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THE EFFECT OF STERILIZATION ON PLASTICS AND ELASTOMERS

Third Edition

Laurence McKeen

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Preface

This book has is an extensive update and extension of *The Effect of Sterilization Methods on Plastics and Elastomers*, 2nd Edition by Liesl K. Massey. The second edition was published in 2004. Since that time, new plastic materials have been introduced. There has been an expanded interest in green materials; those made from renewable resources and those that decompose relatively quickly in the environment. There has been a turnover in ownership of the plastic producing companies. There has been a lot of consolidation, which of course means discontinued products. This update is much more extensive than the usual "next edition". It has been reorganized from a polymer chemistry point of view. Plastics of mostly similar polymer types are grouped into ten chapters. A brief explanation of the chemistry of the polymers used in the plastic films is discussed at the start of each plastic section.

An extensive introduction has been added as three chapters. The initial chapter is a review of sterilization processes used for food irradiation and medical sterilization. It covers some history, some biology and an overview of many sterilization processes. In most cases it is explained how each process kills microbes, and where the processes are most used.

The second chapter covers polymer chemistry, plastics and films composition and how it relates to plastic and film properties. This book will narrow the plastics field down to those used in food packaging and medical applications requiring sterilization. The second chapter includes a brief discussion of polymerization chemistry and the different types of polymers and how they can differ from each other. Since plastics are rarely "neat", reinforcement, fillers and additives are reviewed. A basic understanding of plastic and polymer chemistry will make the discussion of properties of specific plastics easier to understand and it also provides a basis for the introductions of the plastic families in later chapters. This section is based upon the earlier books by this author in the series including *The Effect of Temperature and Other Factors on Plastics*[1] and *Permeability Properties of Plastics and Elastomers*,[2] but it has been rewritten, expanded and refocused on polymers as they relate to food packaging and medical uses.

The third chapter focuses on physical, mechanical, and thermal properties of plastics. Many properties are discussed including how the properties are measured and data is presented. Sterilization and irradiation processes may be expected to change plastic properties and it is important to understand how the property measurements are made and what they mean. First discussed are the physical properties of plastics, such as specific gravity and color. Second are the mechanical properties such as tensile strength, elongation, modulus, tear resistance. Third are thermal properties such as melting point, glass transition temperature and melt index.

Chapters 4 through 13 are a databank that serves as an evaluation of how sterilization and radiation processes affect the performance of plastics. Each of these chapters starts with a brief outline of the chemistry of the polymer in that section. There are hundreds of uniform graphs and tables for more than 70 generic families of plastics used to make films are contained in these chapters.

The data in each chapter is generally organized with chemistry, a manufacturer and trade name list, an applications and uses list followed by the data. Ionizing radiation is generally covered first followed by the chemical approaches. The tabular data in the second edition has been verified and reformatted to take up much less space in this edition, and whereas this new edition does not have many more pages, there is far more information contained. An appendix covers the general suitability of various sterilization processes for many classes of plastics.

Numerous references are included. Only limited data from the first edition has been removed. Removed data primarily was for discontinued products. Product names and manufacturers have been updated.

I am appreciative of the confidence and support of my Plastics Design Library series editor and friend Sina Ebnesajjad. He was also the primary proofreader of the manuscript. I am especially appreciative of Dr. Kayvon Modjarrad MD who practices infectious disease medicine in Chapel Hill, North Carolina. He provided a valuable expert review of Chapter 1 and made many suggestions and corrections. I would not have been given the opportunity to do this work had it not been for the support of Matthew Deans, Senior Publisher at Elsevier. His staff at Elsevier is knowledgeable and easy to work with. My family has been particularly supportive through the long hours of writing and research from my home office.

Laurence McKeen 2012

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[1] L.W. McKeen, The Effect of Temperature and Other Factors on Plastics, 2nd Edition, William Andrew (2008).

[2] L.W. McKeen, Permeability Properties of Plastics and Elastomers, 3rd Edition, Elsevier (2011).

1 Introduction to Food Irradiation and Medical Sterilization

This first chapter primarily focuses on the processes used to destroy microbiological life. Microbiological life, microbes, or pathogens in food contribute to food spoilage, disease, illness, and even death. Similarly, microbes in a health care environment may cause disease, infections, sickness, illness, and death. The elimination, killing, or control of microbes is therefore critically important. The processes used for microbe control can affect the properties of materials, especially plastics. That effect is the subject of the bulk of this book. This introductory chapter will be split up into three parts. First will be background on the biology and types of microbes. Then the processes used to control microbial life in the food supply are discussed. That is followed by the control of microbes in the health care environment.

1.1 Pathogens

Sterilization processes are intended to deal with contamination of food, surfaces, or equipment by potentially harmful life forms. These life forms are primarily bacteria, viruses, and endospores, but could also include parasites, prions, molds, fungi, yeasts, protozoa, etc. Organisms that cause disease are called pathogens. This section briefly summarizes what these life forms are, which leads to a better understanding of how sterilization processes kill or control them.

1.1.1 Bacteria

Bacteria consist of only a single cell. Bacteria fall into a category of life called the *prokaryotes*. Prokaryotes' genetic material, or DNA, is not enclosed in a cellular compartment called a nucleus as it is in eukaryotes. Not all bacteria are harmful. However, the subject of this book implies the killing of harmful bacteria. Most people know harmful bacteria best because of the diseases they cause. Some of these diseases are produced when bacteria attack directly the tissues of a plant or animal. For example, fruits and vegetables that become discolored as they are growing may be under attack by bacteria, though discoloration may also be the result of oxidation.

Bacteria also attack cells by releasing chemicals that are poisonous to plants and animals. Such poisons are known as toxins. As an example, *Clostridium botulinum* releases a toxin that causes the most severe form of food poisoning, botulism.

Some forms of dangerous bacteria live on the human skin, but cause no harm unless they are able to enter the body. Among these bacteria is *Staphylococcus*, responsible for the potentially fatal toxic shock syndrome and gastroenteritis. The bacteria may enter the bloodstream through a break in the skin or the digestive tract through contaminated food. And although *Escherichia coli* is helpful within the digestive system, if it is ingested it may cause cramping and diarrhea. If it enters the bloodstream, it causes fever, hypotension, altered mental status, and possibly death.

A diagram of a typical bacterium is shown in Fig. 1.1 and a micrograph of cholera bacteria is shown

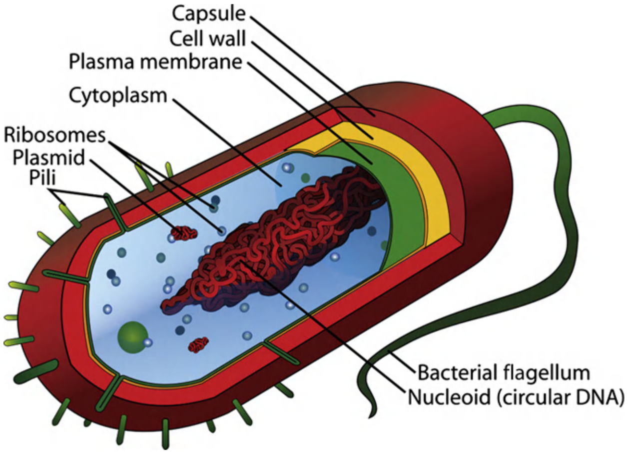


Figure 1.1 Diagram of a typical bacterium.[1] For color version of this figure, the reader is referred to the online version of this book.

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00001-0

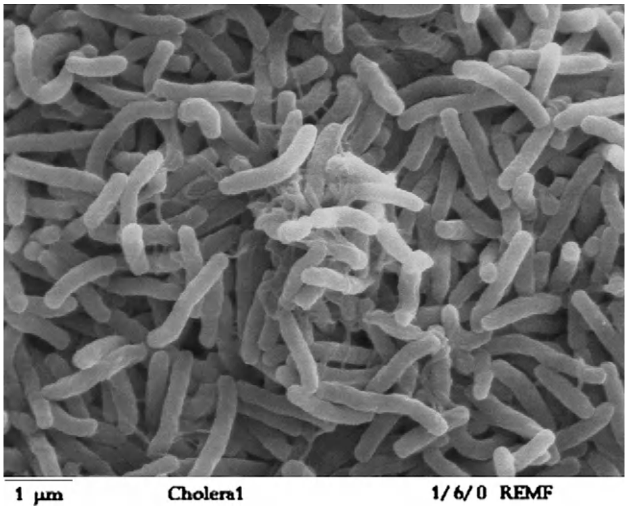


Figure 1.2 Scanning electron micrograph of cholera bacteria.[1]

in Fig. 1.2. Bacteria can be of many other shapes, however, some of which are shown in Fig. 1.3.

Bacteria are often classified as Gram positive and Gram negative. The main difference between the two forms of bacteria is the composition and structure of the cell walls of the two, as shown in Fig. 1.4. Referring to the figure:

- Peptidoglycan, also known as murein, is a polymer consisting of sugars and amino acids that forms a mesh-like layer outside the plasma membrane of bacteria forming the cell wall.
- The periplasm is a space bordered by the two selective permeable biological membranes, which are the inner plasma membrane and the outer membrane in Gram-negative bacteria.
- There is no periplasmic space in Gram-positive bacteria because there is only one biological membrane, but a region called inner wall zone has been observed between the cytoplasmic membrane and the bacterial cell wall.

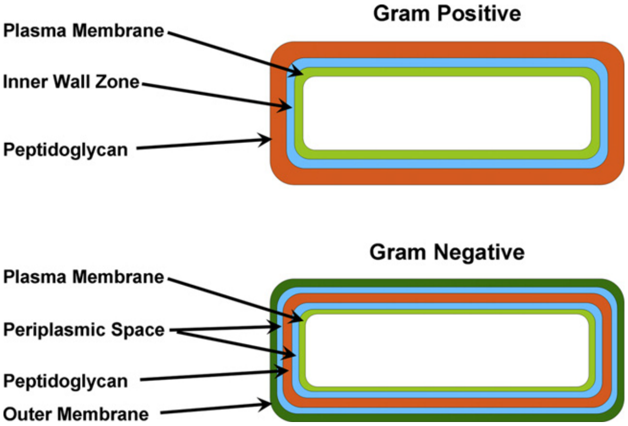
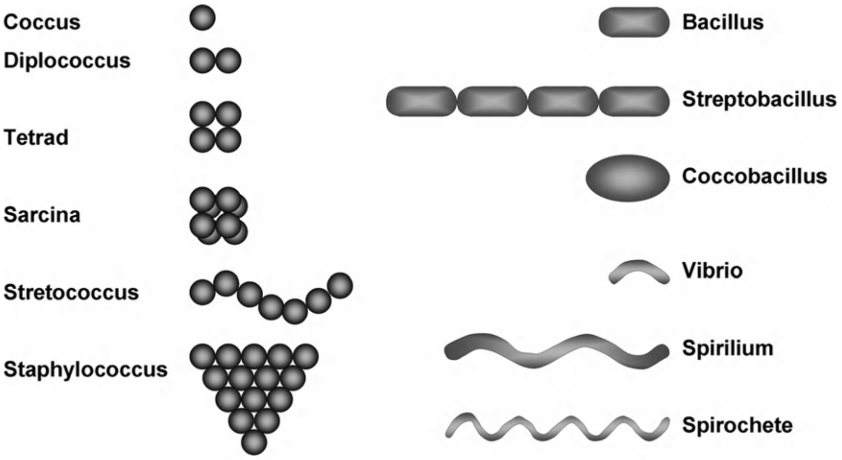


Figure 1.4 The structural difference of the bacterial cell walls of Gram-positive and Gram-negative bacteria.[1] For color version of this figure, the reader is referred to the online version of this book.

The two types of bacteria may respond differently to sterilization processes. Sterilization processes that kill bacteria usually do so by:

- Causing damage to the physical structure, particularly rupture of the cell walls
- Altering the membrane permeability
- Damaging the proteins within the cells
- Damaging the nucleic acids in the DNA or RNA.

Figure 1.3 Common bacterial morphologies.



Other shapes include: Trichome-forming, sheathed, stalked, filamentous, square, star-shaped, spindle-shaped, lobed, and pleomorphic

1.1.2 Viruses

A virus is a small infectious agent that can replicate only inside the living cells of organisms. They are too small to be seen with a light microscope. Viruses are not plants, animals, or bacteria, but they are more like parasites. They are parasites because without a host cell, they cannot carry out their life-sustaining functions or reproduce. Although they may seem like living organisms because of their reproductive abilities, viruses are not living.

The average virus is about one-hundredth the size of the average bacterium. All viruses contain nucleic acid, either DNA or RNA (but not both), and a protein coat, which encases the nucleic acid. Viruses come in a wide diversity of shapes and sizes called morphologies.[2] Viruses are inactive when outside of a living cell, but their nucleic acid once entering the cell can take over the cells' activities, which is primarily to reproduce and break out of the cell to infect other cells. Figure 1.5 shows electron micrographs of two different viruses. The micrograph of the virus on the right side clearly shows the DNA and cell wall structure.

1.1.3 Endospores

An endospore is a dormant, tough, and temporarily nonreproductive structure produced by certain bacteria. It is a stripped-down, dormant form to which the bacterium can reduce itself when conditions are not right for the bacterium to thrive. It is very resistant to harsh environments and can remain viable for very long periods of time, only to spring back to life when conditions are right.

The structure and a micrograph of an endospore are shown in Fig. 1.6. The endospore consists of the bacterium's DNA and part of its cytoplasm, surrounded by a very tough outer coating. The coating consists of multiple layers. The outermost layer is the exosporium, which is a thin protein covering. The next layer is the spore coat which is comprised of

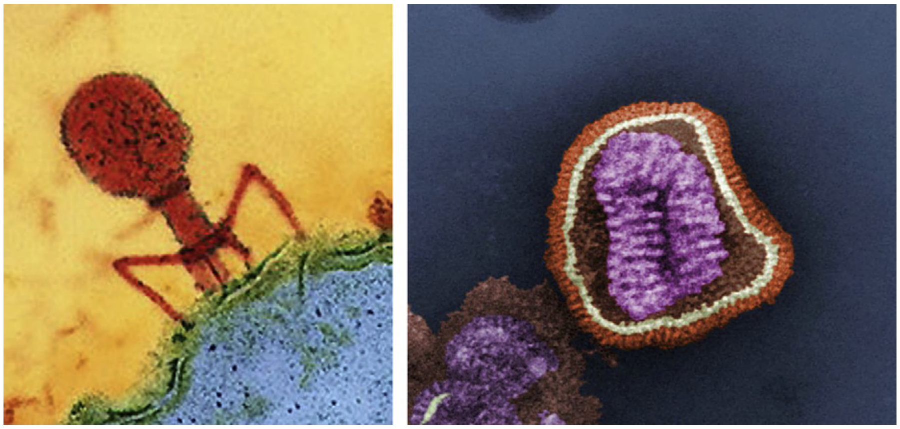


Figure 1.5 Electron micrographs of two viruses, a bacteriophage on the left and an influenza virus on the right.[3] For color version of this figure, the reader is referred to the online version of this book.

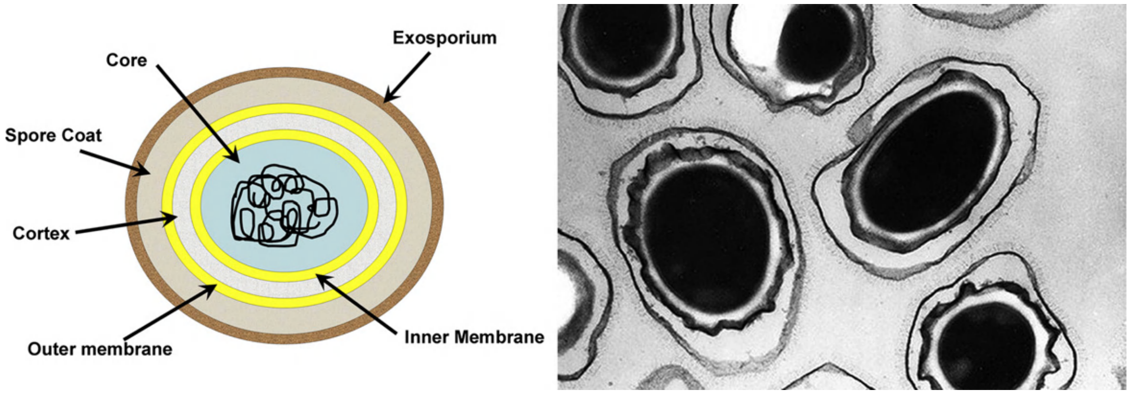


Figure 1.6 Structure of an endospore on the left and a micrograph of anthrax spores on the right. For color version of this figure, the reader is referred to the online version of this book.

spore-specific proteins. An outer membrane surrounds the cortex. The cortex is composed of peptidoglycan containing some dipicolinc acid and calcium ions that cross-link. This creates a highly impenetrable layer that provides the heat resistance properties of the endospore. The core contains the cell wall and cytoplasmic membrane, nuclear material, some ribosomes, RNA molecules, and enzymes. The core contains much less water than the bacterial cell.

Endospores are highly resistant to hostile physical and chemical conditions. They allow a bacterium to survive suboptimal environmental conditions. Because these spores are resistant to heat, radiation, disinfectants, and desiccation, they are difficult to eliminate (but not impossible) from medical and pharmaceutical materials and are a frequent cause of contamination.

1.1.4 Other Infectious Agents

There are other infectious agents may require control. These are listed in the next few sections.

1.1.4.1 Prions

A prion is an infectious agent, rather than a life form, composed of protein in a misfolded form. The group of fatal neurodegenerative diseases are called transmissible spongiform encephalopathies that include bovine spongiform encephalopathy (also known as "mad cow disease") in cattle and Creutzfeldt−Jakob disease (CJD) in humans. They occur in animals (dogs, cows, and primates) as well as humans and are rapidly fatal once symptoms develop. Prions propagate by transmitting a misfolded protein state. When a prion enters a healthy organism, it induces existing, properly folded proteins to convert into the disease-associated, prion form. It acts as a template to guide the misfolding of more protein into prion form. This altered structure is extremely stable and accumulates in infected tissue, causing tissue damage and cell death. CJD poses a unique infection prevention problem because prions, which are protein-containing infectious agents, can survive many common sterilization processes.

1.1.4.2 Helminthes

A parasitical organism is a life form that lives off the host. Helminthes or parasitic worms are a division of eukaryotic parasites. They are worm-like organisms that live and feed off living hosts, receiving nourishment and protection while disrupting their hosts' nutrient absorption, causing weakness and disease. Those that live inside the digestive tract are called intestinal parasites. Figure 1.7 shows one of these parasitic worms. They can live inside humans as well as other animals. The helminthes not only reside in the digestive tract. They may reside in other tissues. Trichinosis is a well-known example. Trichinosis is infection with the microscopic roundworm *Trichinella spiralis*. A micrograph of the trichinosis parasites in muscle tissue is shown in Fig. 1.8.

Figure 1.7 Micrograph of hookworm parasites on intestinal wall.[1] For color version of this figure, the reader is referred to the online version of this book.

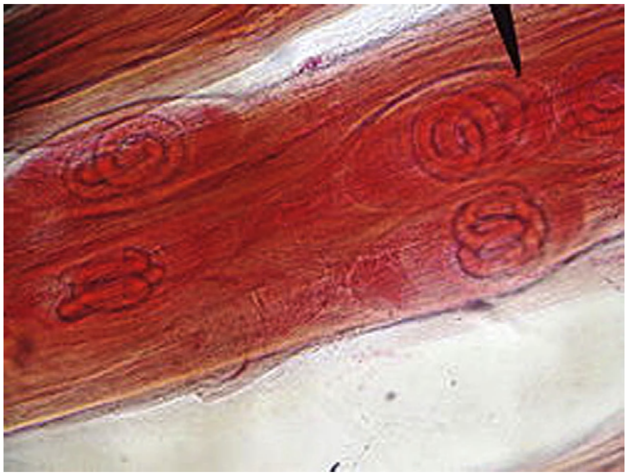


Figure 1.8 Micrograph of trichinosis parasites in muscle tissue.[1] For color version of this figure, the reader is referred to the online version of this book.

1.1.4.3 Fungi: Molds and Yeasts

A fungus is a eukaryotic organism. Fungal cells have cell walls that contain chitin, unlike the cell walls of plants, which contain cellulose. Chitin is a polymer of *N*-acetylglucosamine. Molds are fungi that grow in the form of multicellular filaments called hyphae, such as shown in Fig. 1.9, which shows other labeled features. Microscopic fungi that grow as single cells are called yeasts. Figure 1.10 shows a micrograph of a yeast.

Some molds cause disease or food spoilage. Many fungi produce biologically active compounds, several of which are toxic to animals or plants and are therefore called mycotoxins. Of particular relevance to humans are mycotoxins produced by molds causing food spoilage. Inhaled fungal spores are a well-known cause of allergy and asthma.

Some human diseases caused by fungi include:

- Aspergillosis
- Candidiasis
- Coccidioidomycosis
- Histoplasmosis
- Mucormycosis
- Opportunistic pneumonia
- Thrush.

As such, there is a need to control or kill fungi in the food-processing and in the medical environment.

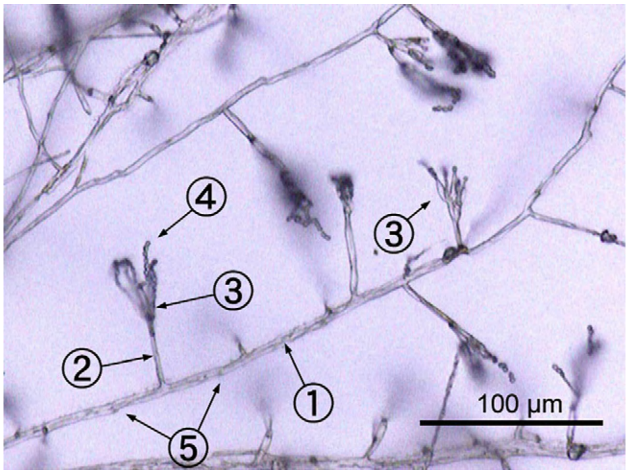


Figure 1.9 Micrograph of *Penicillium* showing (1) hypha, (2) conidiophore, (3) philalide, (4) conidia, and (5) septa.[1] For color version of this figure, the reader is referred to the online version of this book.

1.1.4.4 Protozoans

Protozoa are unicellular eukaryotes, meaning that they have characteristic organelles. They are relatively large and some are visible with the naked eye. Not all protozoa are of concern to public health.

Those that are pathogens include:

- *Toxoplasma*
- *Isospora*
- *Cryptosporidium*
- *Cyclospora*
- *Sarcocystis*
- *Plasmodium*
- *Giardia*
- *Cryptobia* species
- *Enterocytozoon bieneusi*
- *Pleistophora* species.

However, there have been rare infections by amoeba, *Naegleria fowleri*, in the news recently. The news media have called these “brain-eating amoeba.” For the infections in the news, the amoeba entered the brain after contaminated warm water entered the nose, though there were also cases caused by head trauma.

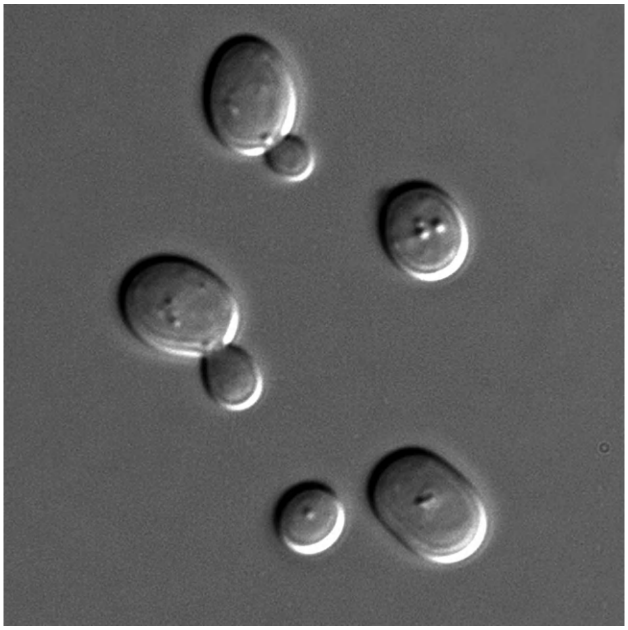


Figure 1.10 Micrograph of yeast species *Saccharomyces cerevisiae*.[1]

1.1.5 Biofilm

A biofilm is an aggregate of microorganisms in which cells adhere to each other on a surface. Dental plaque, the slimy coating that fouls pipes and tanks, and algal mats on bodies of water are examples of biofilms. Biofilms can form on solid or liquid surfaces as well as on soft tissue in living organisms. They are typically resistant to conventional methods of disinfection. These adherent cells in a biofilm are frequently embedded within a self-produced matrix of extracellular polymeric substance (EPS). Biofilm EPS, which is also referred to as slime (although not everything described as slime is a biofilm), is a polymeric conglomeration generally composed of extracellular DNA, proteins, and polysaccharides. Biofilms may form on living or nonliving surfaces and can be prevalent in natural, industrial, and hospital settings.

Biofilms have been found to be involved in a wide variety of microbial infections in the body. Biofilms have been implicated in common problems such as urinary tract infections, catheter infections, middle-ear infections, formation of dental plaque, gingivitis, and coating contact lenses. Though less common but more lethal, biofilms have also been implicated in health problems such as endocarditis, infections in cystic fibrosis, and infections of permanent implanted devices such as joint prostheses and heart valves.

1.2 Food-Borne Disease Control

Concern over food-borne diseases is high. These are the illnesses contracted from eating contaminated foods or beverages. These illnesses include food-borne intoxications and infections and are often incorrectly referred to as food poisoning. There are more than 250 different food-borne diseases and they are caused by viruses, bacteria, parasites, toxins, metals, and prions. According to the US Center for Disease Control (CDC), 31 pathogens are known to cause 20% of the food-borne illnesses, with 80% being caused by unknown agents. Studies by the CDC in 2010 estimated that food-borne diseases each year cause roughly one in six Americans (or 48 million people) to get sick; 128,000 are hospitalized, and 3000 die of food-borne diseases. Symptoms of food-borne illness range from mild gastroenteritis to life-threatening neurologic, hepatic, and renal syndromes. Some of these illnesses are well known and include: botulism, brucellosis, *Campylobacter enteritis*, *E. coli*, hepatitis, listeriosis, salmonellosis, shigellosis, toxoplasmosis, viral gastroenteritis, teniasis, and trichinosis. Food-borne diseases pose a widespread threat to human health and they may lead to reduced economic productivity. Economic losses associated with such food-borne diseases are high estimated between US $6500 million and $33,000 million.

Eight known pathogens account for the vast majority of illnesses, hospitalizations, and deaths. Tables 1.1–1.3 list the top five pathogens causing illness, hospitalization, and death.

Beyond the illnesses, there is the economic cost of high food losses from infestation, contamination, and spoilage caused by insects and bacteria. Killing the microbes and insects that cause these losses by food irradiation can help reduce these losses.

Even though there have been ways to preserve foods for centuries, if not millenia, the cause was not understood until the mid-nineteenth century.

As mentioned in the introduction of this chapter, the killing of microbes in food is a large-scale or bulk process. Heat is one of the best ways to kill microbes, but it is not often desirable to cook the foods prior to sale. The irradiation processes using

Table 1.1 Top Five Pathogens Contributing to Domestically Acquired Food-Borne Illnesses[4]

Pathogen	Estimated Number of Illnesses	90% Credible Interval	% of Total
Norovirus	5,461,731	3,227,078–8,309,480	58
Salmonella, nontyphoidal	1,027,561	644,786–1,679,667	11
Clostridium perfringens	965,958	192,316–2,483,309	10
Campylobacter species	845,024	337,031–1,611,083	9
Staphylococcus aureus	241,148	72,341–529,417	3
Subtotal			91

Table 1.2 Top Five Pathogens Contributing to Domestically Acquired Food-Borne Illnesses Resulting in Hospitalization[4]

Pathogen	Estimated Number of Hospitalizations	90% Credible Interval	% of Total
Salmonella, nontyphoidal	19,336	8545–37,490	35
Norovirus	14,663	8097–23,323	26
Campylobacter species	8463	4300–15,227	15
Toxoplasma gondii	4428	3060–7146	8
Escherichia coli (STEC) O157	2138	549–4614	4
Subtotal			88

Table 1.3 Top Five Pathogens Contributing to Domestically Acquired Food-Borne Illnesses Resulting in Death[4]

Pathogen	Estimated Number of Deaths	90% Credible Interval	% of Total
Salmonella, nontyphoidal	378	0–1011	28
Toxoplasma gondii	327	200–482	24
Listeria monocytogenes	255	0–733	19
Norovirus	149	84–237	11
Campylobacter species	76	0–332	6
Subtotal			88

gamma, electron beam (or beta), infrared (IR), and microwave are used. However, the problem of food preservation has long been accepted and over time have ways have been developed to preserve food. The history of food preservation is interesting.

1.2.1 The History of Food Preservation

Many primitive and tedious methods of food preservation have been used. Some of these were developed thousands of years ago and are still used today. These include:

- **Drying** – Drying was and still is used to preserve fruit, vegetables, meats, and fish. Foods can be dried in the sun (as the ancients did), in an oven or in a food dehydrator by using the right combination of warm temperatures, low humidity, and air current. Drying removes the moisture from the food, so bacteria, yeast, and mold that need water cannot grow and spoil the food.
- **Chemical pickling** – Food for pickling is placed in an edible liquid that inhibits or kills bacteria and other microorganisms. There are many pickling agents including brine (high in salt), vinegar, alcohol, and vegetable oil (particularly olive oil). Many chemical pickling processes also involve heating or boiling so that the food being preserved becomes saturated with the pickling agent. In **fermentation pickling**, the food itself produces the preservation agent, typically by a process that produces lactic acid. This is commonly used to preserve vegetables.
- **Salting** – Salting has been used extensively for pork, beef, and fish. The origins of salt-preserving food can be traced back to at least ancient Egypt, where they used salt as part of the embalming process, as well as in food preservation.

- **Sugaring** – Sugaring is used to preserve fruits for the winter, producing jams and jellies. Sugaring is the process of desiccating a food by first dehydrating it and then packing it with pure sugar. The sugar can be crystalline table or raw sugar, or it can be a high-sugar-density liquid such as honey, syrup, or molasses.
- "**Cold storage**" – Root cellars, ground burial, and iceboxes were cold storage methods used before the development of refrigeration.
- **Smoking** – Smoking is the exposure of cured meat and fish products to smoke for the purposes of preserving them and increasing their palatability by adding flavor and imparting color. The drying action of the smoke tends to preserve the meat, though many of the chemical species present in wood smoke (e.g. formaldehyde and certain alcohols) are natural preservatives as well. Smoking is one of the oldest of food preservation methods.
- **Canning** – Canning is a method of preserving food in which the food contents are processed and sealed in an airtight container. Canning was developed around 1810 by Nicolas Appert in Paris. It revolutionized food preservation.
- **Blanching** – Also known as parboiling, blanching is the method by which foods are partially cooked as a way to preserve their color, texture, and flavor.

1.2.2 The History of Food Irradiation

Antoine-Henri Becquerel (1852–1908) is known for his discovery of radioactivity in 1895, for which he received the 1903 Nobel Prize for Physics jointly with Marie Curie and Pierre Curie. X-rays were also discovered in 1895 by W.K. Roentgen. Ionizing radiation was found to be lethal to living organisms soon after these discoveries. The idea of using ionizing radiation in food preservation almost immediately followed. The suggestion to use ionizing energy to destroy pathogenic and spoilage microorganisms in food was published in a German medical journal the same year. However, the cost and quantity of this radiation inhibited commercial development until much, much later. The basic history of food irradiation follows[5]:

- 1905 – Scientists receive patents for a food preservative process that uses ionizing radiation to kill bacteria in food.
- 1921 – US patent is granted for a process to kill *Trichinella spiral* in meat by using X-ray technology.
- 1953–1980 – The US Government forms the National Food Irradiation Program. Under this program, the US Army and the Atomic Energy Commission sponsor many research projects on food irradiation. The US Army's interest is feeding soldiers during wartime.
- 1958 – The Food, Drug, and Cosmetic Act is amended and defines sources of radiation intended for use in processing food as a new food additive. The Act is administered by Food and Drug Administration (FDA).
- 1963 – FDA approves irradiation to control insects in wheat and flour.
- 1964 – FDA approves irradiation to inhibit sprouting in white potatoes.
- 1964–1968 – The US Army and the Atomic Energy Commission petition FDA to approve the irradiation of several packaging materials.
- 1966 – The US Army and US Department of Agriculture (USDA) petition FDA to approve the irradiation of ham.
- 1971 – FDA approves the irradiation of several packaging materials based in the 1964–68 petitions by the US Army and the Atomic Energy Commission.
- 1976 – The US Army contracts with commercial companies to study the wholesomeness of irradiated ham, pork, and chicken.
- 1980 – USDA inherits the US Army's food irradiation program.
- 1985 – FDA approves irradiation at specific doses to control *Trichinella spiral* is in pork. FDA approves irradiation at specific doses to delay maturation, inhibit growth, and disinfect foods, including vegetables and spices. The Federal Meat Inspection Act is amended to permit gamma radiation to control *Trichinella spiral* is in fresh or previously frozen pork. Law is administered by USDA.
- 1990 – FDA approves irradiation for poultry to control *Salmonella* and other food-borne bacteria.
- 1992 – USDA approves irradiation for poultry to control *Salmonella* and other food-borne bacteria.
- 1997 – FDA's regulations are amended to permit ionizing radiation to treat refrigerated or frozen

uncooked meat, meat by-products, and certain food products to control food-borne pathogens and to extend shelf life.

- 2000 – USDA's regulations are amended to allow the irradiation of refrigerated and frozen uncooked meat, meat by-products, and certain other meat food products to reduce the levels of food-borne pathogens and to extend shelf life. FDA's regulations are amended to permit the irradiation of fresh shell eggs to control *Salmonella*.

1.2.3 Dosage Measures of Radiation

The radiation dose for food irradiation and sterilization generally is measured using the conventional unit rad or the SI unit gray (Gy). The rad, which stands for radiation absorbed dose, was the conventional unit of measurement, but it has recently been replaced by the Gy; 1 Gy is equal to 100 rad. The prefix kilo (k), for 1000×, is commonly used with the gray unit, kGy. Mega (M) for 1,000,000× is often used with the rad unit (Mrad). This is summarized in Table 1.4.

There are other radiation measures: Curie (Ci), Becquerel (Bq), Roentgen (R), Coulomb/kg (C/kg), The rem (rem), and Sievert (Sv). However, these are used for other purposes.

1.2.4 Electron Beam Irradiator

Electron beam irradiation is sometimes referred to as beta irradiation. Beta particles are high-energy, high-speed electrons or positrons emitted by certain types of radioactive nuclei such as potassium-40. Beta particles are subatomic particles ejected from the nucleus of some radioactive atoms. They are equivalent to electrons. The difference is that beta particles originate in the nucleus and electrons originate outside the nucleus.

Electron beam radiation breaks the DNA or damages other critical molecules in bacteria, either killing them or preventing them from reproducing.

The procedure for electron beam irradiation is relatively simple. In practice, a continuous process is used to improve the economics of the process. The source of electron beams is an "accelerator." The accelerator converts electricity through a tungsten filament source.

Accelerators generate and accelerate electrons and direct them toward the food product needing irradiation. An accelerator (see Fig. 1.11) consists of four major systems:

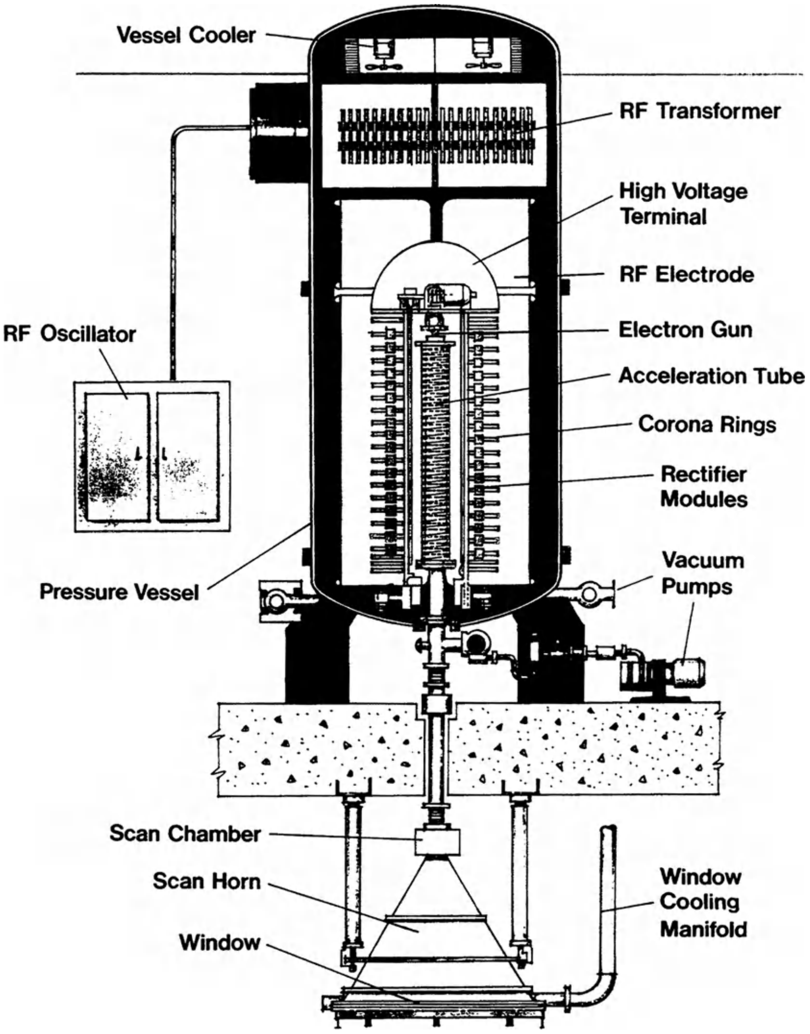
1. Voltage generator
2. Acceleration tube and electron gun
3. Scan chamber and scan horn
4. A control system.

Each segment plays a key role and is briefly described. Low voltage power, typically three-phase, 440 V AC, is converted to high-frequency (100 kHz) radio frequency (RF) power by an oscillator. A number of rectifiers in series along with an RF resonant transformer convert the RF power into ultra high voltage (2–5 MM V) direct current (DC) power. The DC voltage is sent to the acceleration tube. This tube is a hollow vacuum cylinder made from glass and metal. Glass rings are positioned as insulation rings in between metal rings, called dynodes. An electron gun is positioned at the entry point of the tube. A tungsten filament is the source of electrons that are emitted by heating the filament. The continuous electron stream is accelerated through a vacuum tube, supplying a high-energy beam with a diameter of 2–3 cm. The accelerated beam is transmitted through an oscillating magnetic field with a frequency of 200 Hz that converts the tight beam cone into a wide curtain of electrons with

Table 1.4 Conversion of Common Rad and Gray Units of Irradiation

The Rad (rad) is Replaced by the Gray (Gy)	The Gray (Gy) Replaces the Rad (rad)
1 megarad (Mrad) = 10 kilogray (kGy)	1 kilogray (kGy) = 0.1 (Mrad)
1 kilorad (krad) = 10 gray (Gy)	1 gray (Gy) = 100 rad (rad)
1 rad (rad) = 10 milligray (mGy)	1 milligray (mGy) = 100 millirad (mrad)
1 millirad (mrad) = 10 microgray (μGy)	1 microgray (μGy) = 100 microrad (μrad)
1 microrad (μrad) = 10 nanogray (nGy)	1 nanogray (nGy) = 100 nanorad (nrad)

Figure 1.11 Diagram of an electron beam generator.



a width of 1–2.5 m. A thin titanium window acts as a window or a filter before the beam reaches the food to be irradiated. A control system monitors all the functions of the various systems of accelerator to insure proper and consistent operation.

An accelerator operates based on a number of factors including voltage (electron energy), beam current, and beam power. Because electrons have mass, they can only penetrate about 1.5 inches (3.8 cm) into a typical food product or about 3.5 inches (8.9 cm) if the food product is irradiated on both sides. Electrons also have an electric charge. This charge allows the stream of accelerated electrons to be scanned by magnets to track across the product. A commercial food electron beam irradiator accelerates the electrons to an energy of up to 10,000,000 electron volts [10 million electron volts (MeV)]. Electron beam irradiators typically use massive concrete, steel, or lead shielding. Electron beam accelerators can be turned on and off. Safety interlocks ensure that a person cannot enter the radiation chamber where the food is being irradiated when the accelerator is "on." Product is usually passed through the scanned "beam" on roller-type conveyors as shown in Fig. 1.12. A picture of the electron beam scan horn and conveyor system in the irradiation area is shown in Fig. 1.13.

1.2.5 Gamma Irradiator

Gamma radiation, signified by the Greek letter γ, is one of the three types of natural radioactivity. Gamma rays are electromagnetic radiation, like X-rays, except even more energetic. They have enough energy to ionize matter and can damage or destroy living cells, which is of course why they are useful for sterilization. The source of gamma rays in a gamma irradiator is Cobalt-60. Cobalt-60 radioactively beta decays to

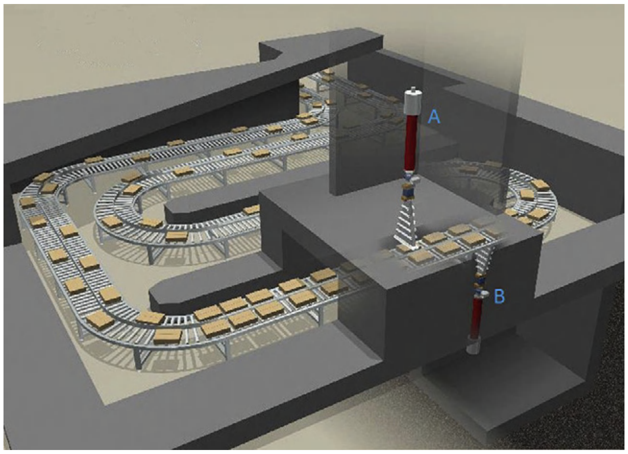


Figure 1.12 A schematic of an electron beam irradiation facility with two-side irradiation for food irradiation. For color version of this figure, the reader is referred to the online version of this book.

Figure 1.13 Scan horn and conveyor system of an Iotron IMPELA® 10/50 Linear Electron Accelerator Installed at Iotron Industries USA Inc., Columbia City, Indiana (photo courtesy of Iotron Industries Canada/USA Inc.). For color version of this figure, the reader is referred to the online version of this book.

Nickel-60 and emits two gamma rays with energies of 1.17 and 1.33 MeV.[6]

Cobalt-60 is not found in nature. It is a synthetic radioactive isotope made by neutron activation of Cobalt-59. Cobalt-60 is produced off site in nuclear reactors and transported in special shipping containers (casks) to the sterilization facility. Cobalt-60 is a solid radioactive metal molded into a cylindrical slug as shown in Fig. 1.14. The slugs are loaded into "sealed source" pencils made of stainless steel. The stainless steel sealed source contains the "radioactive" Cobalt-60, but allows the gamma photons (radiation) to pass through the steel. The pencils are arranged into flat panel arrays. Cobalt-60 continuously emits radiation and cannot be turned "off." The arrays are stored in a deep water pool, which prevents gamma radiation from escaping. The shielding water does not become radioactive.

Large-scale gamma irradiators come in two configurations. In one configuration, the Cobalt arrays are hoisted out of the water into a radiation chamber that typically has shields made out of massive concrete or steel. This is shown in Fig. 1.15. The concrete walls are typically 2-feet thick or more. When the irradiators are out of the protective storage pool, all workers are outside the thick walls. Hanging carriers, totes, or roller conveyors are typically employed to move the product through the chamber for irradiation. A typical product container can be 60 cm × 50 cm × 150 cm, and some irradiators are designed to irradiate entire pallets of product measuring 120 cm × 100 cm × 150 cm. Because Cobalt-60 photons have no mass, they can penetrate more than 24 inches (60 cm) of food product if irradiated on both sides.

In the second configuration, unlike a radiation chamber irradiator, an underwater irradiator stores the Cobalt-60 permanently at the bottom of a pool of water. Instead of raising the Cobalt-60 into a shielded chamber, the product, placed in water-free containers, is lowered to the bottom of the pool adjacent to the Cobalt-60 to receive a dose of radiation. No above-ground shielding or radiation chamber is present. Typically, the product is loaded into water-free containers and the containers are lowered/raised using a hoist mechanism.

1.2.6 X-Ray Irradiator

X-rays are photons and have similar properties to gamma rays emitted by Cobalt-60. However, X-rays are generated by using an electron beam accelerator and converting the electron beam (up to 7.5 MeV) to photons by accelerating the electrons into a high-density material such as tungsten, steel, or tantalum. The sudden deceleration of the electrons generates

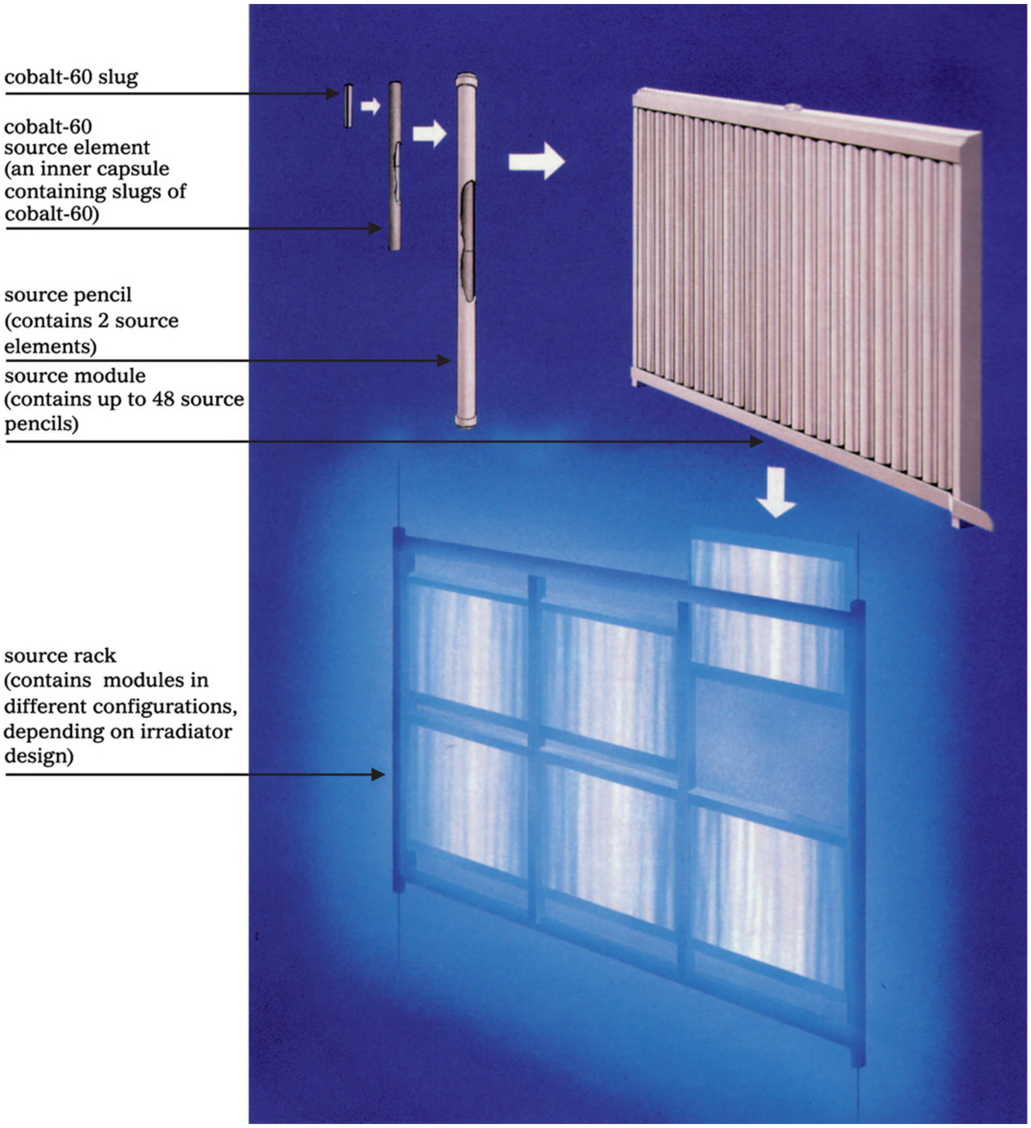


Figure 1.14 Cobalt-60 slugs are arranged into source racks [images/photos courtesy of Nordion (Canada) Inc.]. For color version of this figure, the reader is referred to the online version of this book.

X-rays and waste heat. The shielding and product conveyance are similar to that of a chamber-type gamma irradiator (Fig. 1.15). The advantages of X-rays over electron beams are that they have good product penetration (over 24 inches or 60 cm of food product if irradiated on both sides). The advantage of X-rays over gamma irradiators is that they do not require a shielding storage pool. However, there is a substantial loss of energy during the conversion process. Thus, it suffers a severe cost disadvantage when compared to other types of irradiators for the same product volume throughput. For food irradiation, X-ray machines can have a maximum energy of 5 MeV.

1.2.7 Ultraviolet Germicidal Irradiation

Ultraviolet (UV) is the part of the electromagnetic spectrum between visible light and X-rays. The UV spectrum can be broken down into four parts as shown in Table 1.5. The specific portion of the UV spectrum between 185 and 400 nm (also known as UV-C) has a strong germicidal effect, with peak effectiveness at 265 nm. At these wavelengths, UV kills microorganisms by penetrating their cell membranes and damaging the DNA or RNA, making them unable to reproduce and effectively killing them.

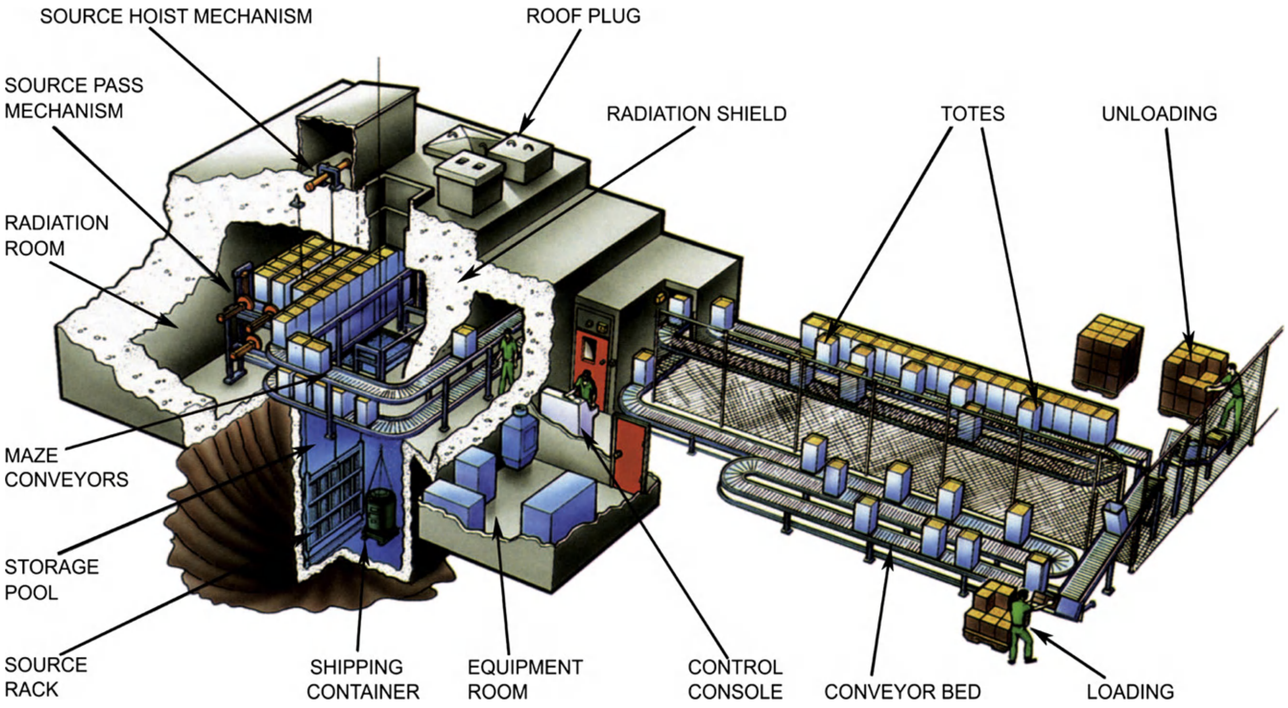


Figure 1.15 A schematic of a gamma irradiation facility [images/photos courtesy of Nordion (Canada) Inc.]. For color version of this figure, the reader is referred to the online version of this book.

Table 1.5 Four Types of Ultraviolet (UV) Light

Wavelength Range	Description
400–315 nm	UV-A – black light UV
315–280 nm	UV-B – dangerous UV
280–200 nm	UV-C – germicidal UV at 254 nm
200–100 nm	UV-V – vacuum UV

Ultraviolet germicidal irradiation (UVGI) is a sterilization method that uses UV light. It is used in a variety of applications, such as food, air, and water purification. It is effective in destroying the nucleic acids in these organisms so that their DNA is disrupted by the UV radiation. This removes their reproductive capabilities and kills them.

The application of UVGI to sterilization has been an accepted practice since the mid-twentieth century. It has been used primarily in medical sanitation and sterile work facilities. Figure 1.16 shows the use of UV irradiation in a laboratory. UVGI technology is particularly suited to the beverage, bottled water, and food processing sectors. The design of these systems is simple as shown in Fig. 1.17. UVGI disinfection has many advantages over alternative methods. Unlike chemical biocides, UVGI does not introduce toxins or residues into the process (which themselves have to be subsequently removed) and does not alter the chemical composition, taste, odor, or pH of the product.

UVGI is employed to sterilize drinking and wastewater, as the holding facilities are enclosed and

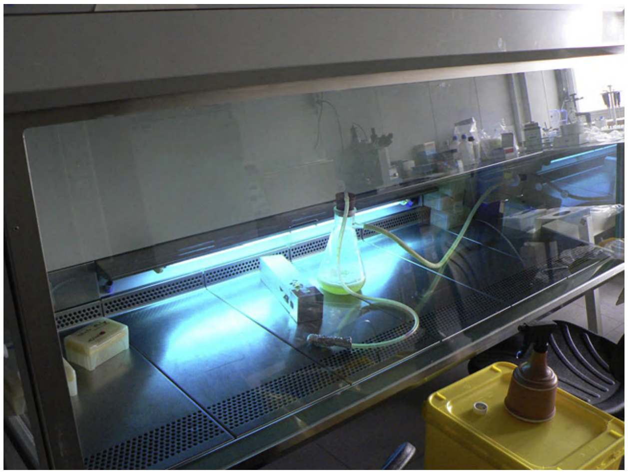


Figure 1.16 Ultraviolet irradiation in use in a laboratory.[1] For color version of this figure, the reader is referred to the online version of this book.

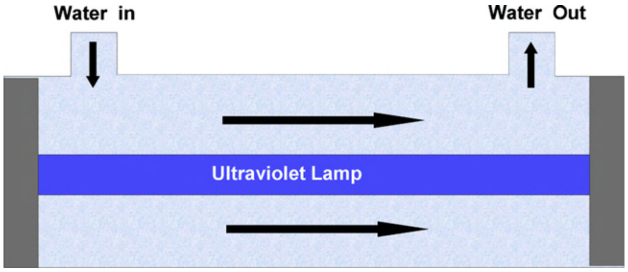


Figure 1.17 The flow-through design of a ultraviolet germicidal irradiation for water purification. For color version of this figure, the reader is referred to the online version of this book.

can be circulated to ensure a higher exposure to the UV. UV sterilizers are commonly used in aquarium circulation systems and hot tub circulation systems. In recent years, UVGI has found renewed application in air sanitization.

Mode of Action: UV photons of different energies have various effects on DNA. The most important damage to DNA is the formation of pyrimidine dimers, which form between two adjacent pyrimidine bases—cytosine (C) and/or thymine (T) as shown in Fig. 1.18. This abnormal link distorts the shape of the DNA double helix and blocks its copying by the DNA replication or RNA transcription machinery. A block in either of these important processes would be very dangerous for a cell; as little as one dimer per cell in fact can be lethal. Dimers are formed in DNA most efficiently by UV-C, less efficiently by UV-B, and very little by UV-A action. The chemical structural changes are shown in Fig. 1.19. UV-A light creates mostly free radicals that lead to indirect DNA damage.[7]

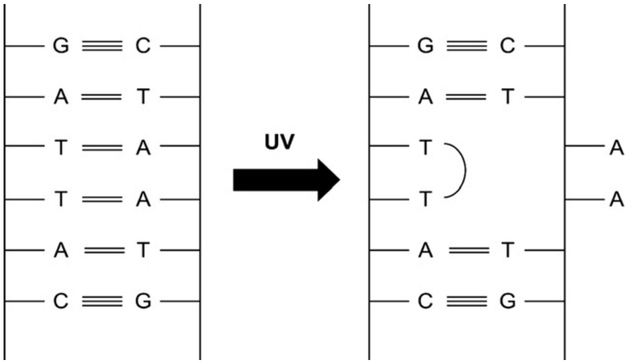


Figure 1.18 Ultraviolet cross-linking of adjacent thymine dimers in a DNA/RNA strand.[7]

1.2.8 Microwave

Microwave sterilization[8] is primarily a thermal process. The heat is generated as microwaves interact with polar water molecules and charged ions. The water molecules align rapidly in alternating the electromagnetic field induced by the microwaves; the friction resulting from the oscillating molecules generates the heat within food. The temperature achieved is limited to about that of boiling water, unless the food is being held under pressure. Because the heat is produced directly in the food, the thermal processing time is sharply reduced compared to processes applying external heat. The food is not necessarily cooked because the times are short. For commercial food applications, this is a developing technology. The microwave sterilization technology developed at Washington State University uses the combination of 915 MHz microwave and conventional heating to improve heating uniformity. Commercial systems performing microwave pasteurization and/or sterilization of foods are currently available in Europe[9] (e.g. TOP's Foods); however, the use of microwaves in the United States to produce prepackaged shelf-stable foods is pending upon FDA acceptance.

Consumers have been able to use their microwaves to sterilize baby bottles in time as short as 90 s. One such unit is shown in Fig. 1.20. Steam from boiling water does the sterilizing.

Mode of Action: The mechanism of germicidal action is essentially heating. Other possible nonthermal mechanisms have been proposed. One of these is electroporation, cell membrane damage and rupture, and direct electromagnetic energy coupling leading to cell lysis (the destruction of cells by disruption of the bounding membrane, allowing the cell contents to escape). However, scientific support for these mechanisms is not entirely convincing.

1.2.9 Infrared

IR heating can be used to inactivate bacteria, spores, yeast, and mold in both liquid and solid foods. Efficacy of microbial inactivation by IR heating depends on several parameters including:

- IR power level
- Temperature of food sample
- Peak wavelength of IR radiation
- Bandwidth of IR heating source

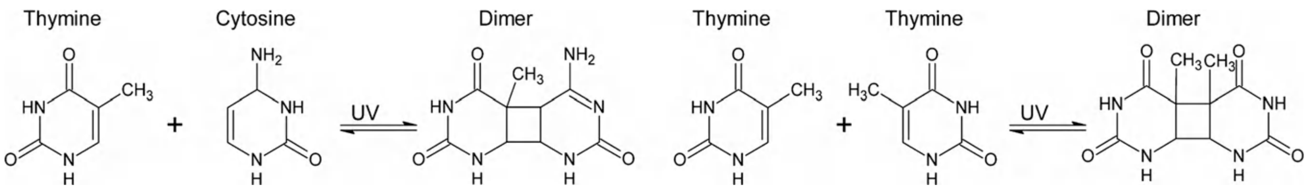


Figure 1.19 Ultraviolet cross-linking structural details of adjacent thymine–cytosine in a DNA/RNA strand on the left, with thymine–thymine dimerization or cross-linking on the right.

- Sample depth
- Types of microorganisms
- Moisture content
- Types of food materials.

Inactivation mechanism by IR heating may include DNA damage in addition to thermal effect. Thermal inactivation can damage DNA, RNA, ribosome, cell envelope, and proteins in microbial cells.

1.2.10 How Does Irradiation Destroy Bacteria?

Radiation breaks the DNA or damages other critical molecules in bacteria, either killing them or preventing them from reproducing. Irradiation is a process that employs ionizing energy. Radiation energy ionizes a very small number of the molecules within the food product and any bacteria within the food product. When a molecule is ionized, it effectively breaks. If a DNA molecule of a bacterium is ionized, it is damaged or destroyed, preventing the bacteria from being able to reproduce.

Figure 1.20 Munchkin® Steam Guard Microwave Sterilizer. For color version of this figure, the reader is referred to the online version of this book.

If a water molecule within a bacterium cell is ionized, it can form peroxide and act as a disinfectant within the bacterium itself. This is covered later in this chapter. These molecular level changes destroy the bacteria by preventing their reproduction. Only a very small fraction of the molecules within a living organism, such as a bacterium, need to be damaged to have this effect. Because only a small fraction of food product molecules are ionized, minimal adverse effects, such as changes in taste, occur.

1.2.11 Doses of Radiation Required

Radiation dose is the quantity of radiation energy absorbed by the food as it passes through the radiation field during processing. International health and safety authorities have endorsed the safety of irradiation for all foods up to a dose level of 10,000 Gy (10 kGy). The bactericidal efficacy of a given dose of irradiation depends on the following[10]:

- The kind and species of the organism (a few are listed in Table 1.6).
- The numbers of organisms (or spores) originally present. The more organisms there are, the less effective a given dose will be.
- The composition of the food. Some constituents may be protective. Compounds that combine with the SH groups would be sensitizing.
- The presence or absence of oxygen. The effect of free oxygen varies with the organism, ranging from no effect to sensitization of the organism. Undesirable "side reactions" are likely to be intensified in the presence of oxygen and to be less frequent in a vacuum.

Table 1.6 Approximate Killing Doses of Ionizing Radiations in Kilograys (kGy)[10]

Organism	Approximate Lethal Dose (kGy)
Insects	0.22–0.93
Viruses	10–40
Yeasts (fermentative)	4–9
Yeasts (film)	3.7–18
Molds (with spores)	1.3–11
Bacteria	
Mycobacterium tuberculosis	1.4
Staphylococcus aureus	1.4–7.0
Corynebacterium diphtheriae	4.2
Salmonella species	3.7–4.8
Escherichia coli	1.0–2.3
Pseudomonas aeruginosa	1.6–2.3
Pseudomonas fluorescens	1.2–2.3
Enterobacter aerogenes	1.4–1.8
Lactobacillus spp.	0.23–0.38
Streptococcus faecalis	1.7–8.8
Leuconostoc dextranicum	0.9
Sarcina lutea	3.7
Bacterial spores	
Bacillus subtilis	12–18
Bacillus coagulans	10
Clostridium botulinum (A)	19–37
Clostridium botulinum (E)	15–18
Clostridium perfringens	3.1
Putrefactive anaerobe 3679	23.50
Bacillus stearothermophilus	10–17

- The physical state of the food during irradiation. Both moisture content and temperature affect different organisms in different ways.
- The condition of the organisms. Age, temperature of growth and sporulation, and state (vegetative or spore) may affect the sensitivity of the organisms.

1.2.12 Dosimetry

The success of radiation processing of food depends to a large extent on the ability of the irradiation processor:

- To measure the absorbed dose delivered to the food product (through reliable dosimetry)
- To determine the dose distribution patterns in the product package (through process qualification procedures)
- To control the routine radiation process (through process control procedures).

This subject is well documented in the literature and will not be discussed further here.[11]

1.3 Medical Sterilization

Until the latter half of the nineteenth century patients undergoing even the most routine operations were at very high risk of infection because surgery was not performed under sterile conditions. The operating room, the surgeon's hands, and the surgical instruments were laden with microbes, which caused high levels of infection and mortality. At the time bad or contaminated air was believed to be the cause of infection. It was not until French scientist Louis Pasteur demonstrated that invisible microbes caused disease, that elimination of them in medical facilities was recognized by numerous doctors.

Ignaz Philipp Semmelweis was a Hungarian physician now known as an early pioneer of antiseptic procedures. Described as the "savior of mothers," Semmelweis discovered that the incidence of puerperal fever could be drastically cut by the use of hand disinfection in obstetrical clinics. Puerperal fever, also known as childbed fever, is a bacterial infection contracted by women during childbirth or miscarriage. It can develop into puerperal sepsis, which is a serious form of septicemia. It was often fatal in mid-nineteenth century hospitals with mortality at 10–35%. Semmelweis proposed washing with chlorinated lime solutions in 1847. He published a book of his findings: *Etiology, Concept, and Prophylaxis of Childbed Fever.*

Heinrich Hermann Robert Koch was a German physician who became famous for isolating *Bacillus anthracis* (1877), the Tuberculosis bacillus (1882), and *Vibrio cholerae* (1883) and for his development of Koch's postulates, which were four criteria to identify the causative agent of a particular disease. He is considered one of the founders of microbiology, inspiring such major figures as Paul Ehrlich and Gerhard Domagk.

Joseph Lister is often considered to be the father of modern surgery, who promoted the idea of sterile surgery while working at the Glasgow Royal Infirmary. Until Lister's studies of surgery, most people believed that chemical damage from exposure to bad air, "miasma," was responsible for infections in wounds. Hospital wards were occasionally aired out at midday as a precaution against the spread of infection via miasma. Hands or a patient's wounds were not washed. While he was a professor of surgery at the University of Glasgow, Lister read a paper published by the French chemist Louis Pasteur, which showed that rotting and fermentation could occur under anaerobic conditions if microorganisms were present. Pasteur suggested three methods to eliminate the microorganisms responsible for gangrene: filtration, exposure to heat, or exposure to chemical solutions. Lister confirmed Pasteur's conclusions with his own experiments and decided to use his findings to develop antiseptic techniques for wounds. Lister successfully introduced carbolic acid (now known as phenol) to sterilize surgical instruments and to clean wounds, which led to reducing postoperative infections and made surgery safer for patients.

Therefore, Lister tested the results of spraying instruments, the surgical incisions, and dressings with a solution of it. Lister found that carbolic acid solution swabbed on wounds remarkably reduced the incidence of gangrene. In August 1865, Lister applied a piece of lint dipped in carbolic acid solution onto the wound of an 11-year-old boy at Glasgow Infirmary, who had sustained a compound fracture after a cart wheel had passed over his leg. After 4 days, he renewed the pad and discovered that no infection had developed, and after a total of 6 weeks, he was amazed to discover that the boy's bones had fused back together, without the danger of formation or discharge of pus. At that time, the mortality rate of a compound fracture was about 60%. He instructed surgeons under his responsibility to wear clean gloves and wash their hands before and after operations with 5% carbolic acid solutions. Instruments were also washed in the same solution and assistants sprayed the solution into the air in the operating theatre.

As the germ theory of disease became more widely accepted, it was realized that infection could be better avoided by preventing bacteria from getting into wounds in the first place. This led to the rise of sterile surgery. Some consider Lister "the father of modern antisepsis." In 1879, Listerine mouthwash was named after him for his work in antisepsis. Also named in his honor is the bacterial genus *Listeria*, typified by the food-borne pathogen *Listeria monocytogenes*.

Hospitals and other medical treatment facilities are now concerned about sterilization. What is sterilization? According to the CDC (Centers for Disease Control and Prevention), "Sterilization means the use of a physical or chemical procedure to destroy all microbial life, including highly resistant bacterial endospores." The processes used to kill microbiological life can affect the materials that are exposed to these processes. For example, when food is irradiated it is often packaged in plastic materials. How does the irradiation process affect the properties of the packaging? When medical devices and facilities are sterilized those processes may affect the plastics used in providing medical care. The plastics may be implants, surgical tools and supplies, or packaging for these items. This book is focused on characterizing and understanding how materials change when they are irradiated or sterilized.

1.3.1 Sterilization, Disinfection, and Asepsis

Medical sterilization is a much broader field than food irradiation. Three terms are often used when talking about this subject and they are: *sterilization*, *disinfection*, and *asepsis*. Sterility and asepsis refer to different conditions. Sterility indicates the elimination (death) of all viable life forms and their germinative elements such as eggs, spores and endospores. Sterility is absolute; there is no such thing as an object being "partially sterile." Asepsis generally means that only certain types of life forms have been removed, excluded or neutralized (rendered nonviable), while the presence of other organisms may be tolerated or even promoted. For example, pasteurization of food does not kill all microorganisms in the food; it does dramatically reduce the number of microorganisms, with the intent that the pasteurized material is stored in conditions that will maintain that low number, such as refrigeration. Disinfection refers to a process whereby many or all pathogenic microorganisms are neutralized or removed. Unlike sterilization, disinfection can be achieved at varying levels as defined by the CDC:

- High-level disinfectants are chemical sterilants that may be used for a shorter exposure period than would be required for sterilization to kill all microorganisms with the exception of high numbers of bacterial spores.
- Intermediate-level disinfectants will kill mycobacteria (causes of tuberculosis and leprosy), vegetative bacteria, most viruses (such as poliovirus), and most fungi but do not kill all bacterial spores.
- Low-level disinfectants kill most vegetative bacteria, some fungi, and some viruses such as *Staphylococcus* species, *Pseudomonas* species, *Salmonella* species, HIV virus, herpes simplex virus, hepatitis B, hepatitis C, and many common cold viruses.

There are hundreds of items that are routinely sterilized or disinfected. In terms of health care/ medical items they are often classified by Spaulding's Classification: critical, semi-critical, and noncritical, as shown in Table 1.7.

Disinfection and sterilization are both decontamination processes. While disinfection is the process of eliminating or reducing harmful microorganisms from inanimate objects and surfaces, sterilization is the process of killing all microorganisms. Sterilization also destroys the spores of various organisms present on surfaces, in liquids, in medication, or in compounds such as biological culture media. Such "extreme" forms of decontamination are needed during critical times like surgery, or in environments like industrial, laboratory or hospital. It is more practical to use disinfection in everyday life.

Disinfection is usually carried out using chemicals, often solutions, but also vapors and gases. When chemicals are used to destroy all forms of microbiologic life, they can be called chemical sterilants. These same germicides used for shorter exposure periods also can be part of the disinfection process (i.e. high-level disinfection).

Sterilization falls into the following three basic categories of which there are several options in each category:

1. High temperature/pressure sterilization (autoclave)
2. Chemical sterilization
3. Radiation sterilization.

Each of these and several less common methods are discussed in later sections.

1.3.2 Thermal Methods of Sterilization

Heat is one of the oldest and cheapest ways to sterilize food, tools, equipment, etc. There are several basic ways to utilize heat and these are described in the following sections.

1.3.2.1 Steam Sterilization/Autoclave

The steam autoclave is the oldest, safest, most widely used and most cost-effective method of sterilization in the medical equipment industry. Steam is generated in a pressure chamber so that it reaches

Table 1.7 Spaulding's Classification

Classification	Definition	Level of Processing Required
Critical equipment/device	Equipment/device that enters sterile tissues, including the vascular system	Cleaning followed by sterilization
Semi-critical equipment/ device	Equipment/device that comes in contact with nonintact skin or mucous membranes but do not penetrate them	Cleaning followed by high-level disinfection as minimum; sterilization if preferred
Noncritical equipment/ device	Equipment/device that touches only intact skin and not mucous membranes or does not directly touch the client/patient/resident	Cleaning followed by low-level disinfection. In some cases, cleaning alone is acceptable

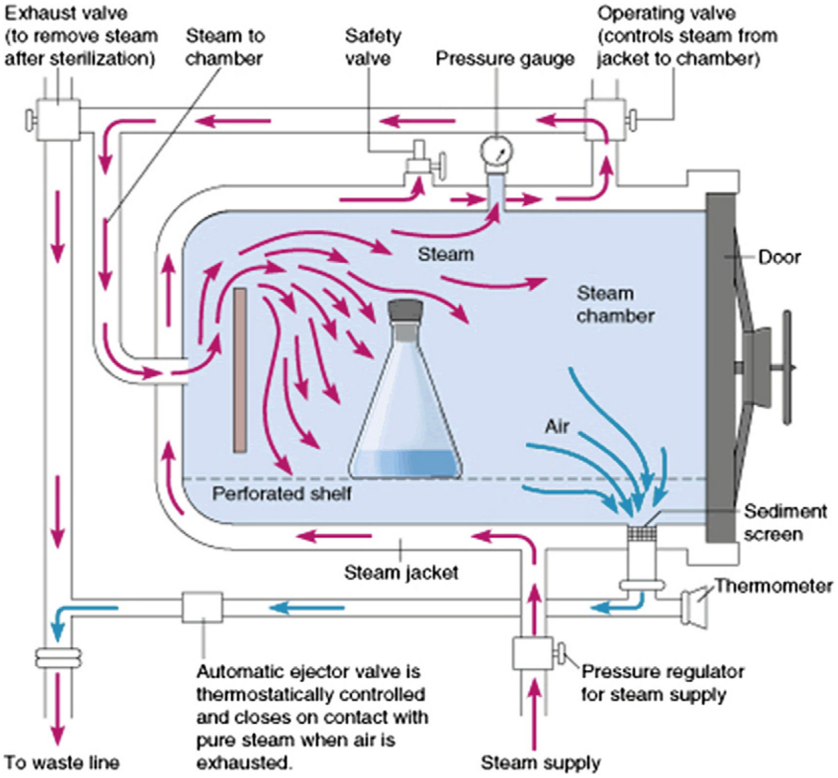


Figure 1.21 Diagram of a gravity displacement steam autoclave (courtesy of Pearson Education). For color version of this figure, the reader is referred to the online version of this book.

a temperature 121–148 °C (250–300 °F) at 15 p.s.i. The time items are kept exposed is dependent on the temperature and size of load and usually ranges from 10 to 60 min. There are two main types of steam autoclaves, gravity displacement and pre-vacuum cycle.

Gravity displacement autoclaves remove air from the chamber by gravity displacement as steam-entering chamber near the top exerts pressure on air forcing it out of the bottom as shown in Fig. 1.21. A photo of an industrial-size steam autoclave is shown in Fig. 1.22.

The high-speed pre-vacuum sterilizers are similar to the gravity displacement sterilizers except they are fitted with a vacuum pump (or ejector) to ensure air removal from the sterilizing chamber and load before the steam is admitted. The advantage of using a vacuum pump is that there is nearly instantaneous steam penetration even into porous loads.

Table 1.8 summarizes the processing parameters for each cycle of the two types of steam autoclaves:

Like all sterilization processes, steam sterilization may have some damaging effects on some materials. At constant temperatures, sterilization times vary depending on the type of item (e.g. metal versus rubber, plastic, items with lumens), whether the item is wrapped or unwrapped, and the sterilizer type.

Figure 1.22 Picture of a large industrial size autoclave. For color version of this figure, the reader is referred to the online version of this book.

Mode of Action: Moist heat destroys microorganisms by the irreversible coagulation and denaturation of enzymes and structural proteins. In support of this fact, it has been found that the presence of moisture significantly affects the coagulation temperature of proteins and the temperature at which microorganisms are destroyed.

Table 1.8 Operating Parameters for Steam Autoclaves

Configuration	Temperature	Time
Gravity displacement	121–123 °C (250–254 °F)	15–30 min
	132–135 °C (270–272 °F)	10–25 min
Pre-vacuum	132–135 °C (270–272 °F)	3–4 min

Uses: Steam sterilization is used whenever possible on all critical and semi-critical items that are heat and moisture resistant (e.g. steam sterilizable respiratory therapy and anesthesia equipment), even when not essential to prevent pathogen transmission. Steam sterilizers also are used in health care facilities to decontaminate microbiological waste and sharps containers but additional exposure time is required in the gravity displacement sterilizer for these items. Steam sterilizers are common in dental facilities.

Advantages:

- Nontoxic to patient, staff, environment
- Cycle easy to control and monitor
- Rapidly microbicidal
- Least affected by organic/inorganic soils among sterilization processes listed
- Rapid cycle time
- Penetrates medical packing, device lumens.

Disadvantages:

- Deleterious for heat-sensitive instruments
- Microsurgical instruments damaged by repeated exposure can corrode surgical alloys and cutting edges
- Development of pitting and dulling of the cutting edges after multiple steam sterilization cycles
- May leave instruments wet, causing them to rust
- Potential for burns.

1.3.2.2 Flash Sterilization

Flash sterilization is often called immediate-use steam sterilization.[12] "Immediate use" is broadly defined as the shortest possible time between a sterilized item's removal from the sterilizer and its aseptic transfer to the sterile field. It is used for sterilizing cleaned patient-care items that cannot be packaged, sterilized, and stored before use. It also is used when there is insufficient time to sterilize an item by the preferred package method. "Flash" steam sterilization was originally defined by Underwood and Perkins as sterilization of an unwrapped object at 132°C for 3 min at 27–28 lbs of pressure in a gravity displacement sterilizer.

Often flash sterilization equipment is located very close to operating rooms to handle urgent needs. However, care must be taken to avoid burns to both the medical staff and the patient. Burns may be prevented by either air cooling the instruments or immersion in a sterile liquid such as saline.

Uses: Flash sterilization should not be used for reasons of convenience. It is not recommended for implantable devices except where unavoidable.

1.3.2.3 Dry Heat Sterilization

Dry heat is effective at inactivating microorganisms, but in general, the temperatures required are higher than is required for steam sterilization to achieve an equivalent level of germicidal action. This method should be used only for materials that might be damaged by moist heat or that are impenetrable to moist heat (e.g. powders, petroleum products, sharp instruments).

There are two types of dry heat sterilizers: the static-air type and the forced-air type. The differences are like two types of ovens common in everyday home kitchens. The static type is like a conventional oven and the forced-air type is like a convection oven. The static-air type has heating coils in the bottom of the unit cause the hot air to rise inside the chamber via convection. This type of dry heat sterilizer is much slower in heating, requires longer time to reach sterilizing temperature, and is less uniform in temperature control throughout the chamber than is the forced-air type. The forced-air or mechanical convection sterilizer is equipped with a motor-driven blower that circulates heated air throughout the chamber at a high velocity, permitting a more rapid transfer of energy from the air to the instruments.

Common time–temperature relationships for sterilization with hot air sterilizers are:

- 170 °C (340 °F) for 60 min
- 160 °C (320 °F) for 120 min
- 150 °C (300 °F) for 150 min.

The advantages for dry heat include:

- It is nontoxic
- Does not harm the environment
- Easy to install
- Relatively low operating costs
- It penetrates materials
- It is noncorrosive for metal.

The main disadvantage is time. Dry heat penetration and microbial killing is time consuming by this method. In addition, the high temperatures are not suitable for most materials.

Mode of Action: The primary lethal process is considered to be oxidation of cell constituents.

1.3.2.4 Glass Bead Sterilizer

Glass bead "sterilization" uses small glass beads (1.2–1.5 mm diameter) and high temperature (217–232 °C) for brief exposure times (e.g. 45 s) to inactivate microorganisms. They are typically used on metal surgical instruments as shown in Fig. 1.23. These devices have been used for several years in the dental profession. FDA believes there is a risk of infection with this device because of potential failure to sterilize dental instruments and their use should be discontinued until the device has received FDA clearance.

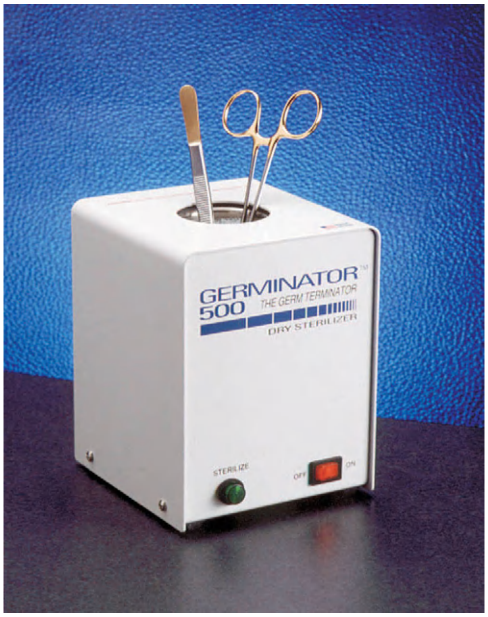


Figure 1.23 Picture of a glass bead sterilizer (photo courtesy of Cellpoint Scientific Inc.). For color version of this figure, the reader is referred to the online version of this book.

1.3.2.5 Microwave

Microwaves are used in medicine for disinfection of soft contact lenses, dental instruments, dentures, milk, and urinary catheters for intermittent self-catheterization. However, microwaves must only be used with products that are compatible (e.g. do not melt). Microwaves are radio frequency waves, which are usually used at a frequency of 2450 MHz. The microwaves produce friction of water molecules in an alternating electrical field. The intermolecular friction derived from the vibrations generates heat and some authors believe that the effect of microwaves depends on the heat produced while others postulate a nonthermal lethal effect. The initial reports showed microwaves to be an effective microbicide. The microwaves produced by a "home-type" microwave oven (2.45 GHz) completely inactivate bacterial cultures, mycobacteria, viruses, and *Geobacillus stearothermophilus* spores within 60 s to 5 min depending on the organism. Another study confirmed these results but also found that higher power microwaves in the presence of water may be needed for sterilization. Microwaves used for sterilization of medical devices have not been FDA cleared.

1.3.2.6 IR Radiation

An IR radiation prototype sterilizer was investigated and found to destroy *Bacillus atrophaeus* spores. IR heating can be effectively used for enzyme inactivation. IR heating can be used to inactivate bacteria, spores, yeast, and mold in both liquid and solid foods. Efficacy of microbial inactivation by IR heating depends on the following parameters: IR power level, temperature of food sample, peak wavelength, bandwidth of IR heating source, sample depth, types of microorganisms, moisture content, and types of food materials.[13] Some of the possible advantages of IR technology include short cycle time, low energy consumption, no cycle residuals, and no toxicological or environmental effects. This may provide an alternative technology for sterilization of selected heat-resistant instruments but there are no FDA-cleared systems for use in health care facilities.

1.3.3 Chemical Disinfectants – Liquids

There are many liquid chemical disinfectants available.[14,15] Some of these may be used in vapor form and that approach is discussed in the next section. All disinfectants act by harming microorganisms in some manner. The different disinfectants have different mechanisms of action. These mechanisms of harm include:

- Protein denaturation
- Membrane disruption
- Nucleic acid damage
- Inhibition of metabolism.

Protein denaturation

It is commonly defined as any noncovalent change in the structure of a protein. This change may alter the secondary, tertiary, or quaternary structure of the molecules. For those proteins that are enzymes, denaturation can be defined as the loss of enough structure to render the enzyme inactive, see Fig. 1.24.

Membrane disruption

The bacterial cytoplasmic membrane is composed of a phospholipid bilayer. It has all the general functions of a cell membrane such as acting as a permeability barrier for most molecules and serving as the location for the transport of molecules into the cell. Membrane disruption by chemical disinfectants is the breakdown of that membrane, which means loss of the permeability barrier and death to the microorganism.

Nucleic acid damage

DNA damage affects the primary structure of the double helix; that is, the bases themselves are chemically modified. These modifications can in turn disrupt the molecules' regular helical structure by introducing nonnative chemical bonds or bulky adducts that do not fit in the standard double helix:

- Oxidation of bases and generation of DNA strand interruptions from reactive oxygen species
- Alkylation of bases (usually methylation)
- Hydrolysis of bases, such as deamination, depurination, and depyrimidination.

Inhibition of metabolism

An enzyme inhibitor is a molecule that binds to enzymes and decreases their activity. Since blocking an enzyme's activity can kill a pathogen or correct a metabolic imbalance.

Many liquid chemical sterilants are discussed in the following sections. Generally for each sterilant, a chemical description or structure is provided. The mode of action is noted and described. Typical uses of the sterilants are listed as are the advantages and disadvantages to it use are summarized.

1.3.3.1 Alcohol

In the health care setting, "alcohol" refers to two water-soluble chemical compounds—ethyl alcohol and isopropyl alcohol. FDA has not cleared any liquid chemical sterilant or high-level disinfectant with alcohol as the main active ingredient. These alcohols are rapidly bactericidal against vegetative forms of bacteria, fungicidal (an agent that destroys fungi), and virucidal (capable of neutralizing or destroying a virus). Alcohols do not destroy bacterial spores. Their cidal activity drops sharply when diluted below 50% concentration, and the optimum bactericidal concentration is 60–90% solution in water (volume/volume).

Mode of Action: The most feasible explanation for the antimicrobial action of alcohol is denaturation of

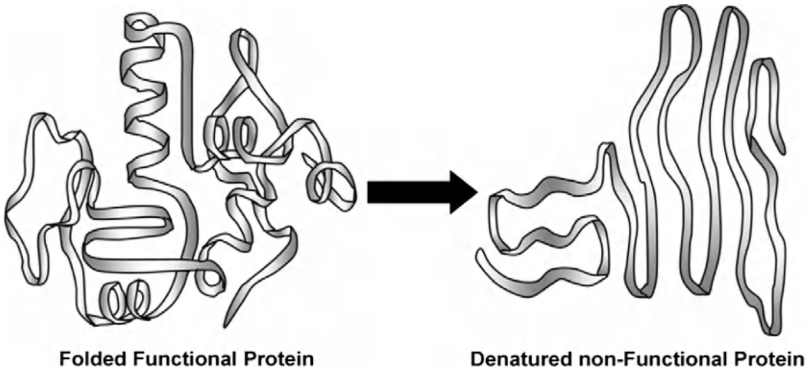


Figure 1.24 Denaturation of a protein can change its shape, which can destroy its function.

proteins. Protein shape is critical to performance of the protein. That shape is maintained by intermolecular forces such as hydrogen bonding (see Section 2.8.1). An example is shown in Fig. 1.25 which shows the hydrogen bonding between two amino acids.

Microbiocidal Activity: Methyl alcohol (methanol) has the weakest bactericidal action of the alcohols and thus seldom is used in health care. The bactericidal activity of various concentrations of ethyl alcohol (ethanol) and isopropanol ranges from 10 s to hours depending on the microorganism.

Uses: A 70% alcohol solution is used as a disinfectant on the skin. This concentration of alcohol is able to penetrate the bacterial cell wall and denature the proteins and enzymes inside of the cell. A 95% alcohol solution merely coagulates the protein on the outside of the cell wall and prevents any alcohol from entering the cell. Alcohols are not recommended for sterilizing medical and surgical materials principally because they lack sporicidal action and they cannot penetrate protein-rich materials. Alcohols have been used effectively to disinfect oral and rectal thermometers, hospital pagers, scissors, and stethoscopes. Alcohol towelettes have been used to disinfect small surfaces such as rubber stoppers of multiple-dose medication vials or vaccine bottles. Furthermore, alcohol occasionally is used to disinfect external surfaces of equipment (e.g. stethoscopes, ventilators, and manual ventilation bags), Cardiopulmonary resuscitation (CPR) manikins, ultrasound instruments or medication preparation areas. Alcohols may damage coatings, plastics, and elastomers.

1.3.3.2 Chlorine and Chlorine Compounds

Chlorine's disinfecting effects are well known as it has been used to disinfect drinking water for many years. Many chlorine compounds release chlorine and are used in the health care setting. The advantage of these compounds over the hypochlorites is that they retain chlorine longer and so exert a more prolonged bactericidal effect. Some of these are discussed in the next sections.

1.3.3.2.1 Hypochlorites

Hypochlorites, the most widely used of the chlorine disinfectants, are available as liquid (household bleach, sodium hypochlorite) or solid (common pool chlorine, calcium hypochlorite). The hypochlorite

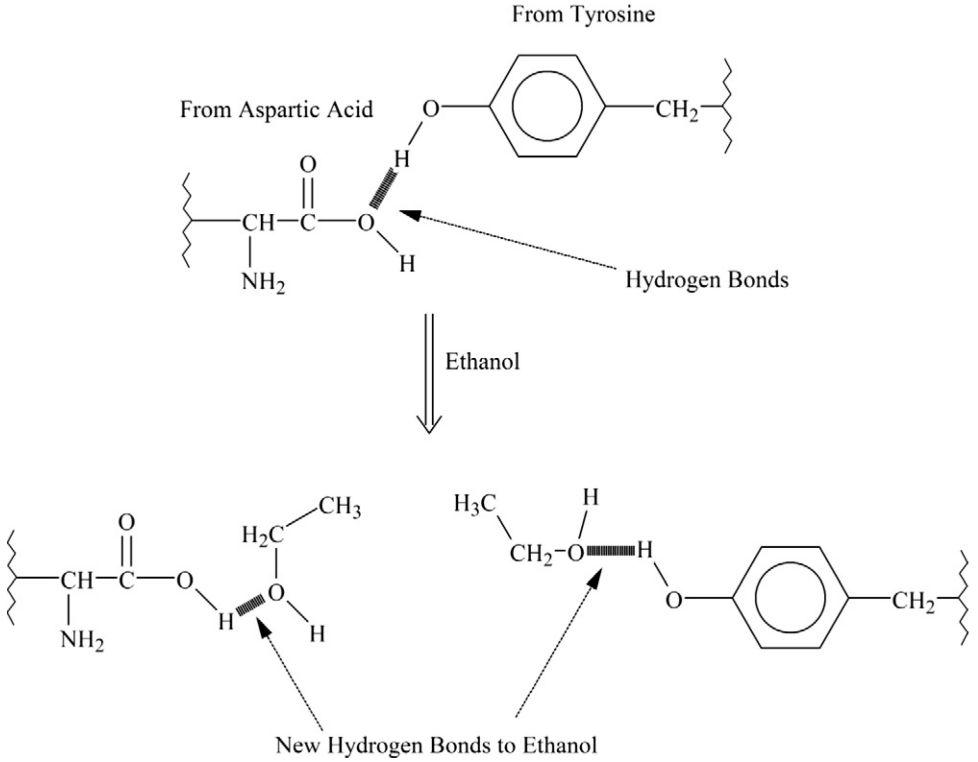


Figure 1.25 Denaturation of hydrogen bonding between two amino acids (aspartic acid, tyrosine) in a protein by ethanol.[16]

ion, also known as chlorate (I) anion, is ClO^-. Household bleach is an aqueous solution of 5.25%−6.15% sodium hypochlorite.

Hypochlorites have a broad-spectrum of antimicrobial activity. They do not leave toxic residues, are unaffected by water hardness, are inexpensive and fast acting. They remove dried or fixed organisms and biofilms from surfaces and have a low incidence of serious toxicity.

One danger is the release of toxic chlorine gas when mixed with ammonia or acid (e.g. household cleaning agents). The microbicidal activity of chlorine is attributed largely to undissociated hypochlorous acid (HOCl). The dissociation of HOCl to the less microbicidal form (hypochlorite ion OCl−) depends on pH. The disinfecting efficacy of chlorine decreases with an increase in pH that parallels the conversion of undissociated HOCl to OCl−.

1.3.3.2.2 Chlorine dioxide

Chlorine dioxide (CD, ClO_2) is greenish yellow and is an oxidizing agent with a chlorine-like odor. ClO_2 is effective against bacteria, yeasts, molds, and viruses. The rapid sterilizing activity of ClO_2 is present at ambient temperature and at relatively low gas concentration, 1−30 mg/l.

Traditionally, chlorine dioxide for disinfection applications is made where it is to be used by one of three methods using sodium chlorite or the sodium chlorite−hypochlorite method:

$$2NaClO_2 + 2HCl + NaOCl \rightarrow 2ClO_2 + 3NaCl + H_2O$$

or the sodium chlorite−hydrochloric acid method:

$$5NaClO_2 + 4HCl \rightarrow 5NaCl + 4ClO_2 + 2H_2O$$

Mode of Action: Chlorine dioxide acts as an oxidizing agent and reacts with several cellular constituents, including the cell membrane of microbes. The potency of chlorine dioxide is attributable to the simultaneous, oxidative attack on many proteins thereby preventing the cells from mutating to a resistant form.

Uses: Drinking water, poultry process water, swimming pools, and mouthwash preparations. It is used to sanitize fruit and vegetables as well as equipment for food and beverage processing. It is used in the life sciences industry to decontaminate animal research facilities. It is also employed in the health care industries to decontaminate rooms, pass-throughs, isolators, and also as a sterilant for product and component sterilization.

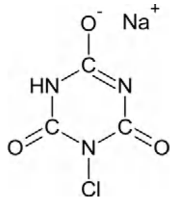


Figure 1.26 Chemical structure of sodium dichloroisocyanurate.

1.3.3.2.3 Sodium dichloroisocyanurate

Sodium dichloroisocyanurate is used as a disinfectant in water. Its structure is shown in Fig. 1.26. It is considered to be a halogen donor, a chemical that releases active chlorine. After release, the halogen reaction is similar to that of chlorine or bromine from other sources. Chlorine donor chemicals do not release the active chlorine all at once, but make it slowly available.

1.3.3.2.4 Chloramine-T

Chloramine-T, the structure of which is shown in Fig. 1.27, is available in tablet or powder form and has to be dissolved before use. It is sprayed on a surface and allowed to stand for at least 15 min before being wiped off or allowed to dry.

Mode of Action: The molecular structure of chloramine-T is similar to para-aminobenzoic acid which is an intermediate in bacterial metabolism. Chloramine-T disrupts bacterial metabolism inhibiting growth. The hypochlorite moiety can destroy the DNA structure via oxidation and thereby prevents microbes from reproducing.

1.3.3.2.5 Superoxidized water

"Superoxidized water" has been examined as a disinfectant. The concept of electrolyzing saline to

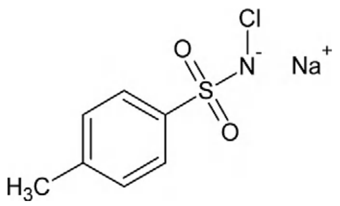


Figure 1.27 Chemical structure of chloramine-T (*N*-chloro 4-methylbenzenesulfonamide, sodium salt).

create a disinfectant or antiseptics is appealing because the basic materials of saline and electricity are inexpensive and the end product (i.e. water) does not damage the environment.[17] The main products of the electrolysis are hypochlorous acid (e.g. at a concentration of about 144 mg/l) and chlorine. As with any germicide, the antimicrobial activity of superoxidized water is strongly affected by the concentration of the active ingredient (available free chlorine). One manufacturer, PuriCore, generates the disinfectant at the point of use by passing a saline solution over coated titanium electrodes at 9 amps. The product generated has a pH of 5.0−6.5 and an oxidation−reduction potential (redox) of >950 mV. Although superoxidized water is intended to be generated fresh at the point of use, when tested under clean conditions, the disinfectant was effective within 5 min when 48 h old. Unfortunately, the equipment required to produce the product can be expensive because parameters such as pH, current, and redox potential must be closely monitored. The solution is nontoxic to biologic tissues.

In October 2002, the FDA cleared superoxidized water as a high-level disinfectant (FDA, personal communication, September 18, 2002).

Mode of Action: The exact mechanism by which free chlorine destroys microorganisms has not been elucidated. Inactivation by chlorine can result from a number of factors: oxidation of sulfhydryl enzymes and amino acids, ring chlorination of amino acids, loss of intracellular contents, decreased uptake of nutrients, inhibition of protein synthesis, decreased oxygen uptake, oxidation of respiratory components, decreased adenosine triphosphate production, breaks in DNA, and depressed DNA synthesis. The actual microbicidal mechanism of chlorine might involve a combination of these factors or the effect of chlorine on critical sites.

Uses: Hypochlorites are widely used in health care facilities in a variety of settings.

1.3.3.3 Liquid Formaldehyde

Formaldehyde is used as a disinfectant and sterilant in both its liquid and gaseous states. The gaseous method is discussed in a later section of this chapter. Formaldehyde is sold and used principally as a water-based solution called formalin, which is 37% formaldehyde by weight. The aqueous solution is a bactericide, tuberculocide, fungicide, virucide, and sporicide.

Mode of Action: Formaldehyde is an extremely reactive chemical that interacts with proteins, DNA, and RNA.

Formaldehyde inactivates microorganisms by alkylating the amino ($-NH_2$) and sulfhydral ($-S-H$) groups of proteins and ring nitrogen atoms of purine bases. This is shown in Fig. 1.28. The interaction with protein results from a combination with the primary amide as well as with the amino groups. Formaldehyde acts as an alkylating agent by reaction with carboxyl ($-C{=}O$), sulfhydryl (-SH), and hydroxyl (-OH) groups. Formaldehyde also reacts extensively with nucleic acid. Two of the four bases in nucleic acids, adenine[2] and guanine,[3] are purines. In DNA, these bases form hydrogen bonds with their complementary pyrimidines, thymine and cytosine, respectively. This is called complementary base pairing. In RNA, the complement of adenine is uracil instead of thymine.

Uses: Although formaldehyde−alcohol is a chemical sterilant and formaldehyde is a high-level disinfectant, the health care uses of formaldehyde are limited by its irritating fumes and its pungent odor even at very low levels (<1 ppm). It is also a suspected human carcinogen linked to leukemia,

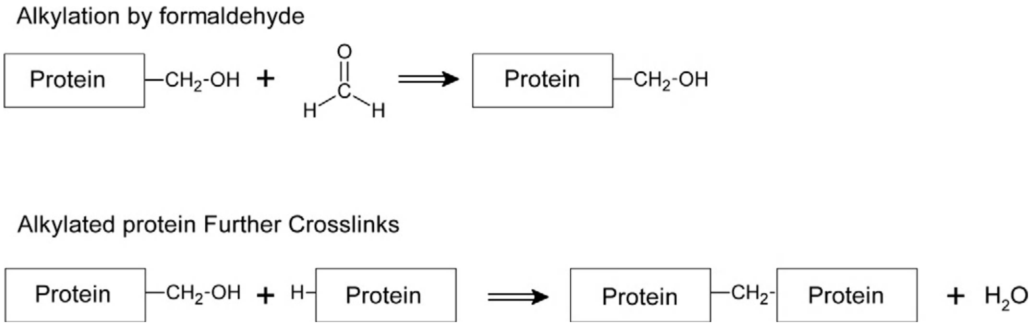


Figure 1.28 Alkylation by formaldehyde can lead to structural changes in proteins.

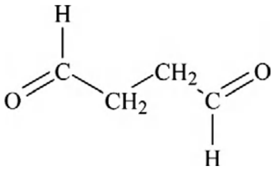


Figure 1.29 Chemical structure of glutaraldehyde.[18]

nasopharyngeal, and lung cancers. Formaldehyde is used in the health care setting to prepare viral vaccines (e.g. poliovirus and influenza), as an embalming agent, and to preserve anatomic specimens, and historically has been used to sterilize surgical instruments, especially when mixed with ethanol.

1.3.3.4 Glutaraldehyde

Glutaraldehyde is a saturated dialdehyde that has gained wide acceptance as a high-level disinfectant and chemical sterilant. Its chemical structure is shown in Fig. 1.29. Aqueous solutions of glutaraldehyde are acidic and generally in this state are not sporicidal. Only when the solution is "activated" (made alkaline) by use of alkalinating agents to pH 7.5−8.5 does the solution become sporicidal. Once activated, these solutions have a shelf life of minimally 14 days because of the polymerization of the glutaraldehyde molecules at alkaline pH levels. This polymerization blocks the active sites (aldehyde groups) of the glutaraldehyde molecules that are responsible for its biocidal activity.

Mode of Action: Like formaldehyde, the biocidal activity of glutaraldehyde results from its alkylation of sulfhydryl, hydroxyl, carboxyl, and amino groups of microorganisms, which alters RNA, DNA, and protein synthesis.

Uses: Glutaraldehyde is used most commonly as a high-level disinfectant for medical equipment such as endoscopes, spirometry tubing, dialyzers, transducers, anesthesia and respiratory therapy equipment, hemodialysis proportioning and dialysate delivery systems, and reuse of laparoscopic disposable plastic trocars. Glutaraldehyde is noncorrosive to metal and does not damage lenses in instruments, rubber, or plastics.

Advantages:

- Numerous use studies published
- Relatively inexpensive
- Excellent materials compatibility.

Disadvantages:

- Respiratory irritation from glutaraldehyde vapor
- Pungent and irritating odor
- Relatively slow mycobactericidal activity
- Coagulates blood and fixes tissue to surfaces
- Allergic contact dermatitis
- Glutaraldehyde vapor monitoring recommended.

1.3.3.5 Hydrogen Peroxide

Good germicidal activity has been ascribed to hydrogen peroxide; it has bactericidal, virucidal, sporicidal, and fungicidal properties. The FDA website lists cleared liquid chemical sterilants and high-level disinfectants containing hydrogen peroxide and their cleared contact conditions.

Mode of Action: Hydrogen peroxide works by producing destructive hydroxyl-free radicals that can attack membrane lipids, DNA, and other essential cell components. Catalase, produced by aerobic organisms and facultative anaerobes that possess cytochrome systems, can protect cells from metabolically produced hydrogen peroxide by degrading hydrogen peroxide to water and oxygen. This defense is overwhelmed by the concentrations used for disinfection. It acts on the microorganisms through its release of nascent oxygen. Hydrogen peroxide produces hydroxyl-free radical that damages proteins and DNA.

Advantages:

- No activation required
- May enhance removal of organic matter and organisms
- No disposal issues
- No odor or irritation issues
- Does not coagulate blood or fix tissues to surfaces
- Inactivates *Cryptosporidium*
- Use studies published.

Disadvantages:

- Material compatibility concerns (brass, zinc, copper, and nickel/silver plating) both cosmetic and functional
- Serious eye damage with contact.

1.3.3.6 Iodophors

Iodine solutions or tinctures long have been used by health professionals primarily as antiseptics on skin or tissue. Iodophors, on the other hand, have been used both as antiseptics and disinfectants. An iodophor is a preparation containing iodine complexed with a solubilizing agent, such as a surfactant or povidone. The structure of povidone−iodine (PVP-I) is shown in Fig. 1.30. A well-known PVP-I product is Betadine®. The result is a water-soluble material that releases free iodine when in solution. Iodine is the active ingredient.

Mode of Action: Iodine can penetrate the cell wall of microorganisms quickly, and the lethal effects are believed to result from disruption of protein and nucleic acid structure and synthesis.

Free iodine, the active ingredient in PVP-I, is rapidly lethal to bacteria, fungi, viruses, and protozoa. These microbial effects are the result of cell wall penetration, oxidation, and substitution of microbial contents with free iodine. It has strong oxidizing effects on the functional groups of amino acids and fatty acids, particularly the $-NH_2$ and -SH groups of amino acids and the double bonds of fatty acids. Iodine reaction with these groups leads to rapid damage to bacterial and fungal cells.

Uses: Besides their use as an antiseptic, iodophors have been used for disinfecting blood culture bottles and medical equipment, such as hydrotherapy tanks, thermometers, and endoscopes. Iodophors formulated as antiseptics contain less free iodine than do those formulated as disinfectants.

1.3.3.7 Ortho-Phthalaldehyde

Ortho-phthalaldehyde (OPA) is a high-level disinfectant that received FDA clearance in 1999. It contains 0.55% 1,2-benzenedicarboxaldehyde (OPA), the structure of which is shown in Fig. 1.31. OPA solution is a clear, pale blue liquid with a pH of 7.5. One popular commercial formulation is Cidex® OPA.[19]

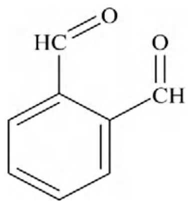


Figure 1.31 Structure of ortho-phthalaldehyde.

Mode of Action: Preliminary studies on the mode of action of OPA suggest that it interacts with amino acids, proteins, and microorganisms. However, OPA is a less potent cross-linking agent that glutaraldehyde. However, the lipophilic aromatic nature of OPA allows its uptake through the outer layers of mycobacteria and Gram-negative bacteria. OPA appears to kill spores by blocking the spore germination process.

Uses: It is used to sterilize a wide range of medical devices.

Advantages:

- Fast-acting high-level disinfectant
- No activation required
- Odor not significant
- Excellent materials compatibility claimed
- Does not coagulate blood or fix tissues to surfaces claimed.

Disadvantages:

- Stains skin, mucous membranes, clothing, and environmental surfaces
- Repeated exposure may result in hypersensitivity in some patients with bladder cancer
- More expensive than glutaraldehyde
- Eye irritation with contact
- Slow sporicidal activity.

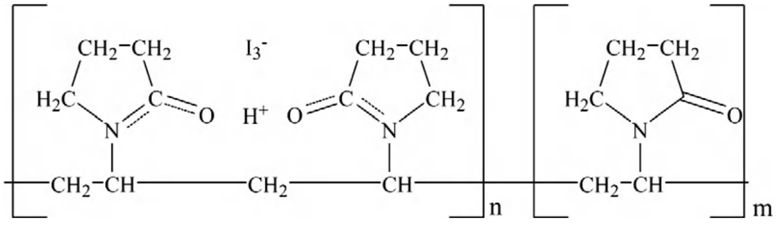


Figure 1.30 Structure of povidone−iodine.

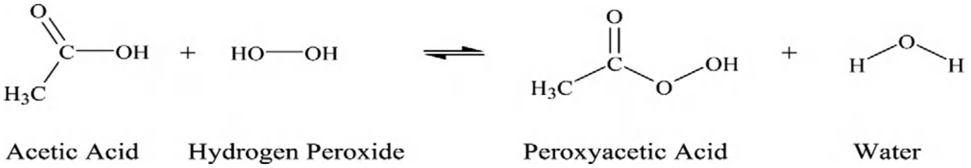


Figure 1.32 Peracetic acid is at equilibrium with acetic acid and hydrogen peroxide in water solutions.

1.3.3.8 Peracetic Acid

Peracetic, or peroxyacetic acid (PAA, see Fig. 1.32), is characterized by rapid action against all microorganisms. The sterilant, 35% peracetic acid, and an anticorrosive agent are supplied in a single-dose container. Special advantages of peracetic acid are that it lacks harmful decomposition products (i.e. acetic acid, water, oxygen, hydrogen peroxide), enhances removal of organic material, and leaves no residue. It remains effective in the presence of organic matter and is sporicidal even at low-temperatures. It is considered unstable, particularly when diluted; for example, a 1% solution loses half its strength through hydrolysis in 6 days, whereas 40% peracetic acid loses 1−2% of its active ingredients per month. One of the common formulations is Envirotech's Perasan®.

Mode of Action: Little is known about the mechanism of action of peracetic acid, but it is believed to function similarly to other oxidizing agents—that is, it denatures proteins, disrupts the cell wall permeability, and oxidizes sulfhydryl and sulfur bonds in proteins, enzymes, and other metabolites.

Advantages:

- Rapid sterilization cycle time (30−45 min)
- Low-temperature (50−55 °C) liquid immersion sterilization
- Environmental friendly by-products (acetic acid, O_2, H_2O)
- Fully automated
- Single-use system eliminates need for concentration testing
- Standardized cycle
- May enhance removal of organic material and endotoxin
- No adverse health effects to operators under normal operating conditions
- Compatible with many materials and instruments
- Does not coagulate blood or fix tissues to surfaces
- Sterilant flows through scope facilitating salt, protein, and microbe removal
- Rapidly sporicidal
- Provides procedure standardization (constant dilution, perfusion of channel, temperatures, exposure)
- PAA breaks down in food to safe and environmentally friendly residues (acetic acid and hydrogen peroxide) and therefore can be used in nonrinse applications.

Disadvantages:

- Potential material incompatibility (e.g. aluminum anodized coating becomes dull). Peracetic acid can corrode copper, brass, bronze, plain steel, and galvanized iron but these effects can be reduced by additives and pH modifications.
- Used for immersible instruments only
- Biological indicator may not be suitable for routine monitoring
- One scope or a small number of instruments can be processed in a cycle
- More expensive (endoscope repairs, operating costs, purchase costs) than high-level disinfection
- Serious eye and skin damage (concentrated solution) with contact
- Point-of-use system, no sterile storage.

1.3.3.9 Peracetic Acid and Hydrogen Peroxide

As shown in Fig. 1.32, peracetic acid may be at equilibrium with hydrogen peroxide and acetic acid. Formulations of the three ingredients are blended and used.

Uses: The combination of peracetic acid and hydrogen peroxide has been used for disinfecting hemodialyzers.

Advantages:

- No activation required
- Odor or irritation not significant.

Disadvantages

- Materials compatibility concerns (lead, brass, copper, zinc) both cosmetic and functional
- Limited clinical experience
- Potential for eye and skin damage.

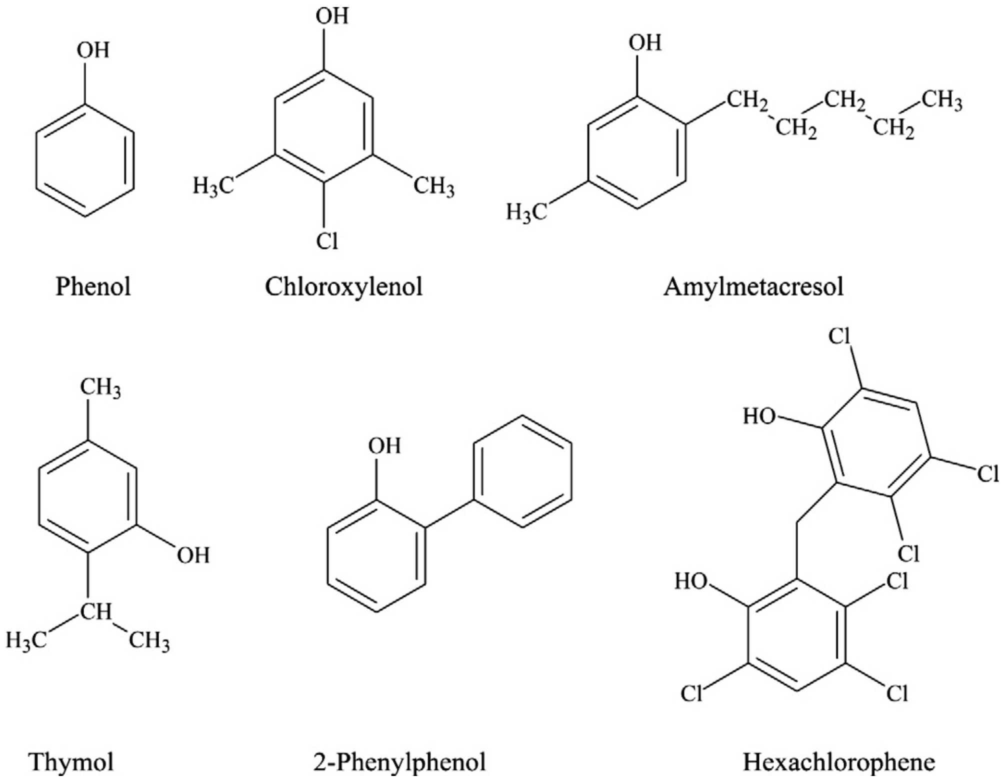
1.3.3.10 Phenolics

Phenol is probably the oldest known disinfectant as it was first used by Lister, when it was called carbolic acid. However, there are many phenol-based materials used as disinfectants. Phenol derivatives originate when a functional group (e.g. alkyl, phenyl, benzyl, halogen) replaces one of the hydrogen atoms on the aromatic ring.

- *o*-Phenylphenol is often used instead of phenol since it is somewhat less corrosive. The primary use of 2-phenylphenol is as an agricultural fungicide. It is generally applied postharvest. It is a fungicide used for waxing citrus fruits.
- Chloroxylenol (4-chloro-3,5-dimethylphenol) is the principal ingredient in Dettol, a household disinfectant and antiseptic.
- Hexachlorophene, also known as Nabac, is a phenolic that was once used as a germicidal additive to some household products but was banned due to suspected harmful effects.
- Thymol, derived from the herb thyme, is the active ingredient in some "broad-spectrum" disinfectants that bear ecological claims. This antibacterial activity is caused by inhibiting growth and lactate production and by decreasing cellular glucose uptake.
- Amylmetacresol is found in Strepsils, a throat disinfectant.

The chemical structures of these materials are shown in Fig. 1.33.

The antimicrobial properties of these compounds and many other phenol derivatives are much improved over those of the parent chemical.



Phenol Chloroxylenol Amylmetacresol

Thymol 2-Phenylphenol Hexachlorophene

Figure 1.33 Structures of several phenol-based disinfectants.

Phenolics are absorbed by porous materials, and the residual disinfectant can irritate tissue.

Mode of Action: In high concentrations, phenol acts as a gross protoplasmic poison, penetrating and disrupting the cell wall and precipitating the cell proteins. Low concentrations of phenol and higher molecular weight phenol derivatives cause bacterial death by inactivation of essential enzyme systems and leakage of essential metabolites from the cell wall. Phenolics generally have poor effectiveness against endospores.

Uses: Many phenolic germicides are EPA registered as disinfectants for use on environmental surfaces (e.g. bedside tables, bedrails, and laboratory surfaces) and noncritical medical devices. Phenolics are not FDA cleared as high-level disinfectants for use with semi-critical items but could be used to preclean or decontaminate critical and semi-critical devices before terminal sterilization or high-level disinfection.

1.3.3.11 Quaternary Ammonium Compounds

Quaternary ammonium compounds (quats), such as benzalkonium chloride (see Fig. 1.34 for the chemical structure), are a large group of related compounds. Some concentrated formulations have been shown to be effective low-level disinfectants. Typically, quats do not exhibit efficacy against difficult-to-kill nonenveloped viruses such as norovirus, rotavirus, or poliovirus. Newer synergous, low-alcohol formulations are highly effective broad-spectrum disinfectants with quick contact times (3−5 min) against bacteria, enveloped viruses, pathogenic fungi, and myco-bacteria.

The quaternary ammonium compounds are widely used as disinfectants. Some of the chemical names of quaternary ammonium compounds used in health care are alkyl dimethyl benzyl ammonium chloride, alkyl didecyl dimethyl ammonium chloride, and dialkyl dimethyl ammonium chloride. The newer quaternary ammonium compounds (i.e. fourth generation), referred to as twin-chain or dialkyl quaternaries (e.g. didecyl dimethyl ammonium bromide and dioctyl dimethyl ammonium bromide), purportedly remain active in hard water and are tolerant of anionic residues.

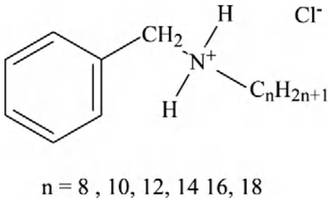


Figure 1.34 Chemical structure of benzalkonium chloride compounds.

Mode of Action: The bactericidal action of the quaternaries has been attributed to the inactivation of energy-producing enzymes, denaturation of essential cell proteins, and disruption of the cell membrane. Evidence exists that supports these and other possibilities. The mechanism of bactericidal/microbicidal action is thought to be due to disruption of intermolecular interactions. Quaternary ammonium compounds are not effective against endospores.

Uses: The quaternaries commonly are used in ordinary environmental sanitation of noncritical surfaces, such as floors, furniture, and walls. EPA-registered quaternary ammonium compounds are appropriate to use for disinfecting medical equipment that contacts intact skin (e.g. blood pressure cuffs).

1.3.3.12 Surfacine

Surfacine Development Company has introduced Surfacine, a persistent antimicrobial agent that may be used on animate or inanimate surfaces. It incorporates a water-insoluble antimicrobial-drug compound (silver iodide) incorporated in a surface-immobilized coating (a modified polyhexamethylene biguanide). Microbial contact with the surface results in transfer of the silver directly from the coating to the organism. Microorganisms contacting the coating accumulate silver until the toxicity threshold is exceeded; dead microorganisms eventually lyse and detach from the surface.

Advantages: It is persistent and has demonstrated vancomycin-resistant *Enterococcus* species, methicillin-resistant *Staphylococcus aureus*, and *Clostridium difficile*.[20]

1.3.3.13 Controlling Biofilm

Biofilm was mentioned in Section 1.2.5 of this chapter. Studies have shown that routine biocides such as chlorine, quats, peracetic acid, chlorine dioxide, and other oxidizers are ineffective against bacteria that live in biofilm. While these agents may be able to kill free-swimming pathogens, these dangerous bacteria will inevitably form biofilms and become resistant to conventional treatment methods.

1.3.4 Gas and Vapor Sterilizing

There are many other sterilization techniques that use gas. Technically, steam could be included as a gas or vapor. Some of the methods discussed in this chapter are used to sterilize medical devices that are already packaged. These may be called terminally sterilized medical devices. ISO 11607-1 details the fundamental attributes required of materials and preformed systems intended for use in packaging systems for terminally sterilized medical devices. ISO 11607-2 describes the validation requirements for forming, sealing, and assembly processes. The development and validation of packaging processes are crucial to ensure that sterile barrier system integrity is maintained until opened by the users of sterile medical devices.

Goals of a terminally sterilized medical device packaging system include:

- Allow sterilization through the packaging. For gaseous sterilants, this means the gas must be able to permeation rapidly through the packaging.
- Provide physical protection during handling, storage, and distribution
- Maintain sterility to the point of use for a specific amount of time
- Allow aseptic presentation

The ASTM tests for packaging include:

- ASTM F1886 Standard Test Method for Determining Integrity of Seals for Medical Packaging by Visual Inspection
- ASTM F88 Standard Test Method for Seal Strength of Flexible Barrier Materials, which is a peel Strength Test
- ASTM F1140 Standard Test Methods for Internal Pressurization Failure Resistance of Unrestrained Packages, which is a Burst Test
- ASTM F1929 Standard Test Method for Detecting Seal Leaks in Porous Medical Packaging by Dye Penetration
- ASTM F1140 Standard Test Methods for Internal Pressurization Failure Resistance of Unrestrained Packages
- ASTM F2096 Standard Test Method for Detecting Gross Leaks in Medical Packaging by Internal Pressurization (Bubble Test)

So in these cases, the effect of the sterilant on both the packaging and the device must be considered.

1.3.4.1 Ethylene Oxide Sterilization

Ethylene oxide (EtO) sterilization is mainly used to sterilize medical and pharmaceutical products that cannot support conventional high temperature steam sterilization — such as devices that incorporate electronic components, plastic packaging or plastic containers.

EtO gas infiltrates packages as well as products themselves to kill microorganisms that are left during production or packaging processes. This gas, mixed with air at a ratio of at least 3% EtO gas, forms an explosive mixture. The pure EtO gas boiling point is 10.73 °C at atmospheric pressure. Most of the time, it is mixed with nitrogen or carbon dioxide (CO_2).

Most EtO sterilization lines involve three different stages.

1. Preconditioning
2. Sterilizer
3. Degasser.

1.3.4.1.1 Preconditioning Stage

First, products need to go through a preconditioning phase to make microorganisms grow. The batch load goes through a dwell time under a controlled environment of temperature and humidity. This is often done in an environmentally controlled room. This part of the process insures the sterilization process will be reproducible.

1.3.4.1.2 Sterilizer Stage

Then the load goes through a long and complex sterilization cycle. Requirements of such a system are:

- Accurate temperature control
- Accurate pressure and vacuum control.

The sterilization phases are:

1. Initial vacuum phase air must be removed or purged from the sterilization chamber because

mixtures of EtO and air can be explosive. For those items that can withstand very low pressure, a vacuum is drawn on the chamber at a controlled rate. Being that many of the items being sterilized are inside a package, a slow evacuation rate is used when that packaging is not very permeable to the components in air. For those devices, components and packaging that are not designed to withstand deep vacuums and/or high pressures, a different approach to air remove is done. A shallow vacuum with nitrogen gas purge is used. An initial shallow vacuum is drawn followed by a nitrogen injection. The combination of the vacuum and nitrogen injection is called a nitrogen wash. The nitrogen wash is repeated several times to assure an adequate removal of air from the vessel.

2. Humidification − When the initial evacuation phase of the process is performed, the product can lose a significant amount of moisture. Moisture is required for the EtO to sterilize properly. The lost moisture must be replaced prior to introducing the ethylene oxide. This is accomplished by adding humidity in the form of steam injections. The amount of steam required is calculated to yield a predetermined relative humidity. After the addition of steam, the product is allowed to dwell or soak for the amount of time required to replace the moisture lost from the evacuation phase.
3. Liquid ethylene oxide is first heated into a gaseous phase and then injected into the chamber. It is often "diluted" with a carrier gas such as Freon [hydrochlorofluorocarbon (HCFC)]. Common dilutions are 8.6% EtO/91.4% HCFC, 10% EtO/90% HCFC, and 8.5% EtO/91.5% CO_2. The amount of gas or gas concentration is dependent on two primary factors that are addressed during cycle design but it is usually 450−1200 mg/l. The most important factor is to assure that the minimum gas concentration required to achieve sterility within the product is attained. This minimum concentration must be balanced against the second factor, which is the maximum amount of gas that can be injected before difficulties arise due to high levels of poststerilization EtO residuals (EtO remaining in the items being sterilized). Additionally, the chamber is kept at a temperature of 37−63 °C and the relative humidity is 40−80%. Exposure time to EtO gas is typically 1−6 h.

1.3.4.1.3 Degassing Stage

4. After the EtO exposure phase of the process, all gas must be removed from the chamber until the levels of EtO fall below the flammable limit for the gas (3% or 30,000 ppm). This is accomplished by performing a series of post-vacuums, each followed with a nitrogen back-fill (wash).
5. After the process, removal of residual EtO is required. This is often done by aeration at elevated temperature. Depending on the substrate materials can take 8−12 h or more. Sometimes this is done in a special room but that may require 7 days if the temperature is around 20 °C.

Mode of Action: The microbicidal activity of EtO is considered to be the result of alkylation of protein, DNA, and RNA. Alkylation or the replacement of a hydrogen atom with an alkyl group, within cells prevents normal cellular metabolism and replication. Ethylene oxide acts more strongly against bacteria, especially Gram-positive bacteria, than against yeast and fungi. The disinfectant effect of ethylene oxide is similar to that of sterilization by heat, but because of limited penetration, it affects only the surface.

Uses: EtO is used in health care facilities to sterilize critical items (and sometimes semi-critical items) that are moisture or heat sensitive and cannot be sterilized by steam sterilization.

Advantages:

For 100% EtO

- Penetrates packaging materials, device lumens
- Single-dose cartridge and negative-pressure chamber minimizes the potential for gas leak and EtO exposure
- Simple to operate and monitor
- Compatible with most medical materials.

For EtO mixtures

- Penetrates medical packaging and many plastics
- Compatible with most medical materials
- Cycle easy to control and monitor.

Disadvantages:

For 100% EtO
- Requires aeration time to remove EtO residue
- Sterilization chamber size from 4.0 to 7.9 ft^3 total volume (varies with model type)
- EtO is toxic, a carcinogen, and flammable
- EtO emission regulated by states but catalytic cell removes 99.9% of EtO and converts it to CO_2 and H_2O
- EtO cartridges should be stored in flammable liquid storage cabinet
- Lengthy cycle/aeration time.

For EtO mixtures
- Some states (e.g. CA, NY, MI) require EtO emission reduction of 90–99.9%
- CFC (inert gas that eliminates explosion hazard) banned in 1995
- Potential hazards to staff and patients
- Lengthy cycle/aeration time
- EtO is toxic, a carcinogen, and flammable.

1.3.4.2 Vaporized Hydrogen Peroxide

Hydrogen peroxide solutions have been used as chemical sterilants for many years. However, the vaporized hydrogen peroxide (HPV or VHP®) approach was not developed for the sterilization of medical equipment and spaces until the mid-1980s. One method for delivering HPV uses a deep vacuum to pull liquid hydrogen peroxide (30–35% concentration) from a disposable cartridge through a heated vaporizer and then, following vaporization, into a sterilization chamber or space. A second approach to HPV delivery is the flow-through approach in which the VHP is carried into the sterilization chamber or space by a carrier gas such as air using either a slight negative pressure (vacuum) or slight positive pressure.

Applications of this technology include vacuum systems for industrial sterilization of medical devices and atmospheric systems for decontaminating for large and small areas, such as laboratory workstations, isolation and pass-through rooms, and even aircraft interiors. VHP offers several appealing features that include rapid cycle time (e.g. 30–45 min), low-temperature, environmentally safe by-products (water, oxygen), good material compatibility, and ease of operation, installation, and monitoring. VHP has limitations including that cellulose cannot be processed, nylon becomes brittle, and VHP penetration capabilities are less than those of EtO. VHP has not been cleared by FDA for sterilization of medical devices in health care facilities.

Mode of Action: See section for a discussion on the mode of action of hydrogen peroxide.

1.3.4.3 Low-Temperature Hydrogen Peroxide Gas Plasma

New sterilization technology based on plasma was patented in 1987 and marketed in the United States in 1993.[21] Gas plasmas have been referred to as the fourth state of matter (i.e. liquids, solids, gases, and gas plasmas). Gas plasmas are generated in an enclosed chamber under deep vacuum using RF or microwave energy to excite the gas molecules and produce charged particles, many of which are in the form of free radicals. The five stages of the process consist of:

1. Vacuum
2. Hydrogen peroxide (H_2O_2) injection
3. Diffusion
4. Plasma
5. Vent.

The sterilization chamber is evacuated to 0.3 mmHg pressure. Hydrogen peroxide solution is injected from a cassette and is vaporized in the sterilization chamber to a concentration of 6 mg/l. The hydrogen peroxide vapor diffuses through the chamber for about 50 min and exposes all surfaces and initiates the inactivation of microorganisms. At the completion of the diffusion phase, the chamber pressure is reduced to 0.5 torr. An electrical field created by an RF is applied to the chamber to create a gas plasma, which lasts for 15 min. Microbicidal free radicals are generated in the plasma. The excess gas is removed and in the final stage of the process the sterilization chamber is returned to atmospheric pressure by introduction of high-efficiency filtered air. The vapor purged from the chamber is vented to the atmosphere through a catalytic filter to decompose all remaining traces of hydrogen peroxide into water and oxygen vapor. The by-products of the cycle (e.g. water vapor, oxygen) are nontoxic and eliminate the need for aeration. The process operates in the temperature range of 37–44 °C and has a cycle time of 75 min.

Multiple plasma cycles are sometimes used. Advanced Sterilization Products' STERRAD® systems utilize this technology.

Mode of Action: Gas plasmas generate charged particles and radicals (hydroxyl and hydroperoxyl free radicals). A free radical is an atom with an unpaired electron and is a highly reactive species. The proposed mechanism of action of low-temperature hydrogen peroxide gas plasma is the production of free radicals within a plasma field that are capable of interacting with essential cell components such as enzymes and nucleic acids. This disrupts the metabolism of microorganisms.

Uses: Materials and devices that cannot tolerate high temperatures and humidity, such as some plastics, electrical devices, and corrosion-susceptible metal alloys, can be sterilized by hydrogen peroxide gas plasma. This method has been compatible with most (>95%) medical devices and materials tested.

Advantages:

- Safe for the environment
- Leaves no toxic residuals
- Cycle time is 28−75 min (varies with model type) and no aeration necessary
- Used for heat- and moisture-sensitive items since process temperature <50 °C
- Simple to operate
- Compatible with most medical devices
- Only requires electrical outlet.

Disadvantages:

- Cellulose (paper), linens, and liquids cannot be processed
- Sterilization chamber size from 1.8 to 9.4 ft^3 total volume
- Some endoscopes or medical devices with long or narrow lumens cannot be processed at this time in the United States
- Requires synthetic packaging (polypropylene wraps, polyolefin pouches) and special container tray
- Hydrogen peroxide may be toxic at levels greater than 1 ppm time-weighted average.

1.3.4.4 Formaldehyde Gaseous Sterilization

Paraformaldehyde, a solid polymer of formaldehyde, can be vaporized by heat for the gaseous decontamination of laminar flow biologic safety cabinets when maintenance work or filter changes require access to the sealed portion of the cabinet. This is shown in Fig. 1.35.

Mode of Action: See Section 1.3.3.3.

1.3.4.5 Formaldehyde Steam

Low-temperature steam with formaldehyde is used as a low-temperature sterilization method in many countries, particularly in Scandinavia, Germany, and the United Kingdom. The process involves the use of formalin (aqueous solution of formaldehyde, i.e. 37% by weight), which is vaporized into a formaldehyde gas that is admitted into the sterilization chamber. A formaldehyde concentration of 8−16 mg/l is generated at an operating temperature of 70−75 °C. The sterilization cycle consists of a series of stages:

1. Initial vacuum to remove air from the chamber and load
2. Steam admission to the chamber with the vacuum pump running to purge the chamber of air and to heat the load
3. Followed by a series of pulses of formaldehyde gas
4. Followed by steam.
5. Formaldehyde is removed from the sterilizer and load by repeated alternate evacuations and flushing with steam and air.

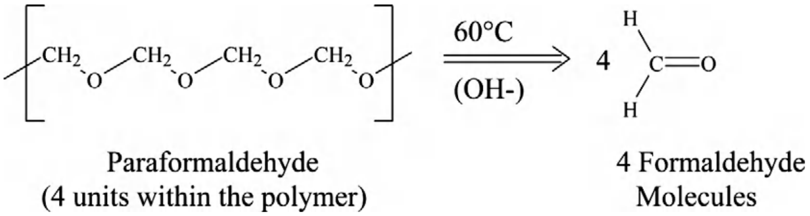


Figure 1.35 Generation of formaldehyde gas from solid polymer.

Mode of Action: See Section 1.4.3.

Advantages:

- Cycle time for formaldehyde gas is faster than that for EtO
- The cost per cycle is relatively low.

Disadvantages:

- EtO is more penetrating and operates at lower temperatures than do steam/formaldehyde sterilizers
- Formaldehyde is a mutagen and a potential human carcinogen, and OSHA regulates formaldehyde
- The formaldehyde steam sterilization system has not been FDA cleared for use in health care facilities.

1.3.4.6 Ozone

Ozone has been used for years as a drinking water disinfectant. Ozone is produced when oxygen is energized and split into two monatomic molecules. The monatomic oxygen molecules then collide with O_2 molecules to form ozone, which is O_3. The additional oxygen atom makes ozone a powerful oxidant that destroys microorganisms but is highly unstable (i.e. half-life of 22 min at room temperature).

A new sterilization process, which uses ozone as the sterilant, was cleared by FDA in August 2003 for processing reusable medical devices. The sterilizer, introduced by TSO3 Inc. (Quebec City, QC, Canada), creates its own sterilant internally from USP-grade oxygen, steam-quality water, and electricity; the sterilant is converted back to oxygen and water vapor at the end of the cycle by a passing through a catalyst before being exhausted into the room.

The ozone sterilization process uses two identical half-cycles. After the chamber is loaded with instruments, the door is closed, and the cycle begins.

1. A vacuum is created within the chamber
2. Humidification
3. Ozone is then injected into the chamber
4. The previous steps are repeated
5. A final ventilation phase is used to remove ozone from the chamber and the packaging within it, the residual ozone is catalytically converted to oxygen.

The duration of the sterilization cycle is about 4 h and 15 min, and it occurs at 30–35 °C.

Advantages:

- Claimed cost per cycle is very low
- Employee safety
- Can used sterilized items immediately.

Disadvantages:

- Several metals may not be used.

Combined hydrogen peroxide and ozone systems have been introduced.

1.3.4.7 Gaseous Chlorine Dioxide

A gaseous chlorine dioxide system for sterilization of health care products was developed in the late 1980s. Chlorine dioxide is not mutagenic or carcinogenic in humans. The process is:

1. Precondition: Raising of relative humidity levels to between 60% and 75%. Increased humidity levels are necessary for all spore reduction.
2. Condition: Hold time once relative humidity set point has been reached. This is to allow spores to swell and crack due to humidity prior to gas introduction.
3. Charge: Generation and delivery of chlorine dioxide gas.
4. Exposure: Hold time once chlorine dioxide gas concentration set point has been reached.
5. Aeration: Removal of chlorine dioxide gas from chamber.

Mode of Action: Chlorine dioxide (ClO_2) acts as an oxidizing agent and reacts with several cellular constituents, including the cell membrane and proteins of microbes.

1.3.4.8 Vaporized Peracetic Acid

The sporicidal activity of peracetic acid vapor at 20%, 40%, 60%, and 80% relative humidity and 25 °C was determined on *Bacillus atrophaeus* spores on paper and glass surfaces. Appreciable activity occurred within 10 min of exposure to 1 mg of peracetic acid per liter at 40% or higher relative humidity. No vaporized peracetic acid system is FDA cleared.

1.3.5 Ionizing Radiation

Sterilization by ionizing radiation, primarily by Cobalt-60 gamma rays or electron accelerators, is a low-temperature sterilization method that has been used for a number of medical products (e.g. tissue for transplantation, pharmaceuticals, and medical devices). Gamma and electron beam (or beta) radiation is discussed in detail in the earlier sections on the irradiation of food. The radiation process is not any different for medical items, but in general only disposable or one-time use items are sterilized by these methods because the facilities large and expensive and are not located on hospital grounds. Major advantages of gamma and electron beam irradiation are that there are no residuals and no radioactivity remaining. As soon as the delivered dose of radiation is verified, products may be released for shipment.

There are no FDA-cleared ionizing radiation sterilization processes for use in health care facilities. Because of high sterilization costs, this method is an unfavorable alternative to EtO and plasma sterilization in health care facilities but is suitable for large-scale sterilization.

1.3.5.1 UV Radiation

The wavelength of UV radiation ranges from 328 nm to 210 nm (3280 Å to 2100 Å). Its maximum bactericidal effect occurs at 240–280 nm. Mercury vapor lamps emit more than 90% of their radiation at 253.7 nm, which is near the maximum microbicidal activity. Inactivation of microorganisms results from destruction of nucleic acid through induction of thymine dimers. This is discussed in Section 1.2.8. UV radiation has been employed in the disinfection of drinking water, air, titanium implants, and contact lenses. Bacteria and viruses are more easily killed by UV light than are endospores.

The application of UV radiation in the health care environment (i.e. operating rooms, isolation rooms, and biologic safety cabinets) is limited to destruction of airborne organisms or inactivation of microorganisms on surfaces. There are two examples of airborne use of UV. Figure 1.36 shows that UV lights may be mounted within air ducts to destroy airborne organisms; such an application might be found in operating room ventilation. Figure 1.37 shows an example of UV use in an isolation room. Table 1.9 shows the UV dose required to reduce the populations of various organisms.

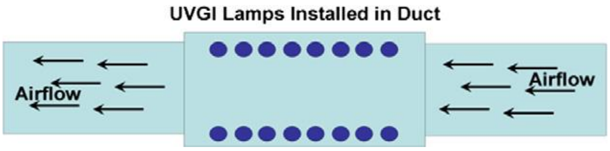


Figure 1.36 Diagram of ductwork-installed ultraviolet germicidal irradiation.[22] For color version of this figure, the reader is referred to the online version of this book.

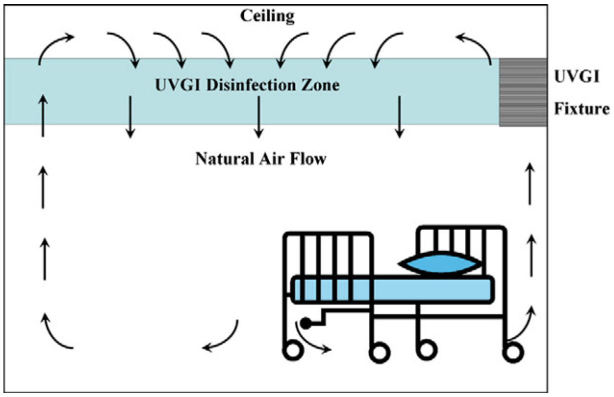


Figure 1.37 Diagram of hospital bed air space ultraviolet germicidal irradiation.[22] For color version of this figure, the reader is referred to the online version of this book.

1.4 Bioterrorism

Bioterrorism is also a constant threat that the public really learned about in September of 2001, when anthrax spores were intentionally sent through the postal system, causing 22 cases of anthrax, including 5 deaths, and forever changing the realm of public health.[24] Mail to government offices was irradiated to prevent anthrax infections and contaminated rooms and buildings were fumigated by methods discussed in this chapter.

The principal means of decontamination of facilities experiencing an anthrax attack is fumigation with chlorine dioxide gas. Delivery of anthrax has been by mail in the past. Irradiation of mail is an effort to disinfect it. The most notable instance of mail irradiation occurred in response to the 2001

Table 1.9 UV Dose Required to Reduce the Population of Various Microorganisms[23]

Organisms	Energy Dosage of Ultraviolet Radiation (UV Dose) in μWs/cm^2 Needed for Kill Factor	
Bacteria	**90% Reduction**	**99% Reduction**
Bacillus anthracis – anthrax	4520	8700
Bacillus anthracis spores – anthrax spores	24,320	46,200
Bacillus megaterium sp. (spores)	2730	5200
Bacillus megaterium species (veg.)	1300	2500
Bacillus paratyphus	3200	6100
Bacillus subtilis spores	11,600	22,000
Bacillus subtilis	5800	11,000
Clostridium tetani	13,000	22,000
Corynebacterium diphtheriae	3370	6510
Eberthella typhosa	2,140	4100
Escherichia coli	3000	6600
Leptospira canicola – infectious jaundice	3150	6000
Micrococcus candidus	6050	12,300
Micrococcus sphaeroides	1000	15,400
Mycobacterium tuberculosis	6200	10,000
Neisseria catarrhalis	4400	8500
Phytomonas tumefaciens	4400	8000
Proteus vulgaris	3000	6600
Pseudomonas aeruginosa	5500	10,500
Pseudomonas fluorescens	3500	6600
Salmonella enteritidis	4000	7600
Salmonella paratyphi – enteric fever	3200	6100
Salmonella typhosa – typhoid fever	2150	4100
Salmonella typhimurium	8000	15,200
Sarcina lutea	19,700	26,400
Serratia marcescens	2420	6160
Shigella dysenteriae – dysentery	2200	4200
Shigella flexneri – dysentery	1700	3400
Shigella paradysenteriae	1680	3400
Spirillum rubrum	4400	6160
Staphylococcus albus	1840	5720
Staphylococcus aureus	2600	6600
Staphylococcus hemolyticus	2160	5500
Staphylococcus lactis	6150	8800
Streptococcus viridans	2000	3800
Vibrio cholerae	3375	6500

(*Continued*)

Table 1.9 (*Continued*)

Organisms	**Energy Dosage of Ultraviolet Radiation (UV Dose) in μWs/cm^2 Needed for Kill Factor**	
Molds	**90%**	**99%**
Aspergillus flavus	60,000	99,000
Aspergillus glaucus	44,000	88,000
Aspergillus niger	132,000	330,000
Mucor racemosus A	17,000	35,200
Mucor racemosus B	17,000	35,200
Oospora lactis	5000	11,000
Penicillium expansum	13,000	22,000
Penicillium roqueforti	13,000	26,400
Penicillium digitatum	44,000	88,000
Rhizopus nigricans	111,000	220,000
Protozoa	**90%**	**99%**
Paramecium	11,000	20,000
Algae		
Chlorella vulgaris	13,000	22,000
Helminthes		
Nematode eggs	45,000	92,000
Virus	**90%**	**99%**
Bacteriophage – *Escherichia coli*	2600	6600
Infectious hepatitis A and E	5800	8000
Influenza	3400	6600
Poliovirus – Poliomyelitis	3150	6600
Tobacco mosaic	240,000	440,000
Yeast	**90%**	**99%**
Brewers yeast	3300	6600
Common yeast cake	6000	13,200
Saccharomyces cerevisiae	6000	13,200
Saccharomyces ellipsoideus	6000	13,200
Saccharomyces spores	8000	17,600

anthrax attacks; the level of radiation chosen to kill anthrax spores was so high that it often changed the physical appearance of the mail. A facility in Bridgeport, NJ, operated by Sterigenics International, uses a Rhodotron continuous wave electron beam accelerator built by IBA Industrial to irradiate the mail. A few facilities were planning to use Cobalt-60 sources, though it is unclear whether this was ever done. During irradiation, an intense stream of electrons (or X-rays if X-ray technology is used) strikes the mail and any anthrax spores it may contain. The radiation dose is very high, about 56 kGy of radiation, which is approximately 2 million times more than a chest X-ray.

List of Potential Bioterrorism Agents[25]

CDC Category A Agents

Highest priority agents: Organisms that pose a risk to national security because:

- ○ They can be easily disseminated or transmitted from person to person
- ○ They result in high mortality rates and have the potential for major public health impact
- ○ They might cause public panic and social disruption
- ○ They require special action for public health preparedness.

- Anthrax (*Bacillus anthracis*)
- Botulism (*Clostridium botulinum* toxin)
- Plague (*Yersinia pestis*)
- Smallpox (*Variola virus*)
- Tularemia (*Franciscella tularensis*)
- Viral hemorrhagic fever (Arenaviruses, Bunyaviruses).

CDC Category B Agents

Second highest priority agents:

- ○ Organisms that are moderately easy to disseminate
- ○ Result in moderate morbidity rates and low mortality rates
- ○ Require enhanced diagnostic capacity and disease surveillance.

- Brucellosis (*Brucella* species)
- Epsilon toxin of *Clostridium perfringens*
- Food safety threats (*Salmonella* species, *Escherichia coli* O157:H7, *Shigella*)
- Glanders (*Burkholderia mallei*)
- Melioidosis (*Burkholderia pseudomallei*)
- Psittacosis (*Chlamydia psittaci*)
- Q fever (*Coxiella burnetii*)
- Ricin toxin from *Ricinus communis* (castor beans)
- *Staphylococcal enterotoxin* B
- Typhus fever (*Rickettsia prowazekii*)
- Viral encephalitis (e.g. Venezuelan equine encephalitis, eastern equine encephalitis, western equine encephalitis)
- Water safety threats (e.g. *Vibrio cholerae*, *Cryptosporidium parvum*).

CDC Category C Agents

These third highest priority agents include emerging pathogens that could be engineered for mass spread in the future because:

- ○ They are easily available
- ○ They are easily produced and spread
- ○ They have potential for high morbidity and mortality rates and major health impact.

- Nipah virus
- Hantavirus
- Severe acute respiratory syndrome virus
- H1N1, a strain of influenza (flu)
- HIV/AIDS.

1.5 Summary

This chapter reviewed briefly dozens of sterilization methods. The effect of sterilization processes on plastic materials is important because most food and many medical supplies are already packaged before being processed for microbe elimination. Packaging is usually made from polymeric plastics. If the sterilization processes weaken the plastic films, they could affect shelf life and damage losses.

The effect of all these methods on plastics is not covered in the data chapters. This is because the effect of many is minimal on the plastic properties. The most commonly used processes get the focus in the data chapters. Appendix A, Guidelines for Component Sterilization based on Material and Process, does contain guidelines on the general suitability of many of the processes on various plastics.

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2 Introduction to Plastics and Polymers

The most basic component of plastic and elastomer materials is the polymer. The word polymer is derived from the Greek term for "many parts." Polymers are large molecules comprised of many repeat units, called monomers, that have been chemically bonded into long chains. Since World War II, the chemical industry has developed a large quantity of synthetic polymers to satisfy the materials needs for a diverse range of products, including paints, coatings, fibers, films, elastomers, and structural plastics. Literally thousands of materials can be called "plastics," although the term today is typically reserved for polymeric materials, excluding fibers, which can be molded or formed into solid or semisolid objects. As of the beginning of 2011, IDES The Plastics Web® (http://www.ides.com) listed over 85,000 different grades of plastic from over 800 suppliers.

This book narrows the plastics field down those used in food packaging and medical applications requiring sterilization.

The subject of this chapter includes polymerization chemistry and the different types of polymers and how they can differ from each other. Since plastics are rarely "neat," reinforcement, fillers, and additives are reviewed. A basic understanding of plastic and polymer chemistry will make the discussion of properties of specific plastics easier to understand and it also provides a basis for the introductions of the plastic families in later chapters. This section is taken from *The Effect of Temperature and Other Factors on Plastics*[1] and *Permeability Properties of Plastics and Elastomers*,[2] but it has been rewritten, expanded, and refocused on polymers as they relate to food packaging and medical uses.

2.1 Polymerization

Polymerization is the process of chemically bonding monomer building blocks to form large molecules. Commercial polymer molecules are usually thousands of repeat units long. Polymerization can proceed by one of several methods. The two most common methods are called addition and condensation polymerization.

2.1.1 Addition Polymerization

In addition polymerization (sometimes called chain-growth polymerization), a chain reaction adds new monomer units to the growing polymer molecule one at a time through double or triple bonds in the monomer. The polymerization process takes place in three distinct steps:

1. Chain initiation – usually by means of an initiator that starts the polymerization process. The reactive initiation molecule can be a radical (free radical polymerization), cation (cationic polymerization), anion (anionic polymerization), and/or organometallic complex (coordination polymerization).
2. Chain propagation – a monomer adds onto the chain and each new monomer unit creates an active site for the next attachment. The net result is shown in Fig. 2.1.
3. Chain termination – the radical, cation, or anion is "neutralized" stopping the chain propagation.

Many of the plastics discussed in later chapters of this book are formed in this manner. Some of the plastics made by addition polymerization include polyethylene, polyvinyl chloride, acrylics, polystyrene, and polyoxymethylene (acetal).

2.1.2 Condensation Polymerization

The other common method is condensation polymerization (also called step-growth polymerization) in which the reaction between monomer units and the growing polymer chain end group releases a small molecule, often water, as shown in Fig. 2.2. The monomers in this case have two reactive groups. This reversible reaction will reach equilibrium and halt unless this small molecular by-product is removed.

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00002-2

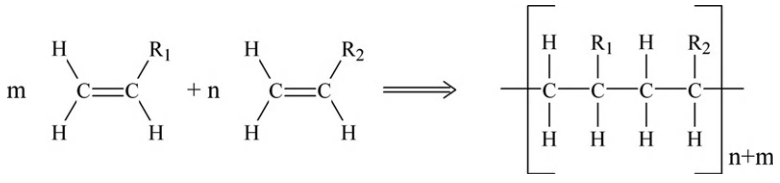


Figure 2.1 Addition polymerization.

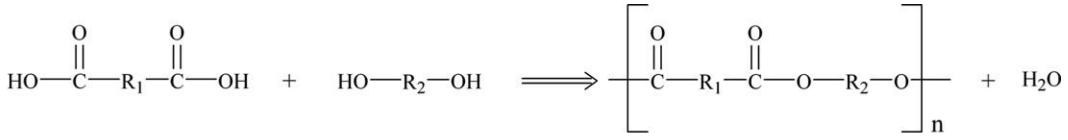


Figure 2.2 Condensation polymerization.

Polyesters and polyamides are among the plastics made by this process.

Understanding the polymerization process used to make a particular plastic gives insight into the nature of the plastic. For example, plastics made via condensation polymerization, in which water is released, can degrade when exposed to water at high temperatures. Polyesters such as polyethylene terephthalate (PET) can degrade by a process called hydrolysis when exposed to acidic, basic, or even some neutral environments severing the polymer chains. The polymer's properties are degraded as a result.

2.2 Copolymers

A copolymer is a polymer formed when two (or more) different types of monomer are linked in the same polymer chain, as opposed to a homopolymer where only one monomer is used. If exactly three monomers are used, it is called a terpolymer.

Monomers are only occasionally symmetric; the molecular arrangement is the same no matter which end of the monomer molecule you are looking at. The arrangement of the monomers in a copolymer can be head-to-tail, head-to-head, or tail-to-tail. Since a copolymer consists of at least two types of repeating units, copolymers can be classified based on how these units are arranged along the chain. These classifications include:

- Alternating copolymer
- Random copolymer (statistical copolymer)
- Block copolymer
- Graft copolymer.

When the two monomers are arranged in an alternating fashion of course, the polymer is called an alternating copolymer:

—A—B—A—B—A—B—A—B—A—B—A—B—A—B—A—B—A—B—

Alternating Copolymer

In the following examples, A and B are different monomers. Keep in mind the A and B do not have to be present in a one to one ratio. In a random copolymer, the two monomers may follow in any order:

—A —A—B—A—B—B—A—B—A—A—B—B—B—A—B—A—A—

Random Copolymer

In a block copolymer, all one type of monomer are grouped together, and all the second monomer are grouped together. A block copolymer can be thought of as two homopolymers joined together at the ends:

—A—A—A—A—A—A—A—A—A—B—B—B—B—B—B—B—B—B—

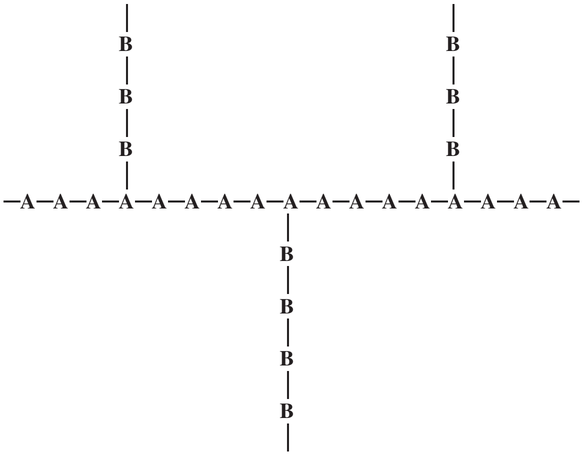
Block Copolymer

A polymer that consists of large grouped blocks of each of the monomers is also considered a block copolymer:

—A—A—A—A—A—A—B—B—B— B—B—B—A—A—A—A—A—

Block Copolymer

When chains of a polymer made of monomer B are connected onto a polymer chain of monomer A, we have a graft copolymer:



Branched/Grafted Copolymer

High-impact polystyrene, or HIPS, is a graft copolymer. It is a polystyrene backbone with chains of polybutadiene grafted onto the backbone. The polystyrene gives the material strength, but the rubbery polybutadiene chains give it resilience to make it less brittle.

2.3 Linear, Branched, and Cross-Linked Polymers

Some polymers are linear, a long chain of connected monomers. Polyethylene, polyvinyl chloride, Nylon 66, and polymethyl methacrylate are some linear commercial examples found in this book. A branched polymer can be visualized as a linear polymer with side chains of the same polymer attached to the main chain. While the branches may in turn be branched, they do not connect to another polymer chain. The ends of the branches are not connected to anything. Special types of branched polymers include star polymers, comb polymers, brush polymers, dendronized polymers,[3] ladders, and dendrimers. A cross-linked polymer, sometimes called network polymer, is one in which different chains are connected. Essentially the branches are connected to different polymer chains on the ends. These three polymer structures are shown in Fig. 2.3.

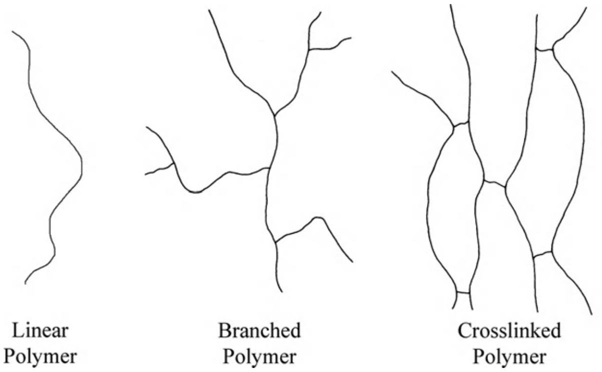


Figure 2.3 Linear, branched, and cross-linked polymers.

2.4 Polarity

A molecule is two or more atoms joined by a covalent bond. Basically, the positively charged atom nuclei share the negatively charged electrons. However, if the atoms are different they may not share the electrons equally. The electrons will be denser around one of the atoms. This would make that end more negatively charged than the other end and that creates a negative pole and a positive pole (a *dipole*), and such a bond is said to be a *polar bond* and the molecule is polar and has a *dipole moment*. A measure of how much an atom attracts electrons is *electronegativity*. The electronegativity of common atoms in the polymers follows:

$$\mathrm{F} > \mathrm{O} > \mathrm{Cl} \text{ and } \mathrm{N} > \mathrm{Br} > \mathrm{C} \text{ and } \mathrm{H}$$

The polarity of a molecule affects the attraction between molecular chains, which affects the structure of the polymer and the attraction of polar molecules, so one would expect polarity to affect solubility that affects permeability.

How does one predict molecular polarity? When there are no polar bonds in a molecule, there is no permanent charge difference between one part of the molecule and another so the molecule is nonpolar. For example, the Cl_2 molecule has no polar bonds because the electron charge is identical on both atoms. It is therefore a nonpolar molecule. The C—C and C—H bonds in hydrocarbon molecules, such as ethane, C_2H_6, are not significantly polar, so hydrocarbons are nonpolar molecular substances and hydrocarbon polymers like polyethylene or polypropylene are nonpolar also.

A molecule can possess polar bonds and still be nonpolar, however. If the polar bonds are evenly (or symmetrically) distributed, the bond dipoles cancel

Table 2.1 Dipole Moments in Some Small Molecules

Molecule	Dipole Moment	Molecule	Dipole Moment	Molecule	Dipole Moment
H_2	0	HF	1.75	CH_4	0.0
O_2	0	H_2O	1.84	CH_3Cl	1.86
N_2	0	NH_3	1.46	CCl_4	0
Cl_2	0	NF_3	0.24	CO_2	0
Br_2	0	BF_3	0		

and do not create a molecular dipole. For example, the three bonds in a molecule of CCl_4 are significantly polar, but they are symmetrically arranged around the central carbon atom. No side of the molecule has more negative or positive charge than another side, and so the molecule is nonpolar. Table 2.1 shows the dipole moments of several small molecules.

Generally, polar polymers are more permeable to water than nonpolar polymers. Figure 2.4 shows a qualitative ranking of some polymers polarities.

2.5 Unsaturation

Up to this point in the discussion of polymer chemistry, the atom-to-atom structure has not been discussed. The covalent bonds between atoms in a polymer can be single, double, triple bonds or even rings. The presence of bonds higher than single bonds generally makes the polymer molecule stiffer and reduces rotation along the polymer chain and that can affect its properties. It is easier to discuss molecules first and then extend that discussion to polymers. Saturated molecules only contain single bonds with no rings.

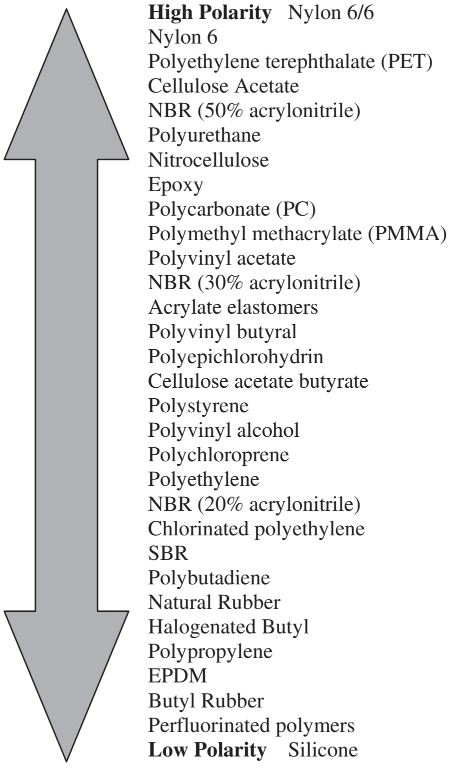


Figure 2.4 Qualitative ranking of polymer polarities.

Often when talking about molecular unsaturation, the degree of unsaturation (DoU) is noted. To calculate the DoU, if the molecular formula is given, it can be calculated using the formula is Eqn (2.1):

$$\mathrm{DoU} = \frac{2\mathrm{C}+2+\mathrm{N}-\mathrm{X}-\mathrm{H}}{2} \tag{2.1}$$

- C = number of carbons
- N = number of nitrogens
- X = number of halogens (F, Cl, Br, I)
- H = number of hydrogens
- Oxygen and sulfur are not included in the formula because saturation is unaffected by these elements.

Examples:
Ethylene: C_2H_4

$$\begin{aligned}\mathrm{DoU} &= \frac{2\mathrm{C}+2+\mathrm{N}-\mathrm{X}-\mathrm{H}}{2}\\ &= \frac{2{*}2+2+0-0-4}{2} = 1\end{aligned} \tag{2.2}$$

Benzene: C_6H_6

$$\begin{aligned}\mathrm{DoU} &= \frac{2\mathrm{C}+2+\mathrm{N}-\mathrm{X}-\mathrm{H}}{2}\\ &= \frac{2{*}6+2+0-0-6}{2} = 4\end{aligned} \tag{2.3}$$

When polymers are used, the formula shown is often the repeating unit. This will often have two bonds that are shown to which the repeating unit is supposed to attach. If applying a DoU formula to the repeating unit, one would remove the "+2" in the formula.

Examples:

Polyethylene (PE): $-(CH_2-CH_2)_n-$

$$\begin{aligned}\text{DoU} &= \frac{2C + N - X - H}{2} \\ &= \frac{2{*}2 + 0 - 0 - 4}{2} = 0\end{aligned} \tag{2.4}$$

Polyphenylene sulfone (PPS): $-(C_6H_4-S)_n-$

$$\begin{aligned}\text{DoU} &= \frac{2C + N - X - H}{2} \\ &= \frac{2{*}6 + 0 - 0 - 4}{2} = 4\end{aligned} \tag{2.5}$$

2.6 Steric Hindrance

As described earlier in this chapter, polymers are long chains of atoms linked together. They may be flexible and bendable. To explain this, one may visual them as a ball-and-stick model. In chemistry, the ball-and-stick model is a molecular model of a chemical substance that aims to display both the three-dimensional (3D) position of the atoms and the bonds between them. The atoms are typically represented by spheres, connected by rods that represent the bonds. Double and triple bonds are usually represented by two or three curved rods, respectively. The chemical element of each atom is often indicated by the sphere's color. The top of Fig. 2.5 shows a drawing of a ball-and-stick model of a molecule. Figure 2.5 also indicates that there is free rotation around the single bonds. If there were a double or triple bond, there would not be any rotation possible around those bonds. Similarly, ring structures, while they might flex a little bit, inhibit rotation. In some cases, such as shown in the bottom of Fig. 2.5, large atoms or bulky side groups might bump into each other as the molecular rotates around single bonds. This is called *sterically hindered* or *steric hindrance*. Hindered or inhibited rotation stiffens the polymer molecule and dramatically affects its physical properties.

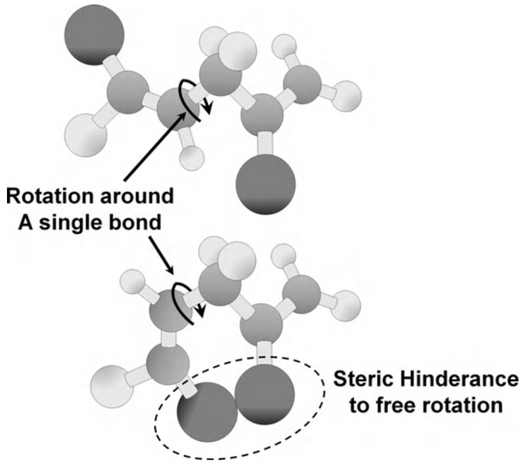


Figure 2.5 Steric hindrance shown with a ball-and-stick molecular model.

2.7 Isomers

Isomers (from Greek isomerès; isos = "equal," méros = "part") are compounds with the same molecular formula but a different arrangement of the atoms in space. There are many kinds of isomers and the properties can differ widely or almost not at all.

2.7.1 Structural Isomers

Structural isomers have the atoms that are arranged in a completely different order as shown in Fig. 2.6. Here both polymer repeating groups have the same formula, -C_4H_8-, but the atoms are arranged differently. The properties of structural isomers may be very different from each other.

Often the repeating group in a polymer is exactly the same formula, but the repeating group is flipped over as shown in Fig. 2.7. If one views the repeating group as having a head and a tail, then the different ways to connect neighboring repeating units is head−tail, head−head, and tail−tail.

2.7.2 Geometric Isomers

When there is a carbon−carbon double bond in a molecule, there might also be two ways to arrange

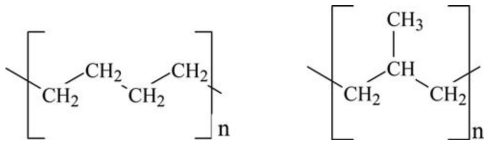


Figure 2.6 Structural isomers.

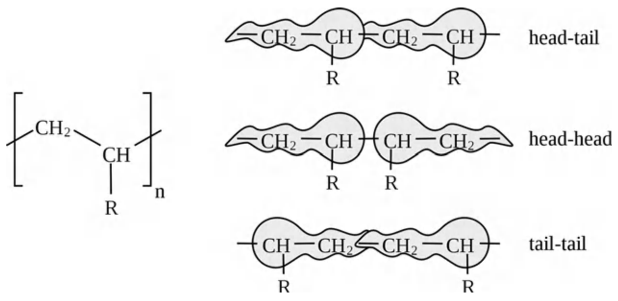


Figure 2.7 Head-to-tail isomers.[4]

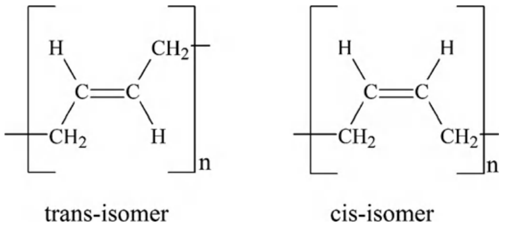


Figure 2.8 *Cis*- and *trans*-isomers.

the groups attached to the double bonds. This is best seen in side-by-side structures such as shown in Fig. 2.8.

These are called *geometric isomers* that owe their existence to hindered rotation about double bonds. If the substituents are on the same side of the double bond, then the isomer is referred to as: *cis*- (Latin: on this side). If the substituents are on the opposite side of the double bond, they are referred to as: *trans*- (Latin: across).

2.7.3 Stereosiomers – Syndiotactic, Isotactic, and Atactic

Stereoisomerism occurs when two or more molecules have identical molecular formula and the same structural formula (i.e. the atoms are arranged in the same order). However, they differ in their 2D or 3D spatial arrangements of their bonds – which mean different spatial arrangement of the atoms – even though they are bonded in the same order. This may best be understood by example.

Polypropylenes all have the same simplified structural polymer formula of polypropene as shown in Fig. 2.9.

However, there are subtle differences in the ways to draw this structure. Figure 2.10 shows a longer structure of polypropene, one that also shows some 3D structure. This structure shows how some bonds (the dotted lines) are behind the plane of the paper and others stick out of the paper (the ones on the ends of the little triangular wedges). In this structure, some of the CH_3 groups are above the paper plane and others are behind the paper plane. This is called *atactic* polypropene.

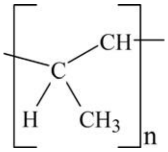


Figure 2.9 The structure of polypropene.

Atactic polypropene has at random about 50% of hydrogen/methyl groups in front/back of C–C–C chain viewing plane. This form of polypropene is amorphous (noncrystalline, discussed in Section 2.9.3) and has an irregular structure due to the random arrangement of the methyl groups attached to the main carbon–carbon chain. It tends to softer and more flexible than the other forms (described below) and is used for roofing materials, sealants, and other weatherproof coatings.

Isotactic polypropene has all the methyl groups in front of C–C–C chain viewing plane and all the H's at back as shown in Fig. 2.11. This stereoregular structure maximizes the molecule–molecule contact and so increasing the intermolecular forces compared to the atactic form. This regular structure is much stronger (than the atactic form above) and is used in sheet and film form for packaging and carpet fibers.

Syndiotactic polypropene has a regular alternation of 50% of hydrogen/methyl groups in front/back of C–C–C chain viewing plane as shown in Fig. 2.12. Its properties are similar to isotactic polypropene rather than the atactic form, i.e. the regular polymer structure produces stronger intermolecular forces and a more crystalline form than the atactic polypropene.

2.8 Inter- and Intramolecular Attractions in Polymers

The attractive forces between different polymer chains or segments within polymer chains play a large part in determining a polymer's properties. As

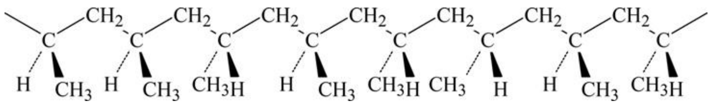


Figure 2.10 The structure of atactic polypropene.

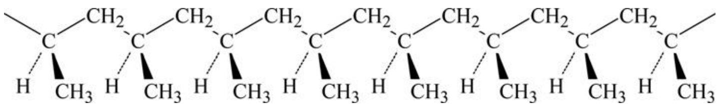


Figure 2.11 The structure of isotactic polypropene.

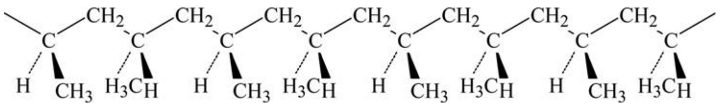


Figure 2.12 The structure of syndiotactic polypropene.

mentioned in Section 2.4, atoms can have polarity or dipole moments. Since negative charges are attracted to the opposite positive charges and repelled by like charges, it is possible to generate attractions that lead to certain structures.

2.8.1 Hydrogen Bonding

One of the strongest dipole interactions is the attraction of some oxygen atoms to hydrogen atoms even though they are covalently bonded to other atoms. This is called hydrogen bonding and a schematic of it is shown in Fig. 2.13. The N—H bond provides a dipole when the hydrogen has a slightly positive charge and the nitrogen has a slight negative charge. The carbonyl group, the C=O, likewise is a dipole, where the oxygen has the slight negative charge and the carbon is slightly positive. When polymer chains line up, these *hydrogen bonds* are formed (indicated by the wide Gy bars in the figure), bonds that are far weaker than the covalent bonds but bonds of significant strength nonetheless.

Other side groups on the chain polymer can lend the polymer to hydrogen bonding between its own chains. These stronger forces typically result in higher tensile strength and higher crystalline melting points. Polyesters have dipole—dipole bonding between the oxygen atoms in C=O groups and the hydrogen atoms in H—C groups. Dipole bonding is not as strong as hydrogen bonding.

2.8.2 Van der Waals Forces

Many polymers, such as polyethylene, have no permanent dipole. However, attractive forces between polyethylene chains arise from weak forces called Van der Waals forces. Van der Waals forces are much weaker than chemical bonds, and random thermal motion around room temperature can usually overcome or disrupt them.

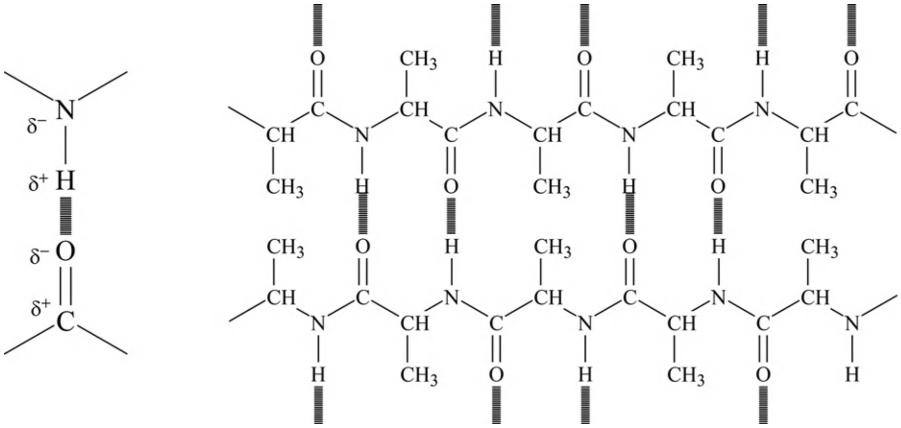


Figure 2.13 Schematic of hydrogen bonding in a pair of polymer chains.

Molecules can be thought of as being surrounded by a cloud of negative electrons. But the electrons are mobile, and at any one instant, they might find themselves toward one end of the molecule, making that end slightly negative (δ−). The other end will be momentarily short of electrons and so becomes (δ+). Basically, temporary fluctuating dipoles are present all molecules and the forces due to these dipoles are the basis for Van der Waals attraction. Van der Waals forces are quite weak, however, so polyethylene can have a lower melting temperature compared to other polymers that have hydrogen bonding.

2.8.3 Chain Entanglement

Polymer molecules are long chains, which can become entangled with one another, much like a bowl of spaghetti. Along with intermolecular forces, chain entanglement is an important factor contributing to the physical properties of polymers. The difficulty in untangling their chains makes polymers and the plastic made from them strong and resilient.

2.9 General Classifications

Besides the chemical structures of the polymers in the plastics, there are several other characterizations that are important including molecular weight, thermoplastics vs. thermosets, and crystallinity.

2.9.1 Molecular Weight

A polymer's molecular weight is the sum of the atomic weights of individual atoms that comprise a molecule. It indicates the *average* length of the bulk resin's polymer chains. All polymer molecules of a particular grade do not all have the exact same molecular weight. There is a range or distribution of molecular weights. There are two important but different ways to calculate molecular weight. The most important one is called the number-average molecular weight, M_n. For all "i" molecules in a sample, the number-average molecular weight is calculated using Eqn (2.6).

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \tag{2.6}$$

where:

i is the number of polymer molecules

N_i is the number of molecules that have the molecular weight M_i.

The weight-average molecular weight is a different calculation as in Eqn (2.7)..

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \tag{2.7}$$

Figure 2.14 shows a molecular weight distribution chart with the two different molecular weight measures noted on it. The ratio M_w/M_n is called the *molar-mass dispersity index*[5] (often called *polydispersity*).[5] If all the polymer chains are exactly the same, then the number-average and weight-average molecular weights are exactly the same and the polydispersity is "1." The larger the molar-mass dispersity index, the wider the molecular weight distribution. The molecular weight range can affect many properties of plastic materials.

Another common means of expressing the length of a polymer chain is the *degree of polymerization*, this quantifies the average number of monomers incorporated into the polymer chain. The average molecular weight can be determined by several means, but this subject is beyond the scope of this book. Low molecular weight polyethylene chains

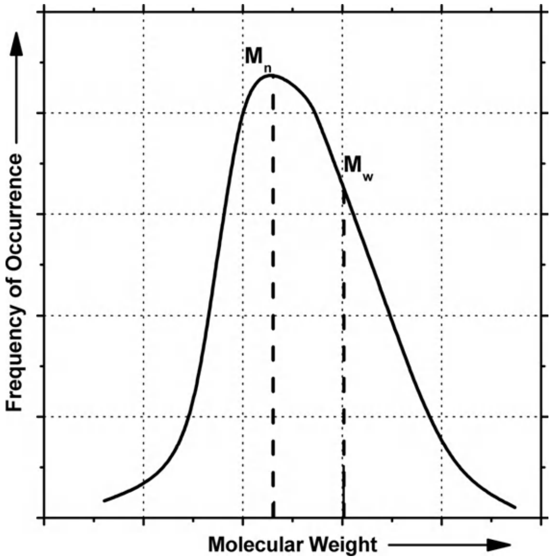


Figure 2.14 Hypothetical molecular weight distribution plot showing number- and weight-average molecular weights.

have backbones as small as 1000 carbon atoms long. Ultrahigh molecular weight polyethylene chains can have 500,000 carbon atoms along their length. Many plastics are available in a variety of chain lengths or different molecular weight grades. These resins can also be classified indirectly by a viscosity value, rather than molecular weight. Within a resin family, such as polycarbonate, higher molecular weight grades have higher melt viscosities. For example, in the viscosity test for polycarbonate, the melt flow rate ranges from approximately 4 g/10 min for the highest molecular weight, standard grades to more than 60 g/10 min for lowest molecular weight, high flow, specialty grades.

Selecting the correct molecular weight for an injection molding application generally involves a balance between filling ease and material performance. If the application has thin-walled sections, a lower molecular weight/lower viscosity grade offers better flow. For normal wall thicknesses, these resins also offer faster mold cycle times and fewer molded in stresses. The stiffer flowing, high molecular weight resins offer the ultimate material performance, being tougher and more resistant to chemical and environmental attack. Higher molecular weight films orient better (see Section 2.9.4 for details on orientation). Lower molecular weight films are often optically clearer.

Molecular weight of the polymers that are used in engineering plastics affects many of the plastics properties. While it is not always known exactly what the molecular weights are, as mentioned above higher flowing plastics of a given series of products generally are lower molecular weight polymers. Molecular weight can affect the permeation properties as shown in Fig. 2.15.

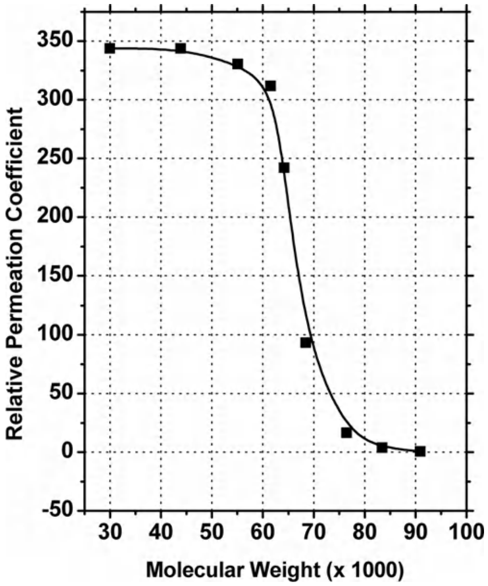


Figure 2.15 Water permeation of ethylene–vinyl alcohol copolymer vs. polymer molecular weight.[6]

Dispersity can also have an effect on permeation rates. For polymers, large molar-mass dispersity index implies a significant amount of low molecular weight polymer is present and that can act like a plasticizer that increases permeation rates (see Section 2.10.3.10 on plasticizers).

2.9.2 Thermosets vs. Thermoplastics

A plastic falls into one of two broad categories depending on its response to heat: thermoplastics or thermosets. Thermoplastics soften and melt when heated and harden when cooled. Because of this behavior, these resins can be injection molded, extruded, or formed via other molding techniques. This behavior also allows production scrap runners and trimmings to be reground and reused. Thermoplastics can often be recycled.

Unlike thermoplastics, thermosets react chemically to form cross-links, as described earlier that limit chain movement. This network of polymer chains tends to degrade, rather than soften, when exposed to excessive heat. Until recently, thermosets could not be remelted and reused after initial curing. Recent advances in recycling have provided new methods for remelting and reusing thermoset materials.

2.9.3 Crystalline vs. Amorphous

Thermoplastics are further classified by their crystallinity or the degree of order within the polymer's overall structure. As a crystalline resin cools from the melt, polymer chains fold or align into highly ordered crystalline structures as shown in Fig. 2.16.

Some plastics can be completely amorphous or crystalline. Often plastics specifications will report what percent of it is crystalline, such as 73% crystallinity. Generally, polymer chains with bulky side groups cannot form crystalline regions. The degree of crystallinity depends upon both the polymer and

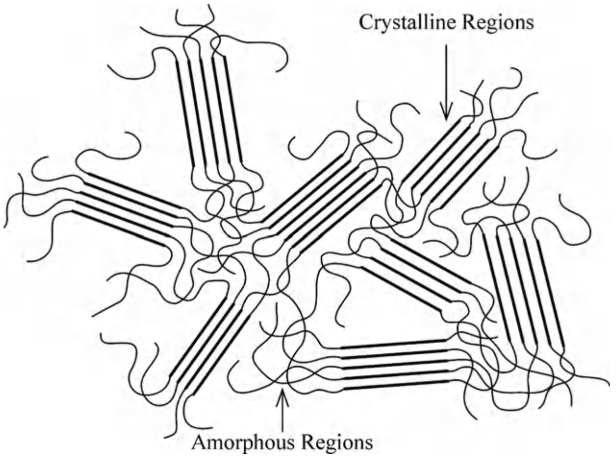


Figure 2.16 Many plastics have crystalline and amorphous regions.

the processing technique. Some polymers such as polyethylene crystallize quickly and reach high levels of crystallinity. Others, such as PET polyester, require slow cooling to crystallize. If cooled quickly, PET polyester remains amorphous in the final product.

Crystalline and amorphous plastics have several characteristic differences. Amorphous polymers do not have a sharp melting point but do have what is called a glass transition temperature, T_g. A glass transition temperature is the temperature at which a polymer changes from hard and brittle to soft and pliable. The force to generate flow in amorphous materials diminishes slowly as the temperature rises above the glass transition temperature. In crystalline resins, the force requirements diminish quickly as the material is heated above its crystalline melt temperature. Because of these easier flow characteristics, crystalline resins have an advantage in filling thin-walled sections of a mold. Crystalline resins generally have superior chemical resistance, greater stability at elevated temperatures and better creep resistance. Amorphous plastics typically have better impact strength, less mold shrinkage, and less final part warping than crystalline materials. Higher crystallinity usually leads to lower permeation rates. End-use requirements usually dictate whether an amorphous or crystalline resin is preferred.

2.9.4 Orientation

When packaging films made from plastic polymers are made, the polymer molecules are randomly intertwined like a bowl of spaghetti. They are amorphous. The polymer molecules are coiled and twisted and have no particular alignment, unless they have crystallized during cooling or aging. However, if the film is drawn or stretched, the amorphous regions of the polymer chains are straightened and aligned to the direction of drawing. The process for doing this is discussed in previously cited literature.[2]

2.10 Plastic Compositions

Plastics are usually formulated products meaning that they are not always neat polymers. They may be blends of polymers and they may have any or many additives used to tailor performance properties.

2.10.1 Polymer Blends

Polymers can often be blended. Occasionally, blended polymers have properties that exceed those of either of the constituents. For instance, blends of polycarbonate resin and PET polyester, originally created to improve the chemical resistance of polycarbonate, actually have fatigue resistance and low-temperature impact resistance superior to either of the individual polymers.

Sometimes, a material is needed that has some of the properties of one polymer and some of the properties of another. Instead of going back into the laboratory and trying to synthesize a brand new polymer with all the properties wanted, two polymers can be melted together to form a blend, which will hopefully have some properties of both.

Two polymers that do actually mix well are polystyrene and polyphenylene oxide. A few other examples of polymer pairs that will blend are:

- Polyethylene terephthalate with polybutylene terephthalate
- Polymethyl methacrylate with polyvinylidene fluoride.

Phase-separated mixtures are obtained when one tries to mix most polymers. But strangely enough, the phase-separated materials often turn out to be rather useful. They are called immiscible blends.

Polystyrene and polybutadiene are immiscible. When polystyrene is mixed with a small amount of polybutadiene, the two polymers do not blend.

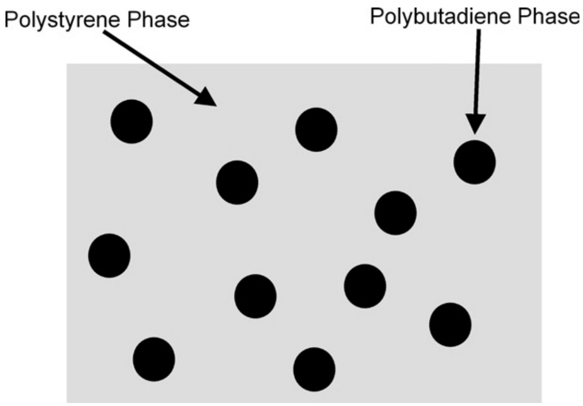


Figure 2.17 Immiscible blend of polystyrene and polybutadiene.

The polybutadiene separates from the polystyrene into little spherical blobs. If this mixture were viewed under a high-power microscope, something that looks like the picture in Fig. 2.17 would be seen.

Multiphase polymer blends are of major economic importance in the polymer industry. The most common examples involve the impact modification of a thermoplastic by the microdispersion of a rubber into a brittle polymer matrix. Most commercial blends consist of two polymers combined with small amounts of a third, compatibilizing polymer, typically a block or graft copolymer.

Multiphase polymer blends can be easier to process than a single polymer with similar properties. The possible blends from a given set of polymers offer many more physical properties than do the individual polymers. This approach has shown some success but becomes cumbersome when more than a few components are involved.

Blending two or more polymers offers yet another method of tailoring resins to a specific application. Because blends are only physical mixtures, the resulting polymer usually has physical and mechanical properties that lie somewhere between the values of its constituent materials. For instance, an automotive bumper made from a blend of polycarbonate resin and thermoplastic polyurethane elastomer gains rigidity from the polycarbonate resin and retains most of the flexibility and paintability of the polyurethane elastomer. For business machine housings, a blend of polycarbonate and ABS (acrylonitrile−butadiene−styrene copolymer) resins offers the enhanced performance of polycarbonate flame retardance and ultraviolet (UV) stability at a lower cost.

Additional information on the subject of polymer blends is available in the literature.[7−9]

2.10.2 Elastomers

Elastomers are a class of polymeric materials that can be repeatedly stretched to over twice the original length with little or no permanent deformation. Elastomers can be made of either thermoplastic or thermoset materials and generally are tested and categorized differently than rigid materials. They are commonly selected according to their hardness and energy-absorption characteristics, properties rarely considered in rigid thermoplastics. Elastomers are found in numerous applications, such as automotive bumpers and industrial hoses.

2.10.3 Additives

The properties of neat polymers are often not ideal for production or the end use. When this is the case, materials are added to the polymer to improve the performance shortfall. The additives can improve the processing and performance of the plastic. For whatever reason the additive is used, it can affect the permeation, diffusion, and solubility properties.

Additives encompass a wide range of substances that aid processing or add value to the final product.[10,11] Found in virtually all plastics, most additives are incorporated into a resin family by the supplier as part of a proprietary package. For example, you can choose standard polycarbonate resin grades with additives for improved internal mold release, UV stabilization, and flame retardance or nylon grades with additives to improve impact performance.

Additives often determine the success or failure of a resin or system in a particular application. Many common additives are discussed in the following sections. Except for reinforcement fillers, most additives are added in very small amounts.

2.10.3.1 Fillers, Reinforcement, Composites

Reinforcing fillers can be added in large amounts. Some plastics may contain as much as 60% reinforcing fillers. Often, fibrous materials, such as glass or carbon fibers, are added to resins to create reinforced grades with enhanced properties. For example, adding 30% short glass fibers by weight to nylon 6 improves creep resistance and increases stiffness by 300%. These glass-reinforced plastics usually suffer some loss of impact strength and ultimate elongation and are more prone to warping because of the relatively large difference in mold shrinkage between the flow and cross flow directions.

Plastics with nonfibrous fillers such as glass spheres or mineral powders generally exhibit higher stiffness characteristics than unfilled resins, but not as high as fiber-reinforced grades. Resins with particulate fillers are less likely to warp and show a decrease in mold shrinkage. Particulate fillers typically reduce shrinkage by a percentage roughly equal to the volume percentage of filler in the polymer, an advantage in tight tolerance molding.

Often reinforced plastics are called *composites*. Often, the plastic material containing the reinforcement is referred to as the matrix. One can envision a number of ways different reinforcing materials might be arranged in a composite. Many of these arrangements are shown in Fig. 2.18.

Particulates, in the form of pigments, to impart color may be added. On occasion particulate, called extender, is added to reduce the amount of relatively expensive polymer used, which reduces overall cost.

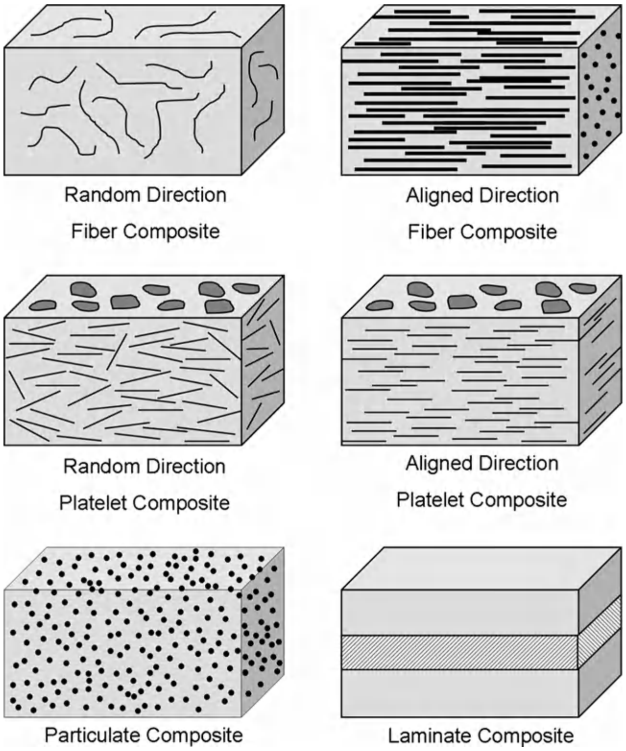


Figure 2.18 Several types of composite materials.

Platelet additives may impart color and luster, metallic appearance or a pearlescent effect, but they also can strongly affect permeation properties. Most of these additives have little or no permeation through themselves so when a film contains particulate additives, the permeating molecule must follow a path around the particulate additive as shown in Fig. 2.19. This is often called a *tortuous path effect*.

2.10.3.2 Combustion Modifiers, Fire, Flame Retardants, and Smoke Suppressants

Combustion modifiers are added to polymers to help retard the resulting parts from burning. Generally required for electrical and medical housing applications, combustion modifiers and their amounts vary with the inherent flammability of the base polymer. Polymers designed for these applications often are rated using an Underwriters Laboratories rating system. Use these ratings for comparison purposes only, as they may not accurately represent the hazard present under actual fire conditions.

2.10.3.3 Release Agents

External release agents are lubricants, liquids, or powders that coat a mold cavity to facilitate part removal. Internal release agents can accomplish the same purpose. The identity of the release agent is rarely disclosed, but frequently they are fine fluoropolymer powders, called micropowders, silicone resins, or waxes.

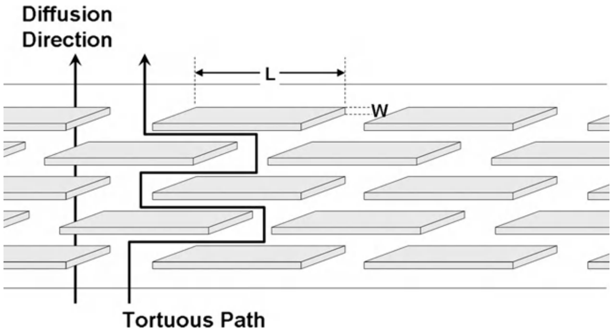


Figure 2.19 Tortuous path of permeant molecule through a particulate-containing film.

2.10.3.4 Slip Additives/Internal Lubricants

When polymeric films slide over each other, there is a resistance that is quantified in terms of the COF. Films with high COF tend to stick together instead of sliding over one another. Sticking makes the handling, use, and conversion of films difficult. To overcome sticking, slip agents are added.

Slip additives can be divided in two types, migrating and nonmigrating. Migrating slip additives are the most common class and they are used above their solubility limit in the polymer. These types of additives are molecules that have two distinct parts, typically pictured as a head and tail as shown in Fig. 2.7. One part of the molecule, usually the head, is designed to be soluble in the polymer (particularly when it is molten during processing) making up the plastic. The other part, the tail, is insoluble. As the plastic cools and solidifies from its molten state, these molecules migrate to the surface, where the insoluble end "sticks up" reducing the COF. This process is shown in Fig. 2.20. These additives are typically fatty acid amides.

There are migrating slip additives that are not of this two-part structure. One additive is perfluoropolyether synthetic oil marketed by DuPont™ under the trademark Fluoroguard®, which is an internal lubricant that imparts improved wear and low friction properties. Silicone fluids, such as those made by Dow Corning, can also act as a boundary lubricant. Both these materials may migrate to the surface of the plastic over time.

Some common nonmigrating slip additives include:

- Polytetrafluoroethylene in micropowder form imparts the lowest COF of any internal lubricant. Manufacturers and suppliers are many, including DuPont™ Zonyl® and 3M Dyneon™.
- Molybdenum disulfide, commonly called "*moly*" is a solid lubricant often used in bearing applications.
- Graphite is a solid lubricant used like molybdenum disulfide.

2.10.3.5 Antiblock Additives

Blocking is a surface effect between adjacent film layers that stick to one another. Blocking is quantified by the force needed to separate two film layers under controlled conditions. Two situations where blocking is an issue are the opening of blown film tubes after extrusion and film layer separation after packing and storage. Antiblock additives are used to overcome these issues.

Antiblock additives can be divided into two classes: inorganic and organic. Chemically inert, inorganic antiblock additives migrate to the film surface and partially stick out of the surface to create a microroughness of the film surface. Figure 2.21 illustrates this principle.

The detailed mechanism of how organic antiblock additives work is not yet understood. It is thought that a barrier layer is formed on the plastic film surface, thus inhibiting the two adjacent plastic film layers' adhesion. Their usage is limited. Organic antiblock additives were partially discussed above and will not be further mentioned here.

2.10.3.6 Catalysts

Catalysts, substances that initiate or change the rate of a chemical reaction, do not undergo a permanent change in composition or become part of the molecular structure of the final product. Occasionally used as setting agents, hardeners, curing agents, promoters, etc., they are added in minute quantities, typically less than 1%.

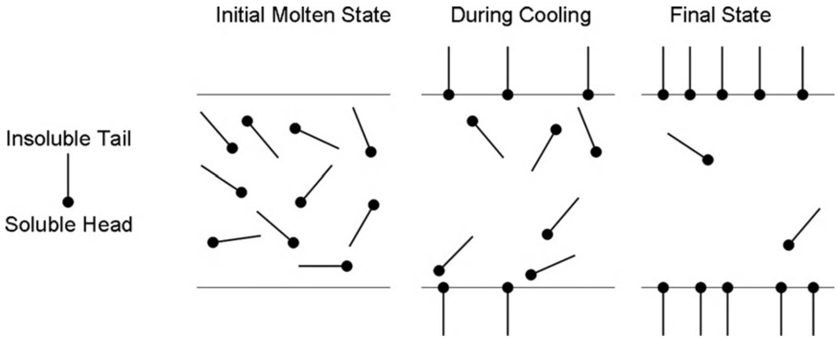


Figure 2.20 Mode of action of a typical migrating slip additive.

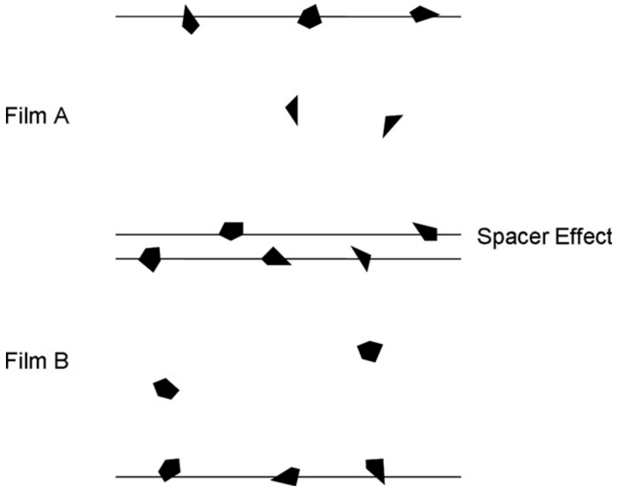


Figure 2.21 Antiblock additives maintain film separation.

2.10.3.7 Impact Modifiers and Tougheners

Many plastics do not have sufficient impact resistance for the use for which they are intended. Rather than change to a different type of plastic, they can be impact modified in order to fulfill the performance in use requirements. Addition of modifiers called impact modifiers or tougheners can significantly improve impact resistance. This is one of the most important additives. There are many suppliers and chemical types of these modifiers.

General-purpose impact modification is a very low level of impact modification. It improves room-temperature impact strength but does not take into account any requirements for low-temperature (below 0 °C) impact strength. For most of these types of applications, only low levels of impact modifier will be required (<10%).

Low-temperature impact strength is required for applications that require a certain level of low-temperature flexibility and resistance to break. This is, for example, the case for many applications in the appliance area. For this purpose, modifier levels between 5% and 15% of mostly reactive modifiers will be necessary. Reactive modifiers can bond chemically to the base polymer.

Super-tough impact strength may be required for applications that should not lead to a failure of the part even if hit at low-temperatures (−30 to −40 °C) under high speed. This requirement can only be fulfilled with high levels (20−25%) of reactive impact modifier with low glass-transition temperature (see Section 3.3.5).

2.10.3.8 Radiation Stabilizers

Radiation stabilizers: Also referred to in the art as "antirads," may be used to mitigate the effects of the gamma ray dose on plastics generally. Stabilizers like antioxidants and free-radial scavengers can prevent degradation and cross-linking. In general, polymers that contain aromatic-ring structures are more resistant to radiation effects compared to aliphatic polymers. However, many stabilizers like phenolics, hindered amine-light stabilizers, and phosphates, may offer some protection against gamma and electron beam radiation.

UV stabilizers: Another way plastics may degrade is by exposure to UV light. UV can initiate oxidation. Plastics that are used outdoors or exposed to lamps emitting UV radiation are subject to photooxidative degradation. UV stabilizers are used to prevent and retard photooxidation. Pigments and dyes may also be used in applications not requiring transparency. Photooxidative degradation starts at the exposed surface and propagates throughout the material.

2.10.3.9 Optical Brighteners

Many polymers have a slight yellowish color. They can be modified to appear whiter and brighter by increasing reflected bluish light (in the range of 400−600 nm). One way to accomplish this is by using an additive that absorbs in the UV range but re-emits the energy at higher wavelength. This effect is called fluorescence and these types of additives are called optical brighteners or fluorescent whitening agents.

2.10.3.10 Plasticizers

Plasticizers are added to help maintain flexibility in a plastic. Various phthalates are commonly used for this purpose. Since they are small molecules, they may extract or leach out of the plastic causing a loss of flexibility with time. Just as deliberately added small molecules may leach out, small molecules from the environment may be absorbed by the plastic and act like a plasticizer. The absorption of water by nylons (polyamides) is an example. Plasticizers increase the space between the polymers.

2.10.3.11 Pigments, Extenders, Dyes, and Mica

Pigments are added to give a plastic color, but they may also affect the physical properties. Extenders are usually cheap materials added to reduce the cost of a plastic resins. Dyes are colorants chemically different than pigments. Mica is a special pigment added to impact sparkle or metallic appearance.

2.10.3.12 Coupling Agents

The purpose of adding fillers is either to lower the cost of the polymer, make it tougher or stiffer or make it flame retardant so that it does not burn when it is ignited. Often the addition of the filler will reduce the elongation at break, the flexibility and in many cases the toughness of the polymer because the fillers are added at very high levels. One reason for the degradation of properties is that the fillers in most cases are not compatible with the polymers. The addition of coupling agents can improve the compatibility of the filler with the polymer. As a result, the polymer will like the filler more, the filler will adhere better to the polymer matrix and the properties of the final mixture (e.g. elongation, flexibility) will be enhanced.

2.10.3.13 Thermal Stabilizers

One of the limiting factors in the use of plastics at high temperatures is their tendency to not only become softer but also to thermally degrade. Thermal degradation can present an upper limit to the service temperature of plastics. Thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to occur. Plastics can be protected from thermal degradation by incorporating stabilizers into them. Stabilizers can work in a variety of ways but discussion of these mechanisms are beyond the purpose of this book.

2.10.3.14 Antistats

Antistatic additives are capable of modifying properties of plastics in such a way that they become antistatic, conductive, and/or improve electromagnetic interference shielding. Carbon fibers, conductive carbon powders, and other electrically conductive materials are used for this purpose.

When two (organic) substrates rub against each other electrostatic charges can build up. This is known as tribocharging. Electrostatic charges can impact plastic parts in several ways; one of the most annoying being the attraction of dust particles. One way to counter this effect is to use antistats (or antistatic additives). This effect is principally a surface effect, although one potential countermeasure (conductive fillers) converts it into a bulk effect.

Tools that decrease electrostatic charges and hence increase the conductivity of an organic substrate can be classified as:

- External antistat (surface effect)
- Conductive filler (bulk and surface effect)
- Internal antistat (surface effect).

An external antistat is applied via a carrier medium to the surface of the plastic part. The same considerations and limitations apply as with non-migrating slip additives. Conductive filler is incorporated into the organic substrates and builds up a conductive network on a molecular level. While both approaches are used in organic substrates, they are not the most common.

An internal antistat is compounded into the organic substrate and migrates to the plastic part surface. The same principle considerations apply as for migrating slip additives (see Fig. 2.20).

The need to protect sensitive electronic components and computer boards from electrostatic discharge during handling, shipping, and assembly provided the driving force for development of a different class of antistatic packaging materials. These are sophisticated laminates with very thin metalized films.

There are other additives used in plastics, but the ones discussed above are the most common.

2.11 Summary

The basis of all plastics is polymers. Most of this chapter did not go into the chemical structures of all the polymers. The data chapters start in Chapter 4 and the chemical structures of the polymers are discussed in the appropriate sections.

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3 Introduction to the Physical, Mechanical, and Thermal Properties of Plastics and Elastomers

Sterilization processes can have an effect on the properties of plastics and elastomers that are used in packaging food or in medical devices. In some cases, the properties may change so much that the plastics may fail during normal use. The properties affected range from appearance properties such as color or haze to mechanical properties relating to strength or flexibility. In some cases, sterilization chemicals can be absorbed by the plastic materials and may be slow to permeate out. The data chapters of this book deal with those details of property change. This chapter summarizes how those properties are measured and in many cases why they are important. The properties are grouped into three groups: physical, mechanical, and thermal.

3.1 Physical Property Testing

Measuring many of the physical properties of films is often done with the same equipment and in the same way as the properties of molded plastics are measured. Often the polymers used to make films are also used to make plastic molding resins. The physical property measurements done on molded samples of the same plastics should yield similar results to those measured on plastic films but are often different because the production of films can produce unique molecular structures as explained in Chapter 2. There are also physical factors that affect the property measurements, particularly the surface area to volume ratio of the test samples.[1] This section will describe how physical property tests are done.

3.1.1 Specific Gravity or Density

Density is the mass per unit volume of a material. Specific gravity is a measure of the ratio of mass of a given volume of material at 23 °C to the same volume of deionized water. Film producers commonly report "yield" on their specifications sheets. Yield is the area of film produced at a specific thickness per unit weight. The metric units are m^2/kg and English units are in in^2/lb. The density is used to calculate this.

One of the standard test procedures is ASTM D792-08 Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement. ISO 1183-1:2004 Plastics − Methods for determining the density of noncellular plastics − Part 1: Immersion method, liquid pycnometer method, and titration method is similar but not exactly the same. There are two basic test procedures in ASTM D792, Method A and Method B. Method A does the measurement in water and Method B uses other liquids. The test specimen is weighed in air and then weighed when immersed in distilled water at 23 °C. A sinker and wire may be use to hold the specimen completely submerged if required. A photograph of the instrument used for these measurement is shown if Fig. 3.1.

The specific gravity and density are calculated by Eqn (3.1) and Eqn (3.2), respectively.

$$\text{Specific gravity} = \frac{a}{((a+w)-b)} \tag{3.1}$$

where:

a = mass of specimen in air.

b = mass of specimen and sinker (if used) in water.

w = mass of totally immersed sinker if used and partially immersed wire.

$$\text{Density}\left(\text{kg/m}^3\right) = \left(\text{specific gravity}\right) \times 997.6 \tag{3.2}$$

Sometimes, the plastic being measured is sensitive to water. Method B of ASTM D792 allows the use of other liquids. In that case, the density of the liquid, *d*, is added to the calculation as shown in Eqn (3.3):

$$\text{Specific gravity} = \frac{a \times d}{((a+w)-b)} \tag{3.3}$$

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00003-4

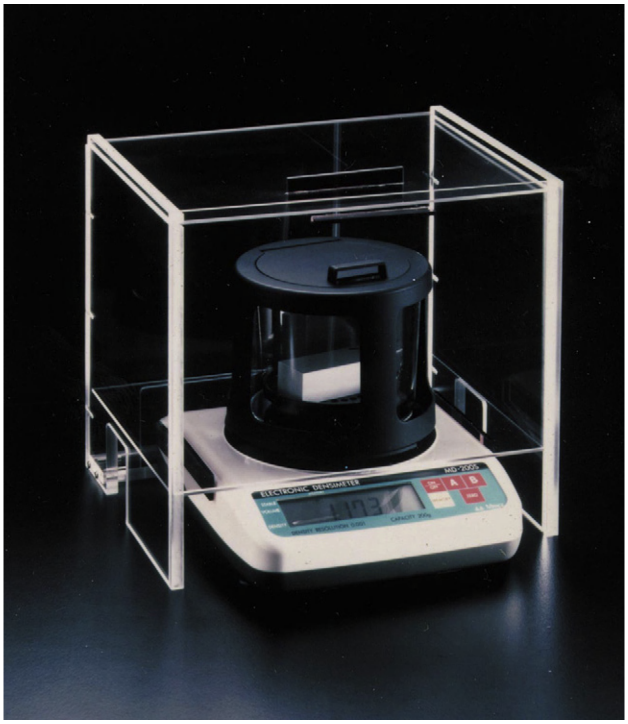


Figure 3.1 Picture of an instrument used to measure specific gravity (photo courtesy of Testing Machines Inc.). For color version of this figure, the reader is referred to the online version of this book.

3.1.2 Appearance: Color, Haze, and Gloss

3.1.2.1 Color

Color perception and measurement is a complex subject. It will be just briefly discussed here, but there are many references for greater detail.[2,3] Three things are required to see color, a light source, and object and an observer.

A *light source* is a real physical source of light, such as the sun or any type of light bulb. An *illuminant* is a plot of the relative energy vs. wavelength and these are different for various light sources. Several common illuminants used in color science are:

A	Incandescent
C	Average daylight
D_{65}	Noon daylight
F2	Cool white fluorescent
U30	Ultralume

By using illuminant to describe a light source, the course is quantified and standardized.

The object interacts with the incident light. It can absorb or reflect light. The reflection can be specular (like a mirror) or diffuse. Diffuse reflection is where incoming light is reflected in a broad range of directions. Some light may pass through as transmitted light. The amount of light reflected or transmitted can be quantified.

The observer may be the human eye. The eye has light sensors in it called cones, some sense red, some green, and some blue. Luminosity is the relative sensitivity of the eye to the various wavelengths of light. The observer needs to be quantified. The standard observer was experimentally derived to quantify the sensitivity of the average human eye to red, green, and blue light. The standard observer was called CIE 1931 2° because the work was done by International Commission on Illumination (CIE) in 1931 and used a 2° field of view. The work was later redone in 1964 and used a 10° field of view and became the CIE 1964 10° standard observer.

Figure 3.2 shows the mathematical forms that mimic the response of the human eye to light. z is the blue cone response, x is the red, and y the green.

When this is all applied to an instrument, it becomes the CIE tristimulus XYZ color scale and is calculated as follows:

$$X = \int (R \text{ or } T) \times \text{illuminant factor} \times x \text{ factor of standard observer}$$

$$Y = \int (R \text{ or } T) \times \text{illuminant factor} \times y \text{ factor of standard observer}$$

$$Z = \int (R \text{ or } T) \times \text{illuminant factor} \times z \text{ factor of standard observer}$$

where

$R = \%$ reflectance
$T = \%$ transmittance.

Sums are across the spectral range for which the instrument reads.

There are other tristimulus color scales, such as Hunter L, a, b and CIE $L^*a^*b^*$, but these can all be mathematically calculated from the XYZ color scale. The advantage to these two scales is that they are more visually uniform and easy to understand as shown in Fig. 3.3.

In a uniform color scale, the differences between points plotted in the color space correspond to visual differences between the colors plotted. The Hunter L, a, b color space, pictured Fig. 3.3, is organized in

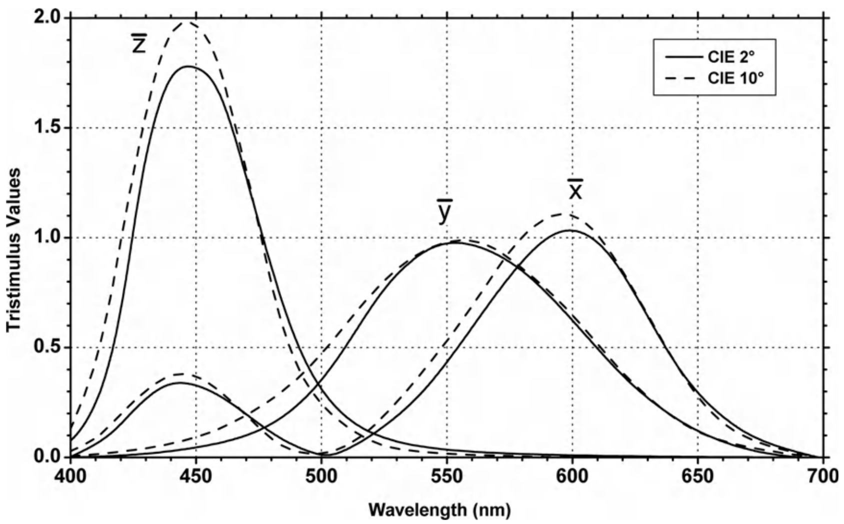


Figure 3.2 The 2° vs. 10° standard observer.

a cube form. The L axis runs from top to bottom. The maximum for L is 100, which would be a perfect white. The minimum for L would be zero, which would be black. The "a" and "b" axes have no specific numerical limits. Positive "a" is red. Negative "a" is green. Positive "b" is yellow. Negative "b" is blue. Often, the values of interest are change in color often due to exposure or aging, the parameters being ΔL, Δa, and Δb.

Hunter L, a, b color space was developed in the 1950s and 1960s.[4] CIE $L^*a^*b^*$ space is similar and was developed around 1964 but is more popular now than Hunter. As stated before, both are mathematically related to XYZ colors space, the formulas relating the two are different.

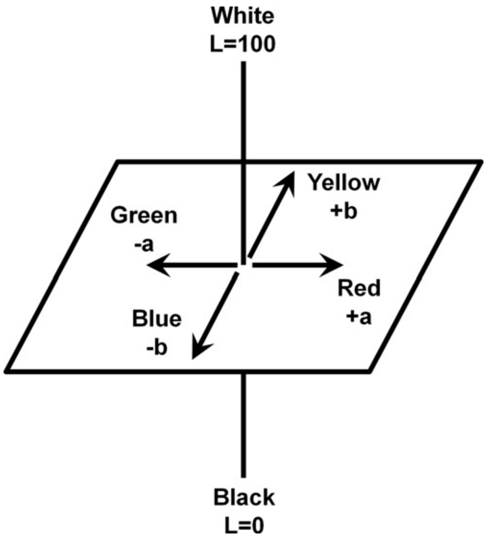


Figure 3.3 Visual representation of the Hunter *L*, *a*, *b* color scale.

The formulas that related Hunter L, a, b to CIE XYZ tristimulus are given in Eqns (3.4)–(3.6).

$$L = 100\sqrt{\frac{Y}{Yn}} \tag{3.4}$$

$$a = K_a\left(\frac{X/X_n - Y/Y_n}{\sqrt{Y/Y_n}}\right) \tag{3.5}$$

$$b = K_b\left(\frac{Y/Y_n - Z/Z_n}{\sqrt{Y/Y_n}}\right) \tag{3.6}$$

where

X, Y, and Z are the CIE tristimulus values.

X_n, Y_n, and Z_n are the tristimulus values for the illuminant.

Y_n is 100.00.

X_n and Z_n are listed in the tables below.

K_a and K_b are chromaticity coefficients for the illuminant and are listed in the Tables 3.1 and 3.2.

Similar formulas are available for CIE $L^*a^*b^*$.[5]

3.1.2.2 Gloss Measurement

Gloss is a measurement of the relative luster or shininess of a film surface. What affects film gloss? Gloss is primarily determined by nature of the material and surface smoothness. Smoothness is affected not only by the product composition but also by the production process. Transparent films have two reflecting surfaces.

Table 3.1 Parameters Relating Hunter *L*, *a*, *b* to CIE *XYZ*, CIE 2° Standard Observer

Illuminant	X_n	Z_n	K_a	K_b
A	109.83	35.55	185.20	38.40
C	98.04	118.11	175.00	70.00
D65	95.02	108.82	172.30	67.20
F2	98.09	67.53	175.00	52.90
TL 4	101.40	65.90	178.00	52.30
UL 3000	107.99	33.91	183.70	37.50
D50	96.38	82.45	173.51	58.48
D60	95.23	100.86	172.47	64.72
D75	94.96	122.53	172.22	71.30

Table 3.2 Parameters Relating Hunter *L*, *a*, *b* to CIE *XYZ*, CIE 10° Standard Observer

Illuminant	X_n	Z_n	K_a	K_b
A	111.16	35.19	186.30	38.20
C	97.30	116.14	174.30	69.40
D65	94.83	107.38	172.10	66.70
F2	102.13	69.37	178.60	53.60
TL 4	103.82	66.90	180.10	52.70
UL 3000	111.12	35.21	186.30	38.20
D50	96.72	81.45	173.82	58.13
D60	95.21	99.60	172.45	64.28
D75	94.45	120.70	171.76	70.76

A glossmeter measures specular reflection. Unpolarized white light is concentrated by a condenser lens onto a field aperture, which is located in the focal plane of the source lens. The reflected beam at the surface is later collected by the receptor lens. The intensity of the beam is then measured with a photodetector. The common angles of incidence for gloss measurement are 20°, 60°, and 85°. Low-gloss surfaces are recommended to be measured with 85° settings.

The typical standards for gloss measurements are:

- ASTM D2457-08e1 Standard Test Method for Specular Gloss of Plastic Films and Solid Plastics
- ISO 2813:1994 Paints and varnishes – Determination of specular gloss of nonmetallic paint films at 20°, 60°, and 85°
- DIN 67530 Reflectometer as a means for gloss assessment of plane surfaces of paint coatings and plastics.

A high gloss requires a smooth surface. Surface imperfections may be introduced by the processing. Excessive drawing into the strain-hardening region will usually reduce the gloss. Blown film usually has a lower gloss since crystallization of the film at the frost line introduces surface roughness. Rapid crystallization of the film by the use of chilled air impinging on the bubble reduces the size of crystals

Table 3.3 Tristimulus Coefficients

Coefficient	C/2°	D65/2°	C/10°	D65/10°
C_X	1.2769	1.2985	1.2871	1.3013
C_Z	1.0592	1.1335	1.0781	1.1498

and improves the gloss. Extrusion cast film passes through chilled rollers after leaving the extruder. The rapid cooling minimizes crystallization and the polished surface of the rollers provides a high-gloss surface. Extrusion cast films have the higher gloss, but the extrusion blown process produces film at a lower cost. The rheology of the polymer will affect the surface of the film.

3.1.2.3 Haze Measurement

Haze is the internal scattering of light and so it is an internal bulk property. Crystallinity, optical defects, "fish eyes," phase separation of blends, contaminants, gel particles, and dispersion of pigments are structures that increase haze. Haze makes it difficult to clearly see objects through a film as a result of the interference from randomly scattered light reaching the viewer in addition to light coming straight from the object. Smaller crystals provided by a nucleating agent will decrease haze.

The test standards are:

- ASTM D1003-11 Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics
- ISO/DIS14782 Plastics — Determination of Haze of Transparent Materials.

3.1.2.4 Yellowness Index

As plastic materials degrade, especially from high heat, they tend to turn yellow or brown. Rather than measure and report full color change data, a parameter to characterize this change is called yellowness index (YI). YI is a number calculated from spectrophotometric data that describes the change in color of a test sample from clear or white toward yellow. This is one of the most common tests done on plastics exposed to sterilization processes. A Hunter *L*, *a*, *b* color measurement instrument may be used to measure YI. The illuminant should be D65 for ASTM E313. Illuminant C may be used for other standards. The standard observer function is 2° or 10°. Transmittance or reflectance modes may be used.

YI per ASTM Method E313 is calculated as per Eqn (3.7):

$$\mathrm{YI} = 100(C_x X - C_z Z)/Y \tag{3.7}$$

where:

X, *Y*, and *Z* are the CIE tristimulus values and the coefficients depend on the illuminant and observer as indicated in Table 3.3. YI may only be calculated for illuminants D65 and C.

YI per ASTM Method D1925 is calculated as follows:

for all instruments except UltraScan XE:

$$\mathrm{YI} = 100(1.274976795X - 1.058398178Z)/Y \text{ under C/2° conditions} \tag{3.8}$$

for UltraScan XE:

$$\mathrm{YI} = 100(1.274641506X - 1.057434092Z)/Y \text{ under C/2° conditions} \tag{3.9}$$

The YI formula is shown in ASTM D1925 as:

$$\mathrm{YI} = 100(1.28X_{\mathrm{CIE}} - 1.06Z_{\mathrm{CIE}})/Y_{\mathrm{CIE}} \text{ under C/2° conditions} \tag{3.10}$$

The tristimulus values of clear air (for CIE illuminant C and the 1931 CIE 2° standard observer) are $X = 98.041$, $Y = 100.000$, and $Z = 118.103$. Using these values, the ASTM formula yields $\mathrm{YI} = 0.303$ for clear air because the factors are truncated to three significant figures. In order to set the YI for air equal to 0.0, the constant multipliers for X_{CIE} and Z_{CIE} have been expanded slightly. The ASTM D1925 method was withdrawn in 1995, but this formula still provides useful information. This index is always calculated for C/2°, regardless what illuminant and observer are chosen. The focus of this index was on evaluation of transparent plastics.

3.2 Mechanical Testing of Plastics

The data chapters of this book contain tables and plots of various mechanical properties of plastics before and after being exposed to a sterilization process. Many but not all of these may be as a function of temperature, strain, humidity, etc. This section will summarize the standard mechanical tests. Details on some of the more common test methods will follow.

Standard plastics tests are generally specified primarily by two standards organizations. ASTM International, originally known as the American Society for Testing and Materials, is one organization; its standards are the well-known ASTM standards. The second organization is the International Organization for Standardization, abbreviated as ISO, that is also well known. These organizations do not specify just plastics tests, but they both develop technical standards in whatever fields need them. They are both well accepted, but unfortunately they do not always agree exactly. While there is often one-to-one correlation of ASTM and ISO standards, they may differ in procedure and conditions, which may lead to slightly different measures. While reported values are similar, they are rarely exactly the same. These standard tests are listed in Tables 3.4–3.9.

Table 3.4 Standard Mechanical Tests

Measurement	American Society for Testing and Materials (ASTM)	International Organization for Standardization (ISO)
Apparent bending modulus	ASTM D747	–
Coefficient of friction	ASTM D1894	–
Compressive modulus	ASTM D695	ISO 604
Compressive strength	ASTM D695	ISO 604
Deformation under load	ASTM D621	–
Flexural creep	ASTM D2990	–
Flexural creep modulus	–	ISO 6602
Flexural modulus	ASTM D790	ISO 178
Flexural strength	ASTM D790	ISO 178
Flexural strength at break	ASTM D790	–
Flexural strength at yield	ASTM D790	–
Nominal tensile strain at break	–	ISO 527-1, -2
Poisson's ratio	ASTM E132	–
Shear modulus	ASTM D732	
Shear strength	ASTM D732	–
Tensile creep modulus	–	ISO 527-1, -2
Tensile elongation at break	ASTM D638	ISO 527-1, -2
Tensile elongation at yield	ASTM D638	ISO 527-1, -2
Tensile modulus	ASTM D638	ISO 527-1, -2
Tensile strength	ASTM D638	–
Tensile strength at break	ASTM D638	ISO 527-1, -2
Tensile strength at yield	ASTM D638	ISO 527-1, -2
Tensile strength, ultimate	ASTM D638	ISO 527-1, -2

Table 3.5 Standard Elastomer Tests

Measurement	American Society for Testing and Materials (ASTM)	International Organization for Standardization (ISO)
Compression set	ASTM D395	ISO 37
Elongation at break	ASTM D412	–
Elongation at yield	ASTM D412	–
Elongation set after break	ASTM D412	–
Tear strength	ASTM D624	ISO 34-1
Tear strength, split	ASTM D412	–
Tensile set	ASTM D412	–
Tensile strength at break	ASTM D412	ISO 37
Tensile strength at yield	ASTM D412	ISO 37
Tensile stress at 100%	ASTM D412	ISO 37
Tensile stress at 200%	ASTM D412	ISO 37
Tensile stress at 300%	ASTM D412	ISO 37
Tensile stress at 50%	ASTM D412	–

Table 3.6 Standard Impact Tests

Measurement	American Society for Testing and Materials (ASTM)	International Organization for Standardization (ISO)
Charpy notched impact strength	ASTM D256	ISO 179
Charpy unnotched impact strength	–	ISO 179
Drop impact resistance	ASTM D4226	–
Gardner impact	ASTM D5420 & D5628	–
Instrumented dart impact	ASTM D3763	–
Multiaxial instrumented impact energy	–	ISO 6603-2 MAII
Multiaxial instrumented impact peak force	–	ISO 6603-2 MAII
Notched Izod impact strength	ASTM D256	ISO 180
Reverse notch Izod impact strength	ASTM D256	–
Tensile impact strength	ASTM D1822	ISO 8256
Unnotched Izod impact strength	ASTM D256	ISO 180

Table 3.7 Standard Hardness Tests

Measurement	American Society for Testing and Materials (ASTM)	International Organization for Standardization (ISO)
Ball indentation hardness	–	ISO 2039-1
Durometer (Shore) hardness	ASTM D2240	ISO 868
Rockwell hardness	ASTM D785	ISO 2039-2

Table 3.8 Standard Electrical Tests

Electrical	American Society for Testing and Materials (ASTM)	International Organization for Standardization (ISO)
Dielectric constant	ASTM D150	IEC 60250
Dielectric strength	ASTM D149	IEC 60243-1
Dissipation factor	ASTM D150	IEC 60250
Surface resistivity	ASTM D257	IEC 60093
Volume resistivity	ASTM D257	IEC 60093

Table 3.9 Standard Thermal Tests

Thermal	American Society for Testing and Materials (ASTM)	International Organization for Standardization (ISO)
Brittleness temperature	ASTM D746	ISO 812 & ISO 974
Coefficient of linear thermal expansion	ASTM D696 & ASTM E831	ISO 11359-1, -2
Heat deflection temperature (HDT) at 8.0 MPa	–	ISO 75 Method C
HDT at 1.80 MPa	ASTM D648	ISO 75 Method A
HDT 0.45 MPa	ASTM D648	ISO 75 Method B
Ductile/brittle transition temperature	–	ISO 6603-2 Ductile Brittle
Glass transition temperature	ASTM E1356	–
Melting temperature (differential scanning calorimetry)	–	ISO 3146
Specific heat	ASTM C351	–
Thermal conductivity	ASTM C177	ISO 8302
Vicat softening temperatue	ASTM D1525	ISO 306
Melt flow rate/melt flow index	ASTM D1238	ISO 1133

Many plastics families have their own ASTM and ISO guidelines for testing. These guidelines provide standard testing procedures including sample preparation and often define the subclassification of the plastic products. Some of these standards are given in Table 3.10.

3.2.1 Tensile Properties

Tensile testing is performed by elongating a specimen and measuring the load carried by the specimen. This is done using a test machine known as an Instron Universal Materials Testing Machine. From knowledge of the specimen dimensions, the load and deflection data can be translated into a stress–strain curve. A variety of tensile properties can be extracted from the stress–strain curve. The standard tests are:

- ASTM D638-03 – Standard Test Method for Tensile Properties of Plastics
- ISO 527-1:1993 Plastics – Determination of tensile properties – Part 1: General principles

Table 3.10 International Organization for Standardization (ISO) and American Society for Testing and Materials (ATSM) Standards for Common Polymer Families

Polymer Family	ISO Standards[a]	ASTM Standards
Acrylonitrile–butadiene–styrene resin (ABS)	DIS 2580–1&2: 2003	D4673–02
Styrene–acrylonitrile resin (SAN)	4894–1&2: 1997	D4203–07
Polystyrene (PS)	1622–1&2: 1994	D4549–03
Polystyrene, impact (PS-I)	2897–1&2: 2003	D4549–03
Polypropylene (PP)	1873–1&2: 1997	D4101–06b
		D5857–05a
Polyethylene (PE)	1872–1&2: 2007	D4976–06
Polyvinyl chloride, plasticized (PVC-P)	2898–1&2: 1997	D2287–96
Polyvinyl chloride, unplasticized (PVC-U)	1163–1&2: 1995	D1784–06a
Polymethylmethacrylate (PMMA)	8257–1&2: 2001	D788–06
Polycarbonate (PC)	7391–1&2: 2006	D3935–02
Acetals (POM)	9988–1&2: 2006	D6778–06
Polyamides (PA)	1874–1&2: 2006	D4066–01a
Thermoplastic polyester	7792–1&2: 1997	D5927–03
Polyketone (PK)	15526–1&2: 2000	D5990–00
Polyphenyl ether (PPE, PPO)	15103–1&2: 2000	D4349–96
Thermoplastic polyester elastomer	14910–1&2: 1997	D6835–02
Ethylenechlorotrifluoroethylene copolymer (ECTFE)		D3275–06
Poly(vinylidene fluoride) (PVDF)		D3222–05
Polytetrafluoroethylene (PTFE)		D4894–04
Ethylene–tetrafluoroethylene copolymer (ETFE)		D3159–06
Perfluoroalkoxy (PFA)		D3307–06
Tetrafluoroethylene–hexafluoropropylene copolymer (FEP)		D2116–02

[a] *Part 1 of each ISO material standard addresses the "Designatory Properties" and part 2 describes specific tests, test specimens, and test conditions.*

- ISO 527-2:1993 Plastics – Determination of tensile properties – Part 2: Test conditions for molding and extrusion plastics
- ISO 37 Rubber, vulcanized or thermoplastic – Determination of tensile stress–strain properties
- ASTM D412-98a(2002)e1 – Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers – Tension.

The additional standard tests for film are different from general molded plastics:

- ASTM D88-10 (Standard Test Method for Tensile Properties of Thin Plastic Sheeting)
- ISO 527-3 (Plastics – Determination of tensile properties – Part 3: Test conditions for films and sheets)
- JIS K7127:1999 (Plastics – Determination of tensile properties – Part 3: Test conditions for films and sheets).

Figure 3.4 shows a picture of an Instron® Universal Materials Testing Machine and a diagram

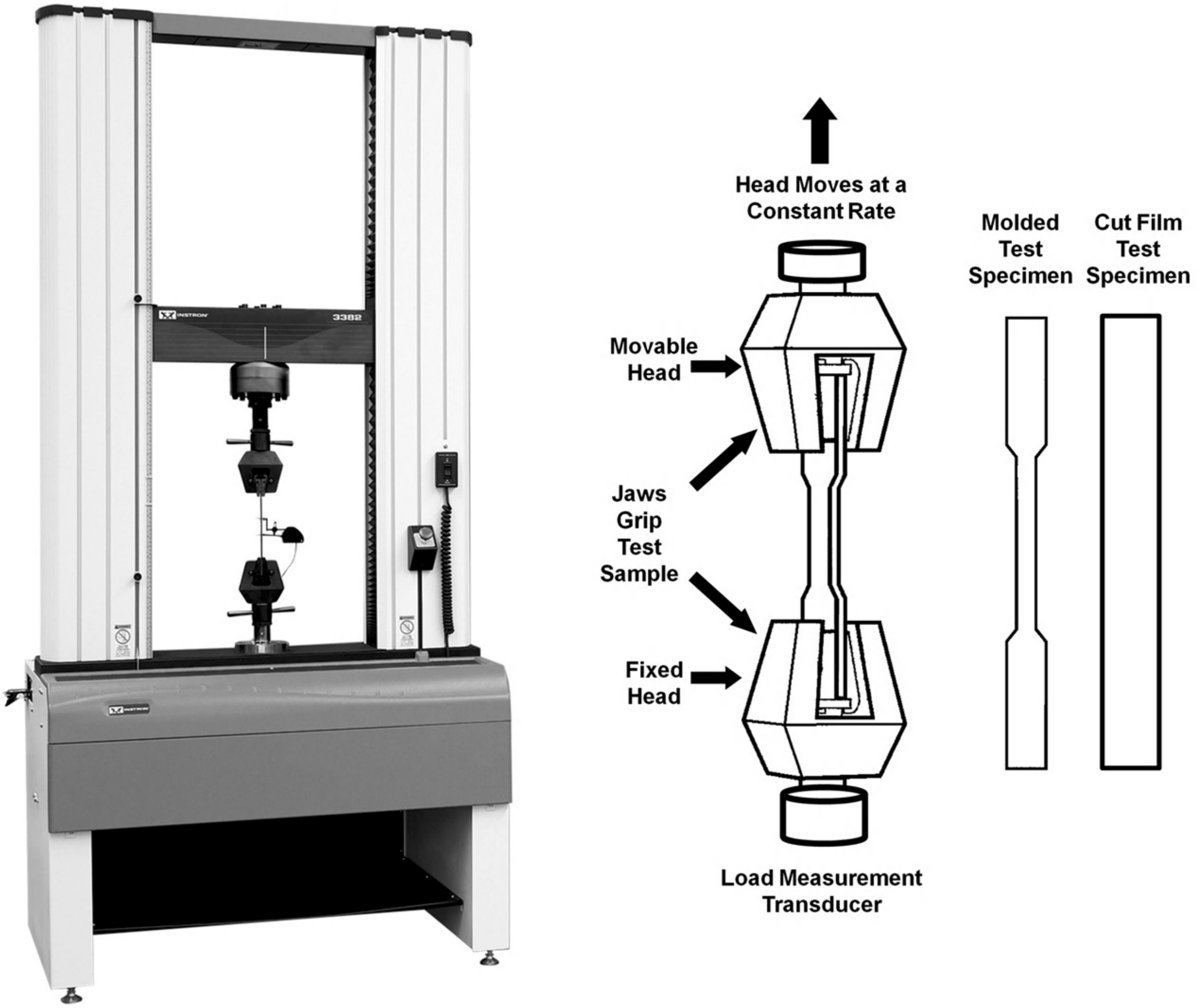


Figure 3.4 Instron Universal Materials Testing Machine (photo courtesy of Instron® Corporation).

of the test plaque and details of the test configuration. The sample jaws for film are slightly different than pictured and typically have rubber surfaced grips to securely hold thin films. The instrument can provide a stress−strain curve such as that shown in Fig. 3.5. Analysis of this curve leads to several useful mechanical measurements.

Figure 3.5 has several points on the curve labeled. These are as follows:

- "A" is the "proportional limit", which is the end of the region in which the resin exhibits linear stress−strain behavior
- "B" is the "elastic limit" after which the part is permanently deformed when the strain is removed
- "C" is the "yield point" after which the material will deform without a further increase in strain
- "D" is the "ultimate strength" which is the maximum stress on the curve
- "E" is the "breakpoint."

Table 3.11 shows how some of the tensile measurements are made from the stress vs. strain curve in Fig. 3.5.

Most plastics when tested will show one of four basic types of stress vs. strain behavior. These are shown in Fig. 3.6. The slopes of the curves and the actual measures of stress and strain may differ, but as the reader views the multipoint curves in the subsequent chapters of this book, he/she will recognized

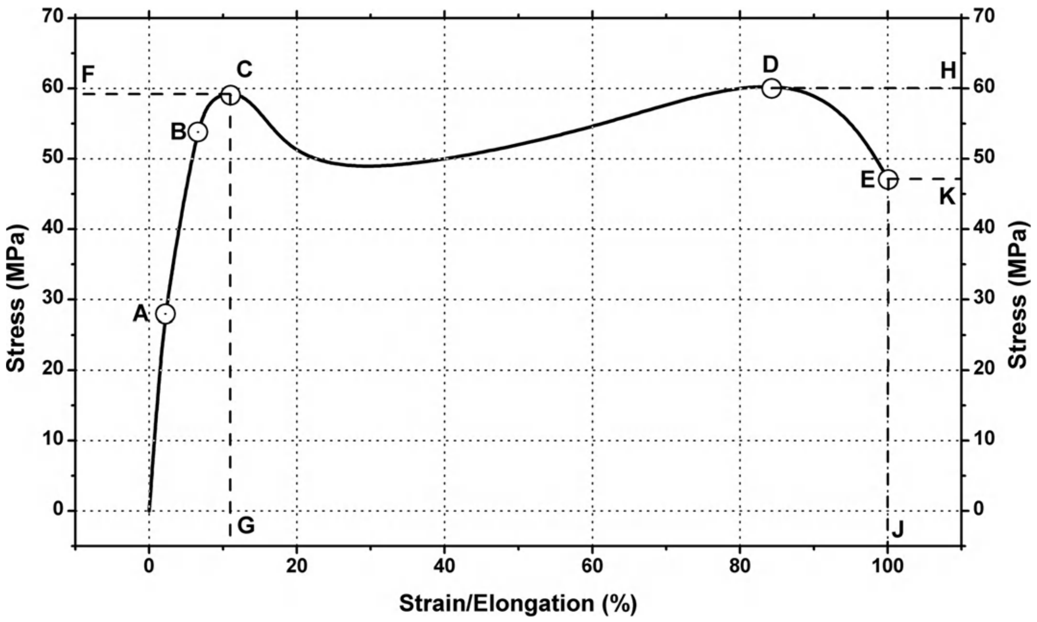


Figure 3.5 Typical stress–strain curve showing some important measurement points.

Table 3.11 Tensile Properties Determined from a Stress–Strain Curve per ASTM D638

Property	**Definition**
Tensile elongation at break	Tensile elongation corresponding to the point of rupture, "J" in Fig. 3.5
Tensile elongation at yield	Tensile elongation corresponding to the yield (an increase in strain does not result in an increase in stress), "G" in Fig. 3.5
Tensile strength at break	Tensile stress corresponding to the point of rupture, "K" in Fig. 3.5
Tensile strength at yield	Tensile stress corresponding to the yield point (an increase in strain does not result in an increase in stress), "F" in Fig. 3.5
Tensile strength	Tensile stress at a specified elongation
Tensile strength, ultimate	The highest tensile stress a material can support before failing, "H" in Fig. 3.5
Tensile modulus	The ratio of tensile stress to tensile strain of a material in the elastic region (from no strain to point "B" in Fig. 3.5) of a stress–strain curve. A "Tangent" tensile modulus value is the slope of the elastic region of the stress–strain curve and is also known as Young's modulus or the modulus of elasticity. A "Secant" tensile modulus value is the slope of a line connecting the point of zero strain to a point on the stress–strain curve at a specified strain

these forms. Table 3.12 lists several plastics that fit each of these behavior types.

3.2.2 Rigidity of Plastics Materials

The rigidity of a plastic is determined by the ease with which the plastic is deformed under load. Modulus is the measure that corresponds to rigidity in plastics. In amorphous plastics at temperatures well below the glass transition temperature, the entire load is absorbed by bond bending and stretching of the polymers making up the plastic. The change in rigidity at the T_g in an amorphous polymer is considerable. The modulus may drop more than three orders of

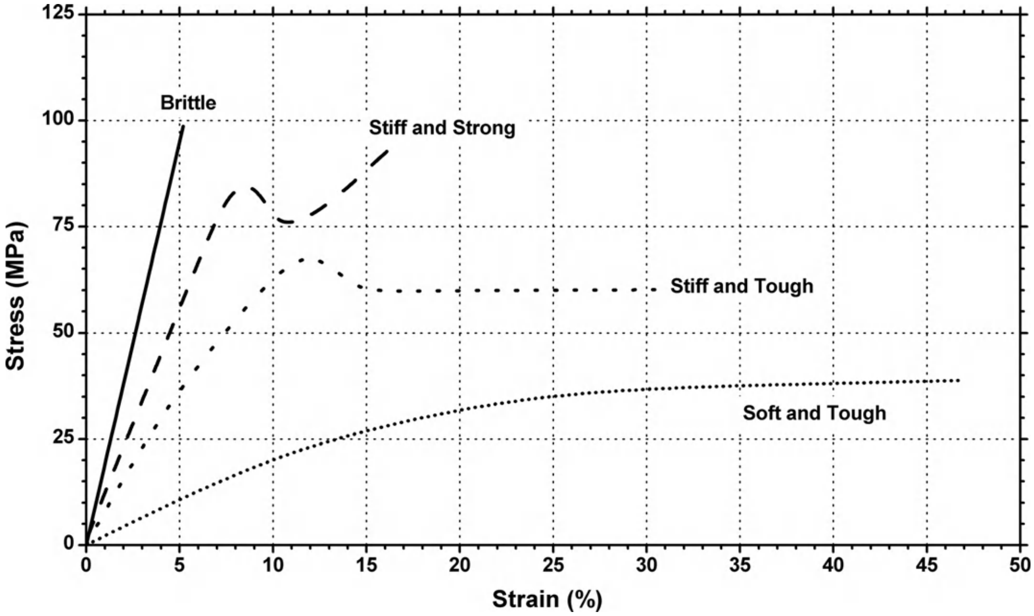


Figure 3.6 The range of stress vs. strain behaviors.

Table 3.12 Examples of Tensile Responses Exhibited by Various Plastics

Behavior	Examples
Brittle	Polystyrene, acrylics, styrene–acrylonitrile, highly reinforced material
Stiff and strong	Acrylonitrile–butadiene–styrene, polycarbonate, polyamides, highly filled resin
Stiff and tough	Impact modified polyamides, impact polystyrene
Soft and tough	Elastomers, low density

magnitude. Further heating of a low-to-moderate uncross-linked plastic past its T_g would rapidly cause a drop of the modulus toward zero. However, in a high molecular weight plastic such as cast poly(methyl methacrylate), the polymer chain entanglements would enable the material to maintain a significant rubbery modulus up to its decomposition temperature. Similar maintenance of the modulus above zero is achieved when the polymer is cross-linked. The more cross-linking present, the higher the modulus.

Crystallinity can also restrict molecular movement of the polymer chains above the T_g raising the modulus. The higher the crystallinity, the more rigid the polymer. Some polymers tend to melt over a wide temperature range, in which case the modulus may fall over a range of temperatures leading up to the melting point T_m. The above effects are summarized in Fig. 3.7.

where:

A is an amorphous polymer of moderate molecular weight
B is of such a high molecular weight that entanglements inhibit flow
C is lightly cross-linked
D is highly cross-linked
E some crystallinity
F higher crystallinity.

3.2.3 Shear Properties

Measurement of properties under shear conditions is described in the standard:

- ASTM D732-02 Standard Test Method for Shear Strength of Plastics by Punch Tool.

The primary measures are shear strength and shear modulus. Shear strength is the maximum load required to completely shear a specimen divided by the sheared area. Shear modulus is the ratio of shear stress to shear strain.

These tests are often done in an Instron® Universal Materials Testing Machine. The sample is typically

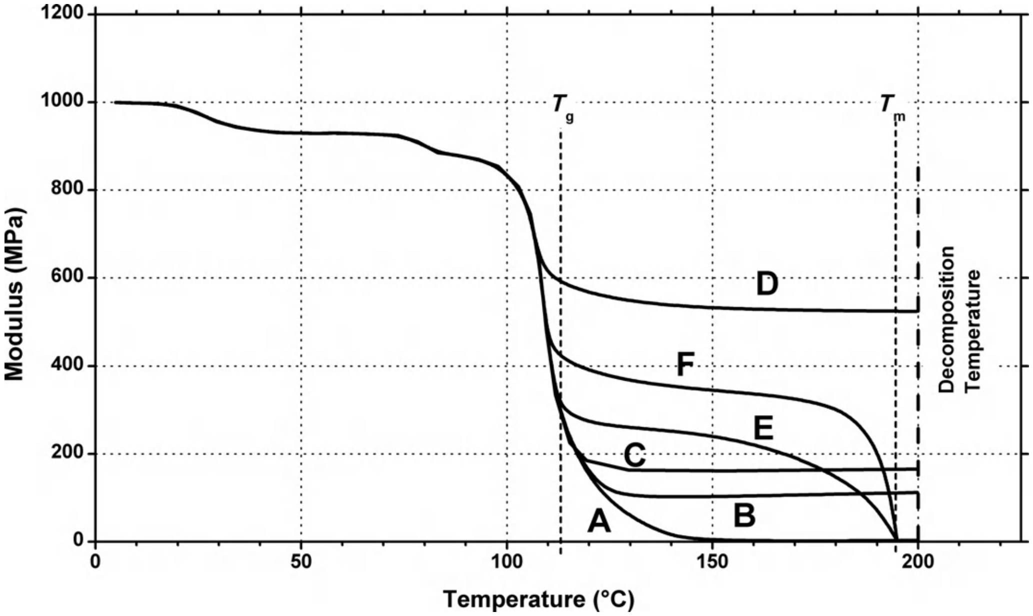


Figure 3.7 Schematic illustration of dependence of the modulus of a polymer on a variety of factors.

molded sheet that has been cut into a disk. The diagram of the apparatus used is shown in Fig. 3.8 for a molded sample and Fig. 3.9 for a film sample.

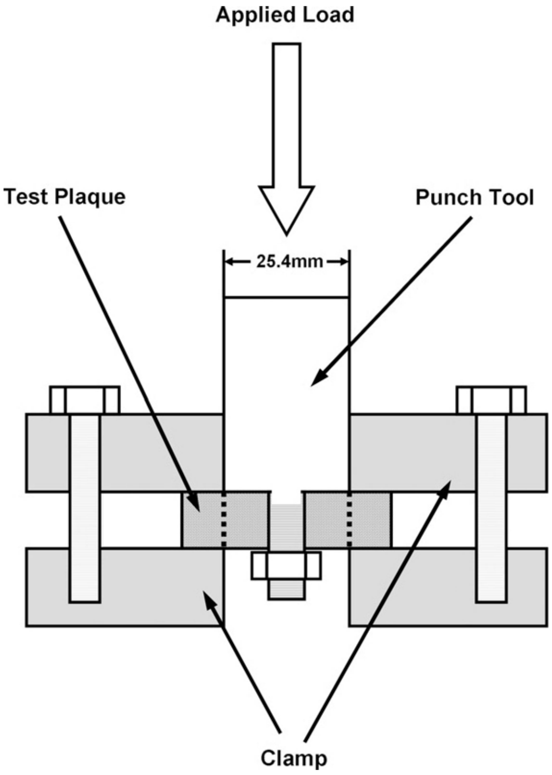


Figure 3.8 Apparatus used for shear property measurements on molded samples.

The test specimen, disk or plaque, is placed in a clamp such that its upper and lower surfaces are securely supported. Specimen thickness should be between 0.127 and 12.7 mm (0.005 in and 0.5 in). A punch type shear tool with a 25.4-mm (1″) diameter is bolted to the specimen through a hole drilled in the center and a load is applied to the punch. The shear strength is calculated as the maximum force encountered during the test divided by the area of the sheared edge (circumference of the punched circle multiplied by the specimen thickness, as indicated by the dotted line in Fig. 3.8).

Referring to Fig. 3.10, the *shear strength* is calculated by Eqn (3.11).

$$\text{Shear strength}\ \left(\text{dyne/cm}^2\right) = \frac{F}{A_{\text{cs}}} \qquad (3.11)$$

where:

F = load required to puncture the film

A_{cs} = the cross-sectional area of the edge of film located in the path of the cylindrical hole of the film holder ($2\pi R \times$ film thickness).

Division by A_{cs} normalizes the data for differences in thickness from film to film.

Energy to shear (ΔE_s) per unit volume is calculated by Eqn (3.12).

$$\Delta E_s\left(\text{erg/cm}^3\right) = \frac{\text{AUC}}{V_c} \qquad (3.12)$$

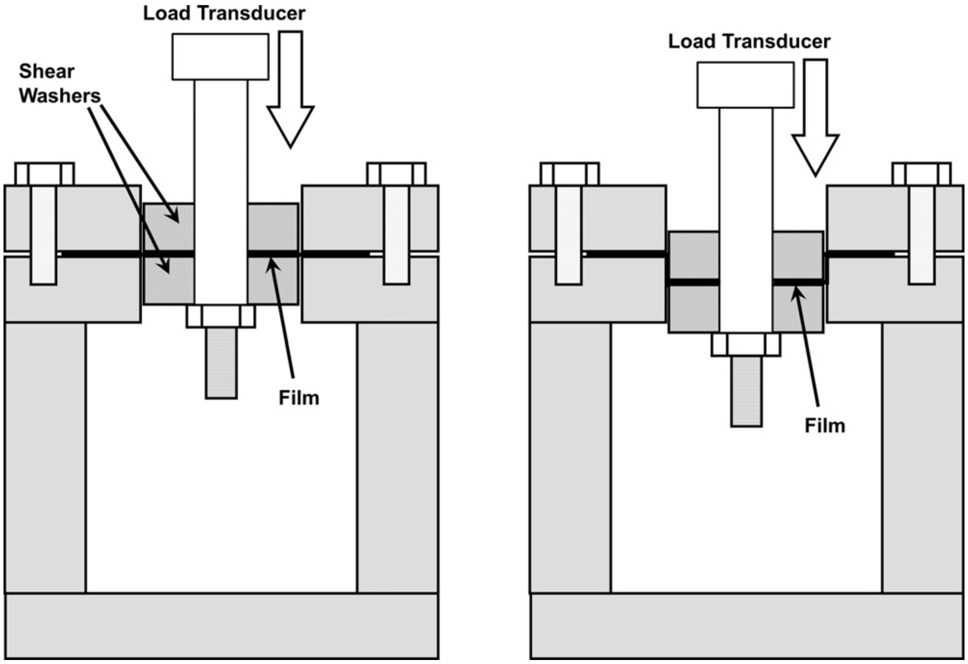


Figure 3.9 Apparatus used for shear property measurements for film samples.

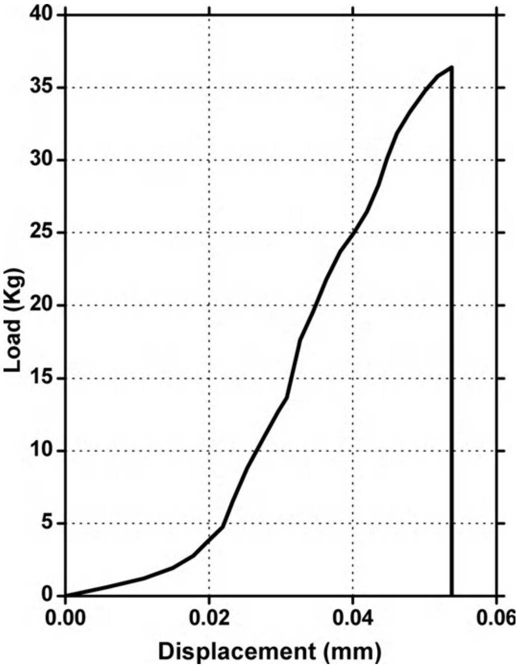


Figure 3.10 Typical recorded measurements for film samples.

where:

AUC = the area under the load vs. displacement curve

V_c = volume of the film in the die cavity.

3.2.4 Flexural Properties

The measurement of flexural properties is described in the standards:

- ASTM D790-03 Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials
- ISO 178:2001 Plastics — Determination of flexural properties.

A test specimen is held as a simply supported beam and is subjected to three-point bending as shown in Fig. 3.11. Typically an Instron® is used. Maximum stress and strain occurs at the underside of the test specimen, directly under the applied force. The preferred test specimen is 80 mm long, 10 mm wide, and 4 mm thick. Other specimens may be used if the length to thickness ratio is equal to 20.

3.2.5 Puncture and Impact Properties

The resistance of packaging film to puncture is a property of interest to users. There are several common tests used to evaluate puncture resistance.

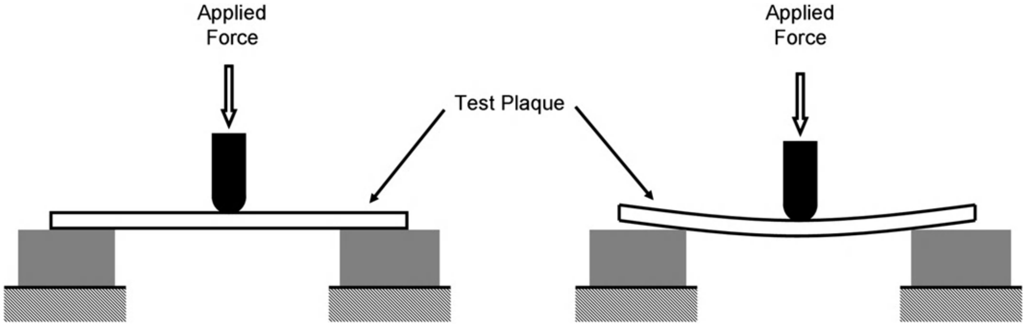


Figure 3.11 Principle used for flexural property measurements.

3.2.5.1 High-Speed Puncture Test

The high-speed puncture test is commonly ASTM D7192-08 High Speed Puncture Properties of Plastic Film Using Load and Displacement Sensors. A schematic of test cell that is used in an Instron type of machine is shown in Fig. 3.12. The high-speed puncture test setup consists of a hydraulic actuator (the drive system), puncture probe (or tup), circular clamp, load sensing device, a set of controllers, data acquisition board and a computer to control, measure, and report.

A typical plot of data acquired in this type of measurement is load vs. displacement as shown in Fig. 3.13.[6] Testing is often done at various impact velocities, and the recommended speeds in the test standard are 2.5, 25, 125, 200, and 250 m/min (0.137, 1.367, 6.835, 10.936 and 13.670 ft/s).

The primary parameters of interest are the displacement of the probe from initial contact to puncture of the film, the area under the curve, and peak load. From this data, elongation to puncture, puncture strength, and energy to puncture may be calculated. *Elongation to puncture* (ϵ_p) is calculated by Eqn (3.13).

$$\epsilon_p(\%) = \frac{\sqrt{(R^2 + D^2)} - R}{R} \times 100 \qquad (3.13)$$

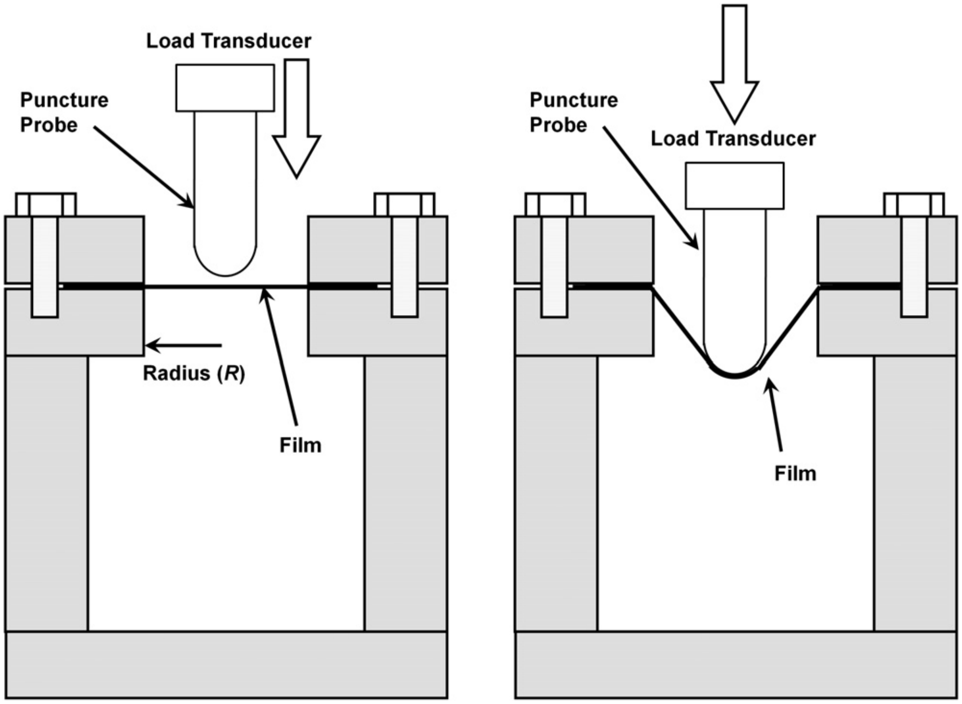


Figure 3.12 Schematic of the high-speed puncture test sample cell.

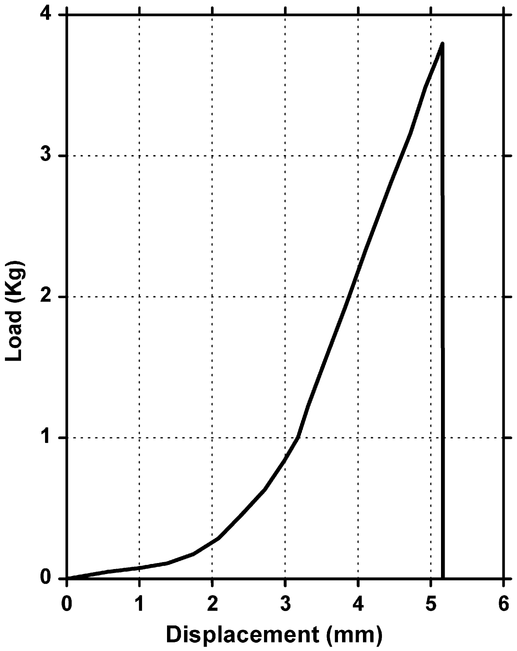


Figure 3.13 Typical load vs. deflection plot obtained from the high-speed puncture test.

where:

R = the radius of the film exposed in the cylindrical hole of the film holder

D = displacement of the probe from point of contact to point of film puncture.

Puncture strength is calculated by Eqn (3.14).

$$\text{Puncture strength}\ \left(\text{dyne/cm}^2\right) = \frac{F}{A_{\text{cs}}} \qquad (3.14)$$

where:

F = load required to puncture the film

A_{cs} = the cross-sectional area of the edge of film located in the path of the cylindrical hole of the film holder ($2\pi R$ × film thickness).

Division by A_{cs} normalizes the data for differences in thickness from film to film.

Energy to puncture (ΔE_p) is calculated by Eqn (3.15).

$$\Delta E_p\left(\text{erg/cm}^3\right) = \frac{\text{AUC}}{V_c} \qquad (3.15)$$

where:

AUC = the area under the load vs. displacement curve

V_c = volume of the film in the die cavity.

A similar standard test is ASTM F1306 Slow Rate Penetration Resistance of Flexible Barrier Films and Laminates.

3.2.5.2 Drop Dart Impact Test for Plastics Film

A dart impact tester is a simple to use stand-alone, noninstrumented tester for measuring impact resistance of film, sheet, and laminated materials per ASTM D1709-09 Standard Test Methods for Impact Resistance of Plastic Film by the Free-Falling Dart Method (Methods A and B). A schematic of a test machine is shown in Fig. 3.14. The test film is clamped securely in a ring at the base of the drop tower. The bracket holding the weight is adjusted to the appropriate drop height, and the dart is inserted into the bracket. The dart weight is adjustable with added weights. The dart is released to drop onto the center of the test specimen. The drop weight and the test result are recorded. This is a pass/fail test. The "Bruceton Staircase" method is used to analyze this test data. A series drops are conducted. If a test specimen passes, the drop weight is increased by one unit. If a test specimen fails, the drop weight is

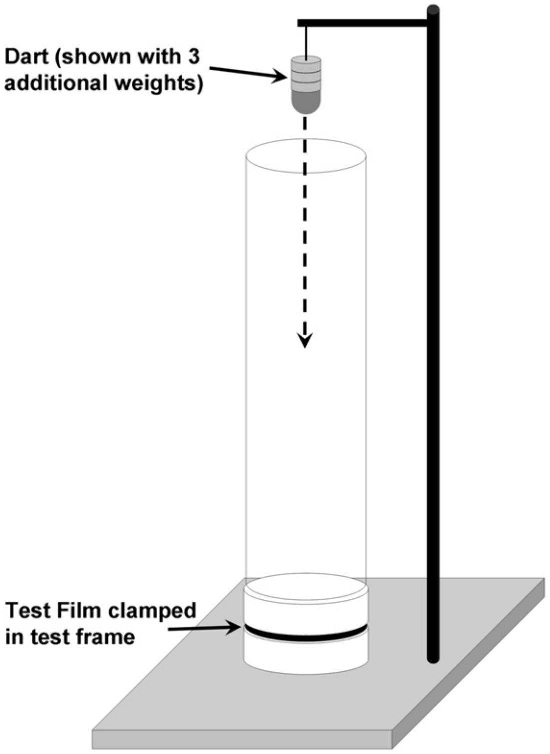


Figure 3.14 Schematic of a falling dart test device.

decreased by one unit. The results from these impacts are used to calculate the impact failure weight — the point at which 50% of the test specimens will fail under the impact.

Depending upon the expected impact strength of the test sample, either Method A or Method B is chosen. Test method A specifies a dart with a 38-mm (1.5″) diameter dropped from 0.66 m (26″) and Test method B specifies a dart with a 51-mm (2″) diameter dropped from 1.5 m (60″).

3.2.5.3 Izod Impact Strength and Charpy Impact Strength

The standard tests for Izod impact strength are:

- ISO 180:2000 Plastics — Determination of Izod impact strength
- ASTM D256-06a Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics.

The standard tests for Charpy impact strength are:

- ISO 179-1:2000 Plastics — Determination of Charpy impact properties — Part 1: noninstrumented impact test.

Both Izod and Charpy tests are based upon a swinging pendulum, such as that shown in Fig. 3.15.

Basically, the pendulum is raised to a measured point, and it is then released. The weighted end of the pendulum gains speed as it swings toward a mounted molded bar of the test plastic. It strikes the bar, breaks it, and the pendulum loses energy while breaking the plastic bar. Therefore, it does not swing as high. The energy lost by the pendulum is equated with the energy absorbed by the test specimen during the breaking process.

There are different ways to mount the test specimen, and there are different specimen sizes and preparation methods. The different sample mounting configurations for the Izod and Charpy tests are shown in Fig. 3.16. Figure 3.17 shows the details of the notch. The sharpness of the bottom of the notch affects the test result. Table 3.13 shows the different notch radii possible.

The impact resistance is usually reported at energy per unit length or per unit area.

3.2.5.4 Gardner and Falling Dart Impact Strength

Another type of impact strength test that uses gravity includes the Gardner impact or falling dart tests. These are described in the following standards:

- D5420-04 Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Striker Impacted by a Falling Weight (Gardner Impact)

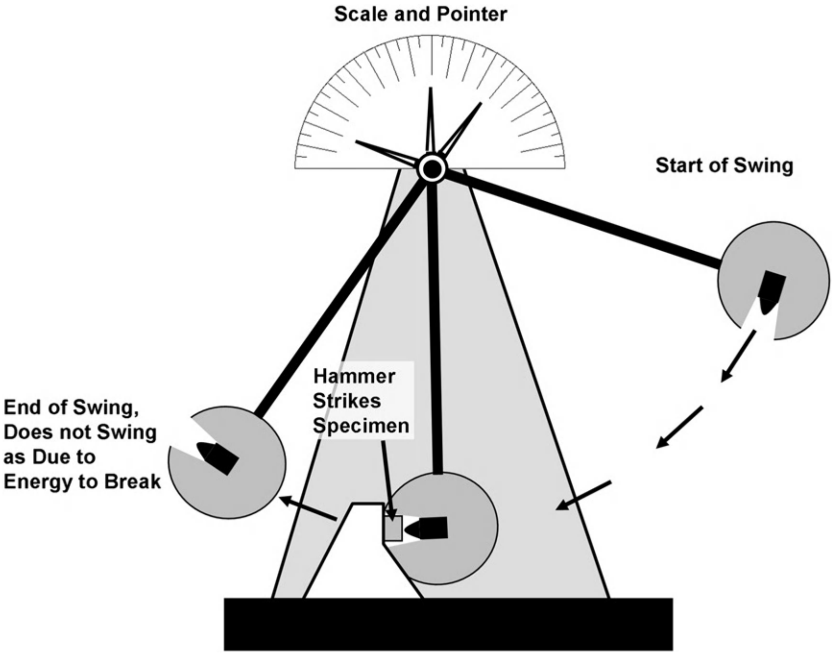


Figure 3.15 Pendulum-type impact strength tester.

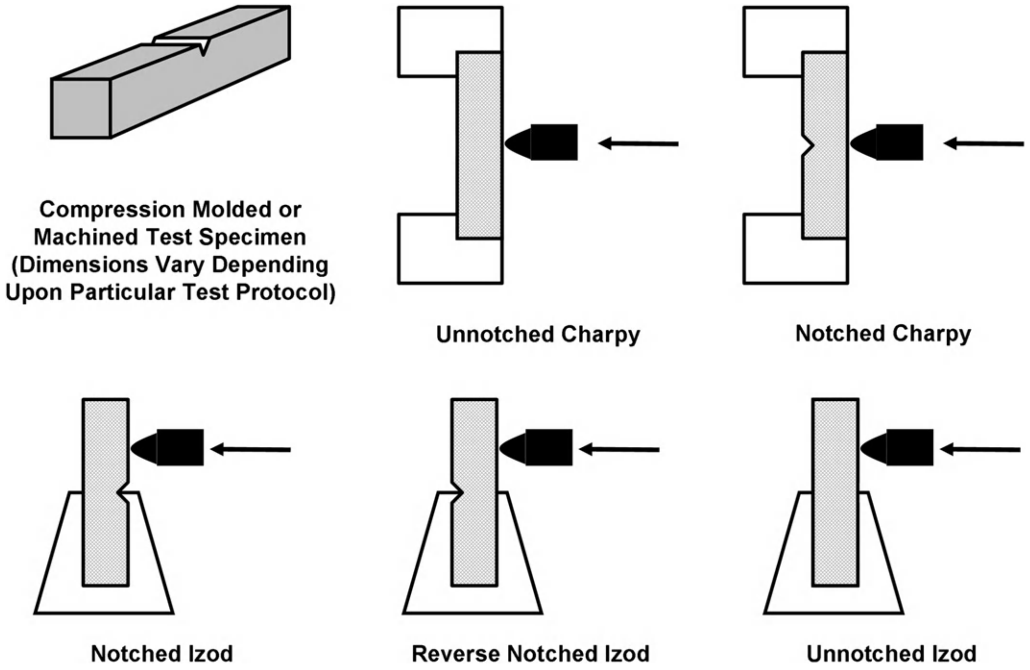


Figure 3.16 Izod and Charpy impact test sample configurations.

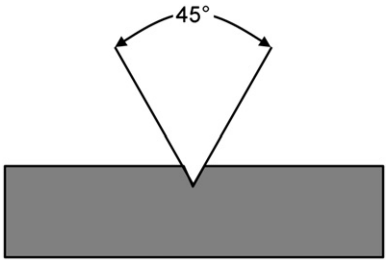


Figure 3.17 Izod and Charpy impact test notch detail.

Table 3.13 Izod and Charpy Impact Notch Radius Options

Notch	Izod Notch Radius (mm)	Charpy Notch Radius (mm)
A	0.25	0.25
B	1.00	1.00
C		0.10

- D5628-06 Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimens by Means of a Falling Dart (Tup or Falling Mass)
- D3763-06 Standard Test Method for High Speed Puncture Properties of Plastics Using Load and Displacement Sensors
- ISO 7765-2:1994 Plastics film and sheeting − Determination of impact resistance by the free-falling dart method − Part 2: Instrumented puncture test.

The Gardner test uses a piece of equipment like that shown in Fig. 3.18. A weight is lifted to a given

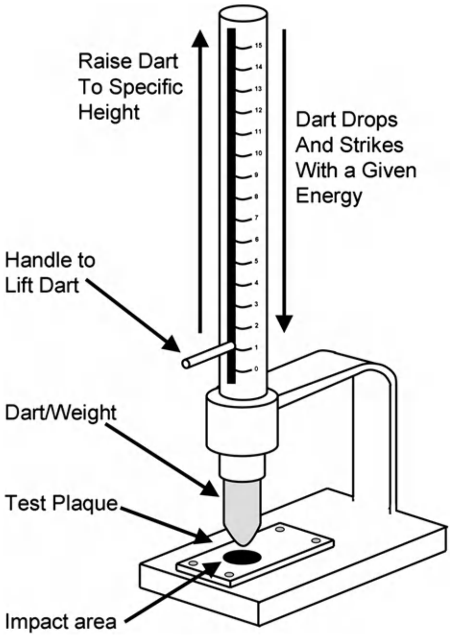


Figure 3.18 Gardner impact test apparatus.

height and it is dropped onto a test plaque. The falling dart is based on the same principle, but the weight is free falling rather than guided through a tube as in the Gardner equipment.

Plastic materials, in general, are blends of polymers with additives and fillers. All the components may well affect the modulus.

In practice one is basically concerned with the rigidity of the product and this involves not only the modulus of the material but also the shape and size of the product. From the points of view of weight saving, economics in material and ease of processing, it is an important aim to keep section thicknesses at a minimum required to achieve performance targets. Since flat or singly curved surfaces have a minimum rigidity, the designer may wish to incorporate domed or other doubly curved surfaces or ribbing into the product in order to increase stiffness. Corrugation can also enhance stiffness but in this case the enhancement varies with position, being greatest when measured at right angles to the corrugation.

3.2.6 Tear Properties

It is natural for film users to be concerned about how easy or difficult it is to tear film materials. There are two common tests for measuring tear strength, the Elmendorf tear strength (a high-speed test) and the Trouser tear strength (a low-speed test).

3.2.6.1 Elmendorf Tear Strength

The Elmendorf tear tester determines the tearing strength by measuring the work done in tearing through a fixed length of the test specimen. It consists of a sector pendulum pivoted on antifriction ball bearings on a vertical bracket fixed on a rigid metallic base. The test principle is fairly simple: The pendulum is lifted up to certain height. When released, the pendulum will have a certain potential energy, at the bottom of the swing the pendulum tears the specimen and the pendulum loses the energy used to tear the sample. The test machine is shown in Fig. 3.19. The test standards are:

- ASTM D1922-09 Standard Test Method for Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method
- ISO 6383-2:1983 Plastics – Film and sheeting – Determination of tear resistance – Part 2: Elmendorf method.

A typical test procedure starts with 10 samples each cut from the plastic film in the machine direction and in the transverse direction. A sample is positioned in the tester and clamped in place. A cutting knife in the tester is used to create a slit in the sample that ends 43 mm from the far edge of the sample. The pendulum is released to propagate the slit through the remaining 43 mm. The energy loss by the pendulum, measured by the machine, is used to calculate an average tearing force.

There are three standard samples for Elmendorf tear testing. The preferred test sample for plastic films is the constant radius sample. This sample provides a constant radius from the start of the tear strength measurement – useful for materials where the tear may not propagate directly up the sample as intended. Another common sample is a 63 mm × 76 mm rectangle. For textiles, a modified rectangle adds height on the ends of the sample to help minimize unraveling of the outside edges.

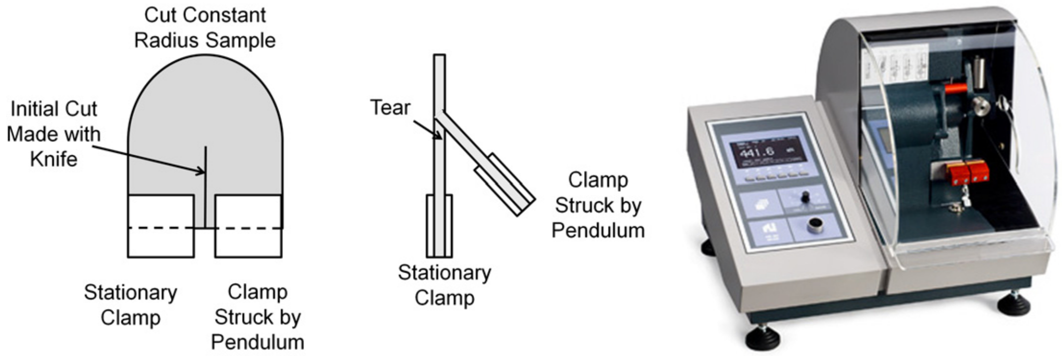


Figure 3.19 Elmendorf tear test, sample schematic on left, photo of a commercial machine right (photo courtesy of Testing Machines Inc.). For color version of this figure, the reader is referred to the online version of this book.

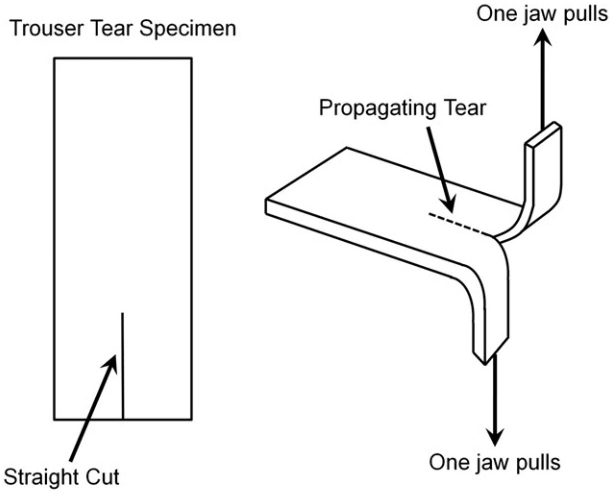


Figure 3.20 Trouser tear test sample configuration.

3.2.6.2 Trouser Tear Resistance

The trouser tear measurement measures the average force required to propagate a tear at a constant tearing speed across a specimen divided by the specimen thickness. This is done in a load frame or tensile test machine, such as an Instron®. The trouser tear sample and tear configuration are shown in Fig. 3.20. The sample is precut as shown. The sample looks like a pair of trousers, hence the name of the test. The tensile machine jaws are set to separate at a rate of either 200 or 250 mm/min.

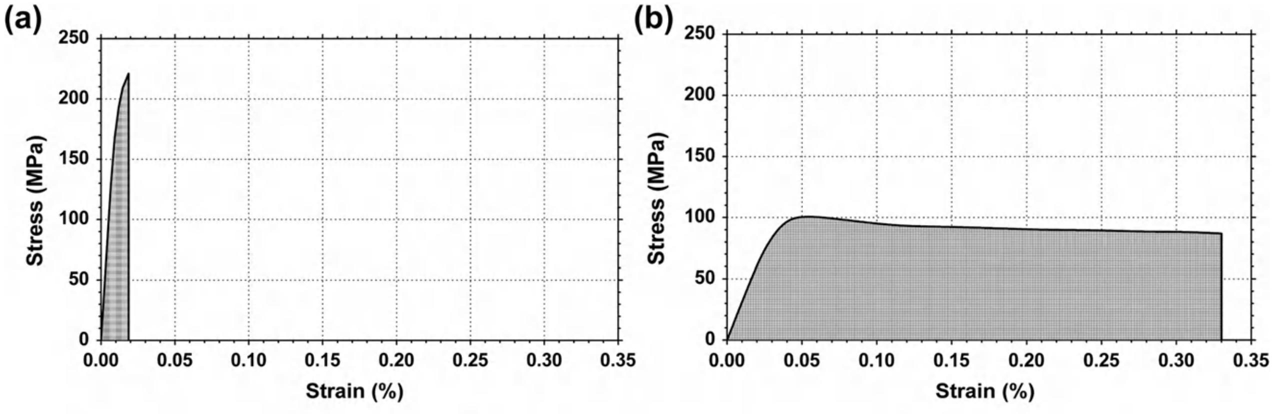
The tests standards are:

- ASTM D1938-08 Standard Test Method for Tear-Propagation Resistance (Trouser Tear) of Plastic Film and Thin Sheeting by a Single-Tear Method
- ISO 6383-1 Film and Sheeting – Determination of Tear Resistance Part 1 Trouser Tear Method.

3.2.7 Toughness

Toughness is complex to define and difficult to understand. Tough thermoplastic resins are usually described as having high elongation to failure or ones that require a large amount of energy to cause failure. If the plastics are reinforced then they need high strength with low elongation. For many applications, the resistance to impact is the most important property of a plastic material. It is also notoriously one of the most difficult to assess.

If a rigid polymer is struck a blow at a temperature well below its glass transition temperature, deformation will be small before break occurs. Nevertheless, because of the high modulus, quite high tensile strengths will be recorded. But the energy required to cause the break will be given by the area under the stress–strain curve and it will not be very large as shown in Fig. 3.21. On the other hand, if an amorphous polymers struck above the T_g, i.e. in the rubbery state, large extensions are possible before



Rigid Polymer, Below T_g has Very High Tensile Strength, but Less Area under the Curve = Less Energy to Break

Rigid Polymer, Above T_g has Lower Tensile Strength, but More Area Under Curve = More Energy to Break

Figure 3.21 Stress vs. strain curves for two plastics.

fracture occurs and, although the tensile strength will be much lower, the energy to break (the area under the curve) will be much more, so that for many purposes the material will be regarded as tough.

A common material performance need is a rigid plastic with the toughness of rubber. This can be achieved in a number of ways:

1. By the use of a moderately crystalline polymer with a T_g well below the expected service temperature (e.g. polyethylene).
2. By block copolymerization, so that one component of the block copolymer has a T_g well below the expected service temperature range (e.g. polypropylene with small blocks of polyethylene or preferably polypropylene with small amorphous blocks of ethylene–propylene copolymer).
3. By blending with semi-compatible materials that have a T_g well below the expected service temperature range (e.g. high-impact polystyrene).
4. By the use of a polymer that has effective transitions at or below the expected service temperature range and which is able to respond to stress by extensive deformation (e.g. polycarbonates).
5. By plasticization. This in effect reduces the T_g and in the case of nylon, which has absorbed small quantities of water, the toughening effect can be quite substantial.

In terms of a stress–strain curve, a brittle material may be considered to be one that breaks without a yield while a tough material yields to give a substantial energy to break. Keep in mind that if a material has not broken after being struck simply because it yielded to an unrecoverable extent the product may still be useless.

Toughness is not simply a function of polymer structure or the mode of stressing. It clearly will also depend on the temperature and the rate of striking but more important still it will depend on the product design and method of manufacture.

Stress tends to concentrate at defects such as the presence of notches, sharp angles, holes, voids, particle inclusions, or small inserts. Different polymers vary in their "notch sensitivity" and this is presumably a reflection of how close they are to their tough–brittle transitions. The aim of the designer and processor must be to reduce such stress concentration to a minimum.

3.3 Thermal Property Testing of Plastics

The properties of plastic films are affected by temperature. There are also several thermal properties of a more basic nature that affect films' performance. This section will discuss what those properties are and how they are measured.

3.3.1 Melt Flow Index

The melt flow index (MFI) is a measure of the ease of flow of the melt of a thermoplastic polymer. It is defined as the weight of polymer in grams flowing in 10 min through a die of specific diameter and length by a pressure applied by a given weight at a given temperature. The method is given in ASTM D1238 and ISO 1133. The test equipment is diagramed in Fig. 3.22.

The conditions of the test depend upon the type of the polymer, some of which are shown in Table 3.14. One does not want a temperature so high that the polymers in the plastic decompose. The melt flow rate is an indirect measure of molecular weight, with high melt flow rate corresponding to low molecular weight. Synonyms of MFI are melt

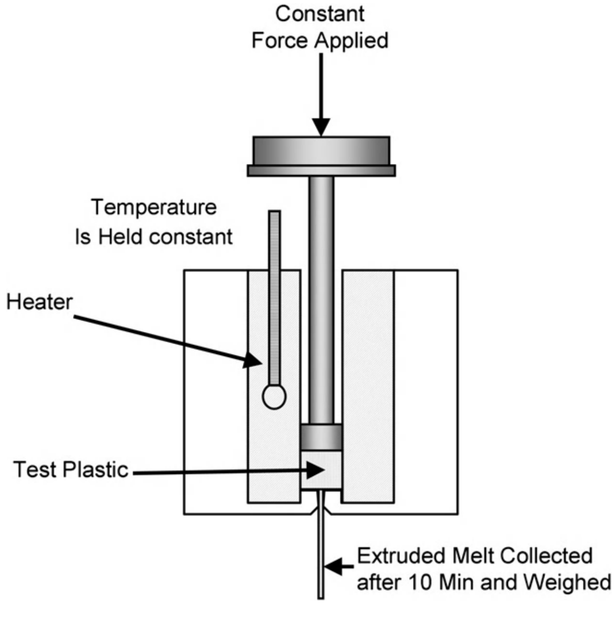


Figure 3.22 Melt flow index test apparatus.

Table 3.14 Recommended Conditions for Determination of Melt Flow Rate and Melt Volume Rate for Common Materials According to International Organization for Standardization (ISO) and American Society for Testing and Materials (ASTM) Guidelines (e.g. 190/2.16 = 190 °C with 2.16 kg Weight)

Plastic/Polymer	ASTM Standard Conditions (°C/kg)	ISO Standard Conditions (°C/kg)
Acetals (copolymer and homopolymer)	190/2.16, 2.16, 1.05	190/2.16
Acrylics	230/1.2, 230/3.8	230/3.8
Acrylonitrile–butadiene–styrene (ABS)	200/5.0, 230/3.8, 220/10	220/10
Acrylonitrile/butadiene/styrene/ polycarbonate blends	230/3.8, 250/1.2, 265/3.8, 265/5.0	
Cellulose esters	190/0.325, 190/2.16, 190/21.60, 210/2.16	
Ethylene–chlorotrifluoroethylene copolymer (ECTFE)	271.5/2.16	
Ethylene–tetrafluoroethylene copolymer (ETFE)	297/5.0	
Nylon	275/0.325, 235/1.0, 235/2.16, 235/ 5.0, 275/5.0	
Perfluoro(ethylene–propylene) copolymer (FEP)	372/2.16	
Perfluoroalkoxyalkane (PFA)	372/5.0	
Polycaprolactone	125/2.16, 80/2.16	
Polychlorotrifluorethylene (PCTFE)	265/12.5	
Polyether sulfone (PES)	380/2.16, 360/10, 343/2.16,	
Polyethylene (PE)	125/0.325, 125/2.16, 250/1.2, 190/0.325, 190/2.16, 190/21.60, 190/10, 310/12.5	190/2.16, 190/21.6, 190/0.325, 190/5
Polycarbonate (PC)	300/1.2	300/1.2
Polypropylene (PP)	230/2.16	230/2.16
Polyphenyl sulfone (PPSU)	365/5.0, 380/2.16	
Polystyrene (PS)	200/5.0, 230/1.2, 230/3.8, 190/5.0	200/5
Polysulfone (PSU)	343/2.16, 360/10	
Polyterephthalate	250/2.16, 210/2.16, 285/2.16	
Poly(vinyl acetal)	150/21.6	
Poly(vinylidene fluoride) (PVF)	230/21.6, 230/5.0,	
Poly(phenylene sulfide) (PPS)	315/5.0	
Styrene–acrylonitrile (SAN)	220/10, 230/10, 230/3.8,	220/10
Styrenic thermoplastic elastomer	190/2.16, 200/5.0	
Thermoplastic elastomer–ether–ester	190/2.16, 220/2.16, 230/2.16, 240/2.16, 250/2.16	
Thermoplastic elastomers (TEO)	230/2.16	
Vinylidene fluoride copolymers	230/21.6, 230/5.0	

flow rate and melt index, which are commonly abbreviated: MFR and MI. When the volume of the extrudate is measured, the melt volume rate is reported.

3.3.2 Heat Deflection Temperature

The heat deflection temperature (HDT) is a measure of a polymer's resistance to distortion under a given load at elevated temperatures. Other terms for this measurement include deflection temperature under load or heat distortion temperature.

The test is performed using an apparatus diagramed in Fig. 3.23. A test bar is molded of a specific thickness and width. The test sample is submerged in oil that is gradually heated. The load is applied to the midpoint of the test bar that is supported near both ends. The temperature at which a bar of material is deformed 0.25 mm is recorded as the HDT.

The ASTM test is ASTM D648 while the analogous ISO test is ISO 75. The test using a 1.8 MPa load is performed under ISO 75 Method A while the test using a 0.46 MPa load is performed under ISO 75 Method B. Less common is the test using an 8 MPa load performed under ISO 75 Method C.

The HDT value obtained for a specific polymer grade will depend on the base resin and on the presence of reinforcing agents. Deflection temperatures of glass fiber or carbon fiber reinforced engineering polymers will often approach the melting point of the base resin.

The HDT test results are a useful measure of relative service temperature for a polymer when used in load-bearing parts. However, the deflection temperature test is a short-term test and should not be used alone for product design. Other factors such as the time of exposure to elevated temperature, the rate of temperature increase, and the part geometry all affect the performance.

3.3.3 Vicat Softening Temperature

The Vicat softening temperature is the temperature at which a flat-ended needle penetrates the specimen to the depth of 1 mm under a specific load. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application.

A test specimen is placed in the testing apparatus such as that diagramed in Fig. 3.24. The penetrating needle rests on its surface. A load of 10 N or 50 N is applied to the specimen. The specimen is then lowered into an oil bath at 23 °C. The bath is raised at a rate of 50° or 120 °C per hour until the needle penetrates 1 mm. The temperature at that moment is called the Vicat softening temperature.

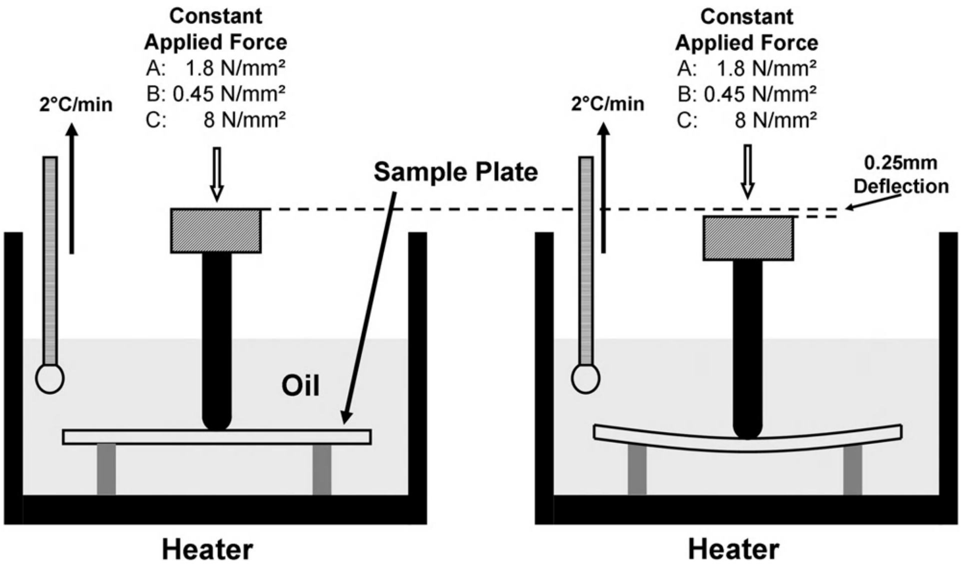


Figure 3.23 Heat deflection temperature test apparatus.

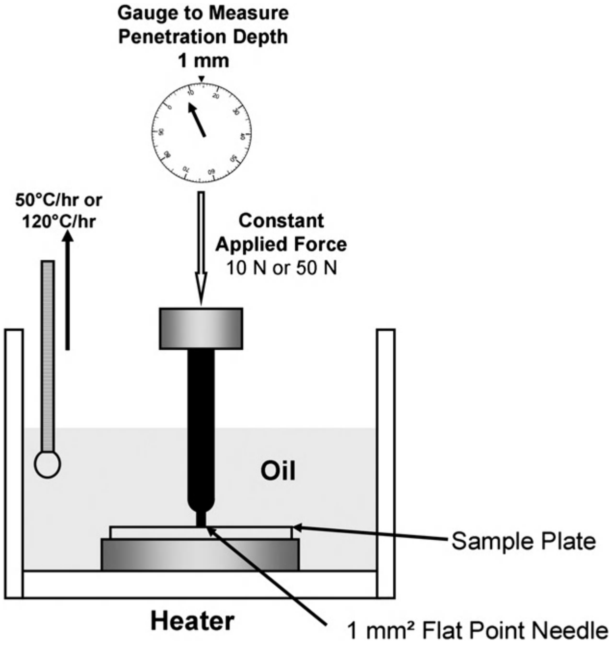


Figure 3.24 Vicat softening temperature test apparatus.

The relevant standards are ISO 306 and ASTM D1525. ISO 306 describes two methods, Method A with a load of 10 N and Method B with a load of 50 N, each with two possible rates of temperature rise, 50 °C per h and 120 °C per h. This results in ISO values reported as A50, A120, B50, or B120.

3.3.4 Melting Point (T_m)

A melting process is illustrated in Fig. 3.25 for the case polyethylene terephthalate polymer, which is slowly heated through its melting temperature, and two other thermal transitions besides.

Again, as the melting temperature is reached, an endothermal peak appears because heat must be preferentially added to the sample to continue this essentially constant temperature process. The peak breadth is primarily related to the size and degree of perfection of the polymer crystals. This differential scanning calorimetry (DSC) also provides additional information: the glass transition temperature, and a crystallization temperature.

Note that if the process were reversed so that the sample was being cooled from the melt, the plot would be approximately inverted at the melt point and glass transition temperature. This corresponds to an exothermal process.

3.3.5 Glass Transition Temperature (T_g)

The glass transition temperature, often called T_g (or "T sub g"), is an important property when considering polymers for a particular end use. The glass transition temperature is the temperature below which the physical properties of plastics change in a manner similar to those of a glassy or crystalline state, and

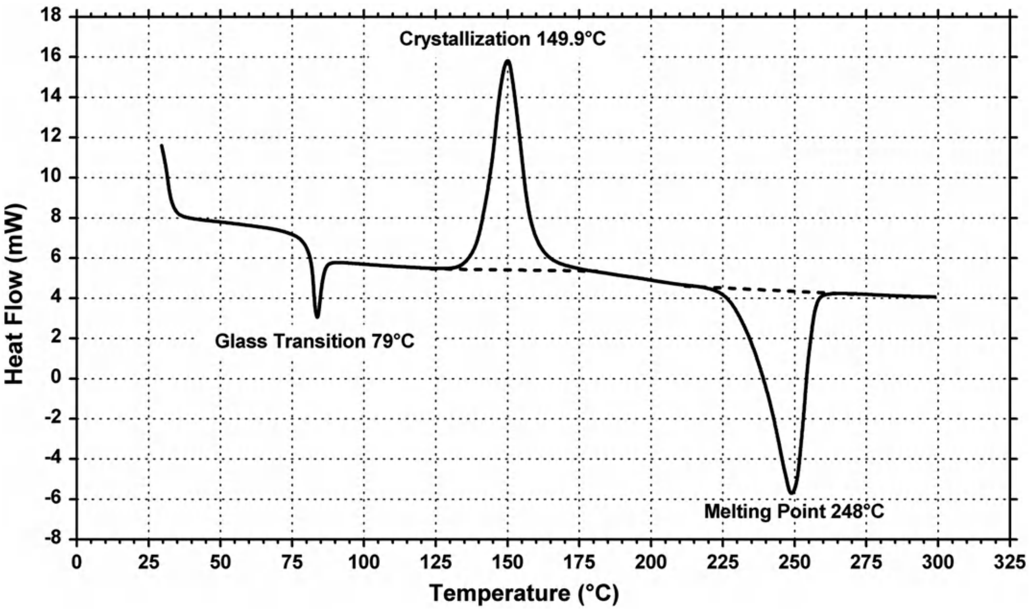


Figure 3.25 Melting point estimation from a differential scanning calorimetry of polyethylene terephthalate.

above which they behave like rubbery materials. A plastic's T_g is the temperature below which molecules have little relative mobility. T_g is usually applicable to wholly or partially amorphous plastics. A plastic's properties can be dramatically different above and below its T_g. The next sections show a number of ways to measure or estimate the T_g. These methods will indicate how some of the properties change around the T_g. The value of the glass transition temperature depends on the strain rate and cooling or heating rate, so there cannot be an exact value for T_g.

3.3.5.1 Mechanical Methods of Estimating T_g

It is possible to calculate a value for the glass transition temperature by measuring the elastic (or Young's) modulus of the plastic as a function of the temperature, e.g. by using a torsion pendulum. Around T_g, there is a large fall in the value of the modulus, as shown in Fig. 3.26. The frequency of the oscillation is important since T_g value depends on the time allowed for chain segment rotation. While this approach is not commonly used, as there are better methods, it does demonstrate one way in which a plastic's physical properties change above and below the T_g.

A more common mechanical method is dynamic mechanical thermal analysis (DMTA). DMTA is also called dynamic mechanical analysis or dynamic thermomechanical analysis. An oscillating force is applied to a sample of material and the resulting displacement of the sample is measured. From this, the stiffness of the sample can be determined, and the sample modulus can be calculated. A plot of loss modulus as a function of temperature shows a maximum at T_g, as shown in Fig. 3.27. Figure 3.27 shows a series of blends of high-impact styrene and polyphenylene oxide (PPO). As the amount of PPO is increased, the T_g increases. The single T_g indicates that these blends are miscible.

3.3.5.2 Thermal Mechanical Analysis

This method of measuring glass transition temperature measures the extension (change in length) of a piece of film as the temperature is raised. The advantage of this technique is that is can be done on a small films sample. The film piece is usually at least 10 μm thick, 2 mm wide, and 15–20 mm long. The equipment is a thermomechanical analyzer such as a Perkin Elmer TMA-7 with a film fixture. It is run in extension mode. A 30-mN load is put on the film and the temperature is slowly raised at a uniform rate and the extension is measured. Extension is plotted vs. temperature as shown in Fig. 3.28. Two tangent lines are draw as shown and the intersection of these two lines is the glass transition temperature. Usually the points at which the tangent lines part from the

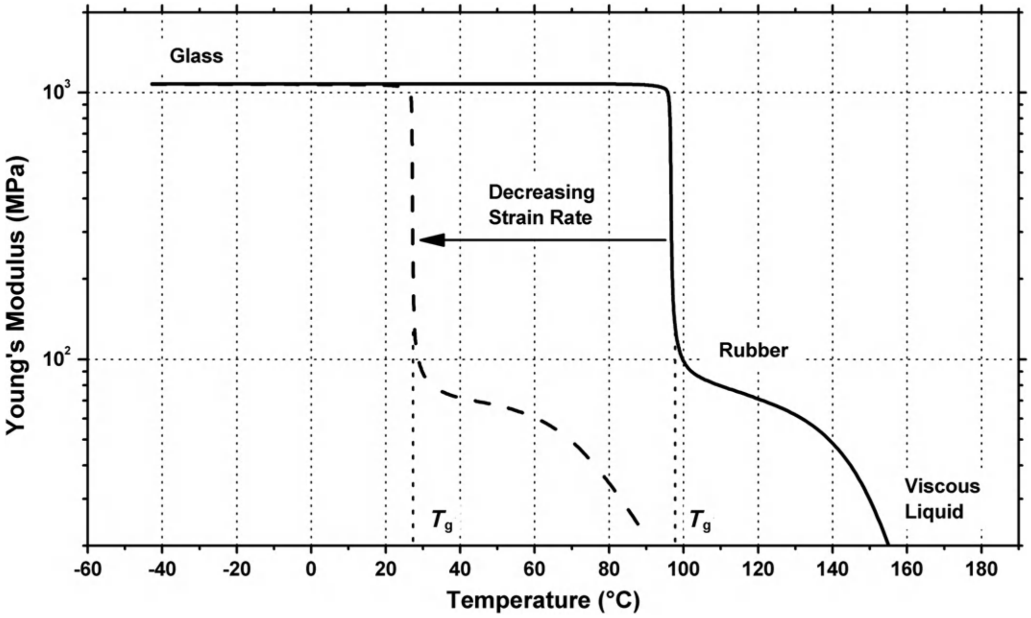


Figure 3.26 T_g estimate from an elastic modulus vs. temperature study.

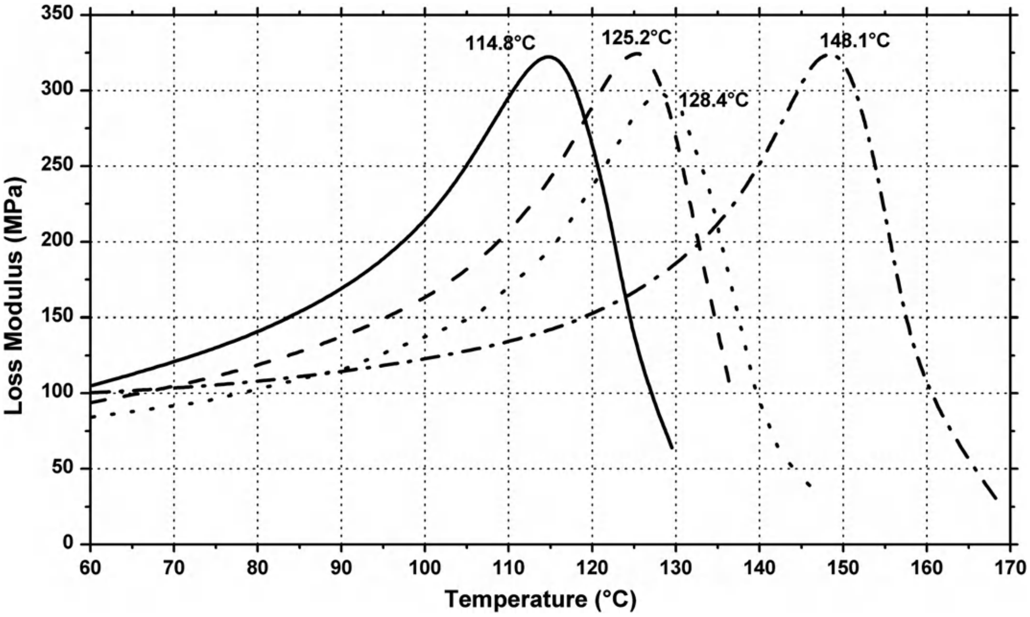


Figure 3.27 T_g estimate from dynamic mechanical thermal analysis study.

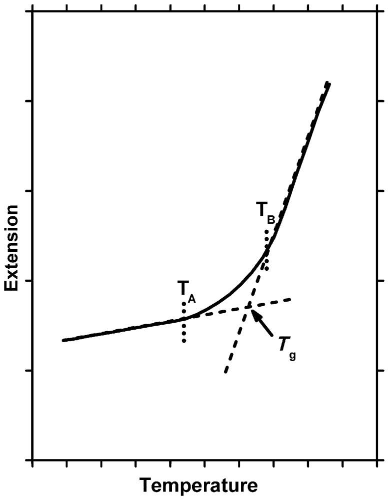


Figure 3.28 Generic thermal mechanical analysis plot used to determine glass transition temperature.

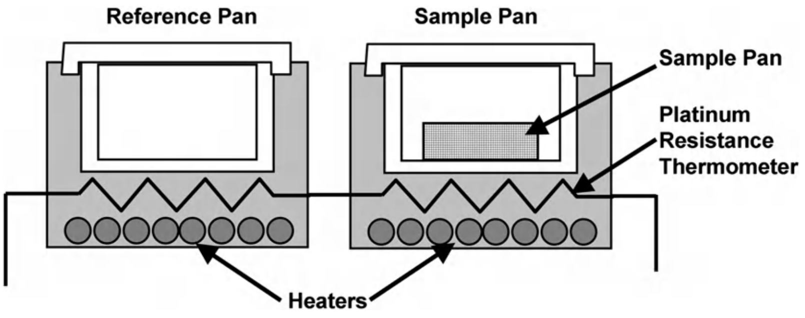
measurements, T_A and T_B, gives a glass transition range that may be reported.

3.3.5.3 Thermal Methods of Estimating T_g

Thermal methods of measuring T_g are based on DSC. In DSC, the thermal properties of a sample are compared against a standard reference material, typically inorganic, which has no transitions such as a melting point in the temperature range of interest. A common reference material is powdered alumina. The sample and reference are each contained in a small holder within an adiabatic enclosure as illustrated in Fig. 3.29.

The temperature of each holder is monitored by a thermocouple and heat can be supplied electrically to each holder to keep the temperature of the two equal. The difference in the amount of heat required

Figure 3.29 Diagram of a differential scanning calorimetry sample and reference cell.



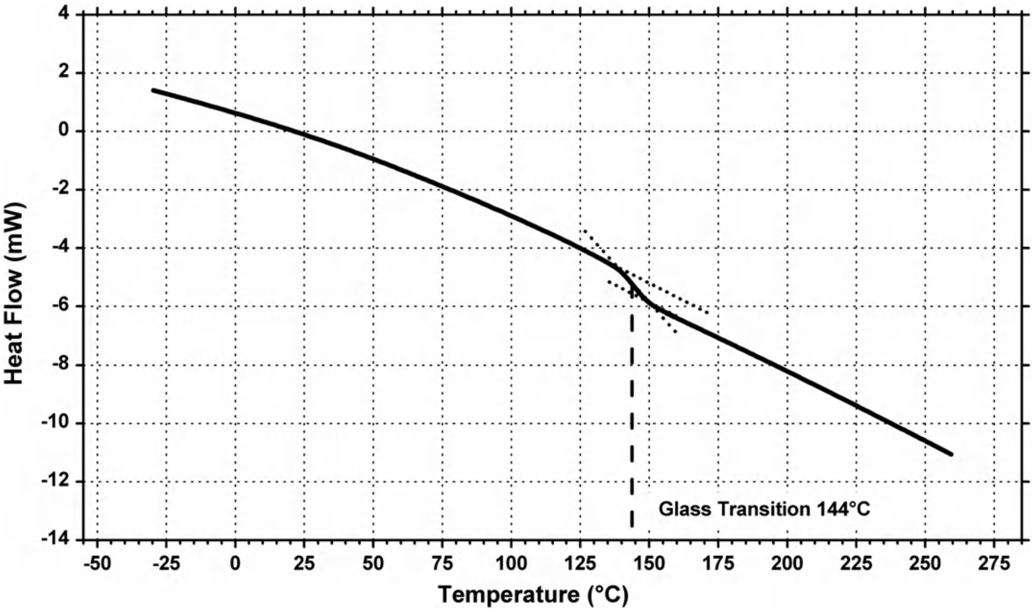


Figure 3.30 Schematic of a differential scanning calorimetry showing a T_g.

to maintain equal temperature is recorded. A plot is recorded of the difference in energy supplied against the average temperature. As the temperature is slowly increased, thermal transitions may be identified.

The glass transition process is illustrated in Fig. 3.30 for a glassy polymer that does not crystallize and is being slowly heated from below T_g.

Here, the drop marked T_g at its midpoint represents the increase in energy supplied to the sample to maintain it at the same temperature as the reference material due to the relatively rapid increase in the heat capacity of the sample as its temperature is raised through T_g. The addition of heat energy corresponds to this endothermal direction.

The specific heat or specific heat capacity, C_p, can be measured using DSC. It can change dramatically at the T_g, as shown in Fig. 3.31. The value of T_g

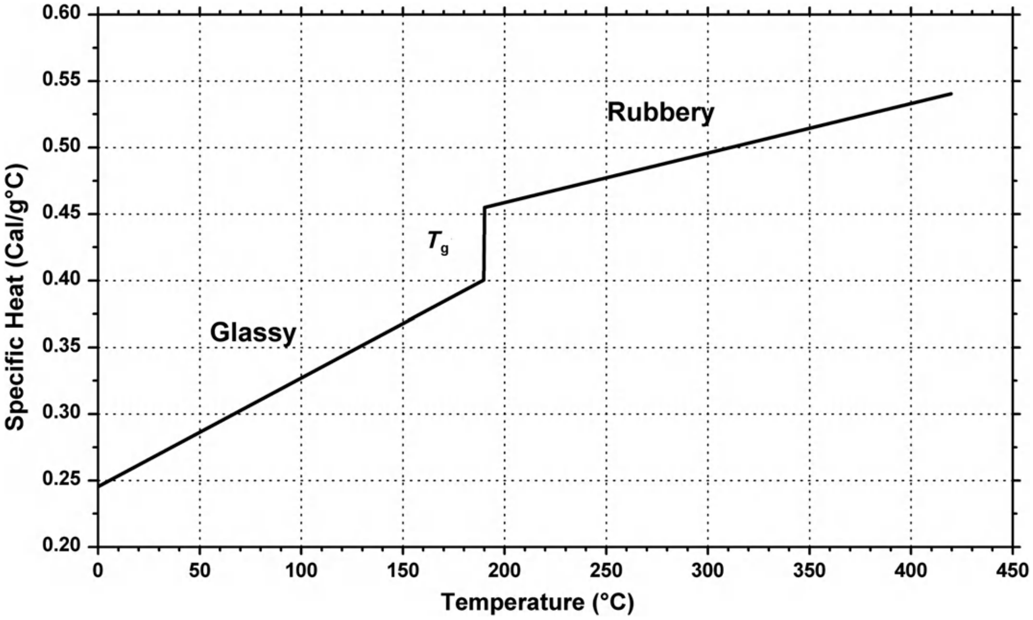


Figure 3.31 T_g estimate from the change in specific heat capacity vs. temperature for a commercial polysulfone.

depends on the heating or cooling rate of the calorimetry experiment.

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4 Styrenic Plastics

This chapter on styrenic plastics covers a broad class of polymeric materials of which an important part is styrene. Styrene, also known as vinyl benzene, is an organic compound with the chemical formula $C_6H_5CH{=}CH_2$. Its structure is shown in Fig. 4.1.

It is used as a monomer to make plastics such as polystyrene, acrylonitrile–butadiene–styrene (ABS), styrene–acrylonitrile (SAN), and the other polymers in this chapter. A summary of the use of primary sterilization methods for styrenic plastics is given in Table 4.1

4.1 Acrylonitrile–Butadiene–Styrene Copolymer

Acrylonitrile–butadiene–styrene, or ABS, is a common thermoplastic used to make light, rigid, molded products.

SAN copolymers have been available since the 1940s and while their increased toughness over polystyrene made them suitable for many applications, their limitations led to the introduction of a rubber, butadiene, as a third monomer, producing the range of materials popularly referred to as ABS plastics. These became available in the 1950s. The availability of these plastics and ease of processing led ABS to become one of the most popular of the engineering polymers.

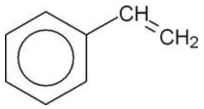


Figure 4.1 Chemical structure of styrene.

The chemical structures of the monomers are shown in the Fig. 4.2. The proportions of the monomers typically range from 15–35% acrylonitrile, 5–30% butadiene, and 40–60% styrene. It can be found as a graft copolymer, in which SAN polymer is formed in a polymerization system in the presence of polybutadiene rubber latex; the final product is a complex mixture consisting of SAN copolymer, a graft polymer of SAN, and polybutadiene and some free polybutadiene rubber. The CAS is 9003-56-9.

Styrenic plastics in general should not be sterilized by steam or autoclave methods. This is due to relatively low heat resistance. The butadiene rubber component of ABS can turn yellow when exposed to ultraviolet (UV) light or high heat and requires

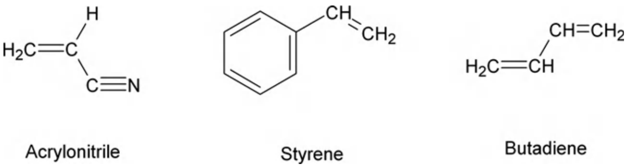


Figure 4.2 Chemical structures of acrylonitrile–butadiene–styrene raw materials.

Table 4.1 General Sterilization Capabilities of Styrenic Plastics

Polymer	Steam	Dry Heat	Ethylene Oxide	Gamma Radiation	E-Beam
ABS	Poor	Poor	Good	Good	Good
MABS	Poor	Poor	Good	Good	Good
ASA	Poor	Poor	Good	Good	Good
Polystyrene	Poor	Poor	Good	Good	Good
SAN	Poor	Poor	Good	Good	Good
SBC	Poor	Poor	Good	Good	Good

Note: ABS, acrylonitrile–butadiene–styrene; MABS, methacrylate–acrylonitrile–butadiene–styrene; SAN, styrene–butadiene; SBC, styrene–butadiene copolymer; ASA, acrylonitrile–styrene–acrylic copolymer.

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00004-6

stabilizers to reduce or eliminate the color shift. ABS can be sterilized by ethylene oxide (EtO), gamma, and electron beam (e-beam) radiation. The dose of radiation one may deliver will depend upon the amount of styrene content in the polymer. The aromatic ring content (benzene ring structure) protects the polymer. However, high-dose radiation should be avoided on high-impact grades. The greater the styrene content, the better the polymer's resistance to high-energy radiation. Sterilization of ABS with ethylene oxide is limited to a few cycles only. ABS is also stable up to 75−100 kGy doses of gamma and e-beam radiation.

Manufacturers and trade names include: SABIC Innovative Polymers Cycolac®; INEOS Lustran® and Novodur®; Perrite Ronfalin®, Dow Magnum, and BASF AG Terulan®.

Sterile applications and uses: Medical devices, intravenous (IV) connectors and valves, inhaler housings, surgical instruments, instrument handles, trays and kits, surgical equipment, surgical staplers, home test kits, roller clamps, and piercing pins.

Gamma radiation resistance: The decrease in impact strength of ABS after gamma radiation sterilization is generally attributed to the radiation cross-linking of the butadiene rubber phase of the ABS, which reduces its ductility.[1] The higher the radiation dosage, the greater the cross-linking, and the lower the ultimate impact strength. At the sterilization exposure level of 10 Mrad, the high-gloss ABS

Table 4.2 Gamma Radiation Sterilization Effects on Dow Chemical Magnum 2642[3]

Sterilization Conditions						
Radiation dose (Mrad)	Unexposed	2.5	2.5	10	10	
Postconditioning (weeks)	–	1	8	1	8	
Properties						**Test Method**
Tensile yield (MPa)	39	34	33	34	34	ASTM D638
Elongation (%)	102	96	86	9	84	ASTM D638
Izod impact (J/m)	192	155	187	133	139	ASTM D256
Peak energy (J)	30	27	27	22	26	ASTM D3763

Table 4.3 Effects of Gamma Radiation Sterilization on Low-Gloss Dow ABS[2]

Sterilization Conditions							
Radiation dose (Mrad)	2.5	2.5	2.5	10	10	10	
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	103.1	106.6	108.7	108.6	111.9	111.6	ASTM D638
Tensile strength at yield	103.1	102.5	102	110.1	110.6	107.5	ASTM D638
Elongation at break	97.3	86.7	86.7	61.3	74.7	73.3	ASTM D638
Dart impact (total energy)	167.2	188.2	175.5	117.2	124.5	106.4	ASTM D3763
Notched Izod impact	96	92	104	80	96	88	ASTM D3763

Note: Cobalt 60 source, 21 °C.

showed losses in impact strength accompanied by a slight increase in tensile strength and a decrease in tensile elongation-at-break. This change is attributed to the cross-linking of the butadiene rubber matrix.[2]

If the rubber content is high enough, cross-linking becomes the dominating factor in determining the physical property characteristics of the polymer upon irradiation. Thus, cross-linked butadiene rubber loses its impact strength at dosages sufficient to cross-link all the rubber, and so the enhanced impact properties originally provided by the rubber modifier are lost. The remaining impact strength of the material will be no better than that of the unmodified polymer. Comparing the notched Izod impact strength at 2.5 Mrad and 10 Mrad, one can see the loss in properties with the increase in radiation dosage.[2]

Electron beam radiation resistance: E-beam radiation will generally cause a decrease in the impact strength of ABS.

Ethylene oxide resistance (EtO): ABS samples exposed to repeated EtO cycles show minor surface attack.[3]

Regulatory status: Magnum 2600 series ABS resins have USP XXIII Class VI test data as well as non-USP for biocompatibility classified testing. Cycolac HP20 and HP30 have USP Class VI rating.

Data for ABS plastics are found in Tables 4.2−4.17 and Figs 4.3−4.18.

The Dow Chemical Magnum® 2600 series includes Magnum 2620 (high gloss), Magnum 2630 (high gloss), and Magnum 2642 (low gloss); these are designated for health care applications. Magnum 9020

Table 4.4 Effects of Gamma Radiation Sterilization on High-Gloss Dow ABS[2]

Sterilization Conditions							
Radiation dose (Mrad)	2.5	2.5	2.5	10	10	10	
Postconditioning time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	99.9	109.5	103.9	104.5	105.3	105.3	ASTM D638
Tensile strength at yield	104.1	121.6	107.5	107.7	110.7	111	ASTM D638
Elongation at break	84.2	60.5	60.5	60.5	50	60.5	ASTM D638
Dart impact (total energy)	216.1	183.4	202.4	159.5	138	105.9	ASTM D3763
Notched Izod impact	71.9	67.2	67.2	45.3	42.2	43.8	ASTM D3763

Note: Cobalt 60 source, 21 °C.

Table 4.5 Effects of Gamma Radiation Sterilization on Dow Magnum 9020 ABS[4]

Sterilization Conditions					
Radiation dose (Mrad)	2.5	10	2.5	10	
Postconditioning type	Storage under fluorescent light		Storage in dark		
Postconditioning time (h)	336	336	336	336	
Properties Retained (%)					**Test Method**
Tensile strength at yield	105.4	114.3	103.6	107.1	ASTM D638
Notched Izod impact	71.9	45.3	71.9	45.3	ASTM D3763

Note: Cobalt 60 source, 21 °C.

Table 4.6 Effects of Gamma Radiation Sterilization on Dow Magnum 2640 and 2642 ABS[1]

Product	**Magnum 2620, High Gloss**				**Magnum 2642, Low Gloss**				
Sterilization Conditions									
Radiation dose (Mrad)	2.5	2.5	10	10	2.5	2.5	10	10	
Postconditioning time (h)	168	1344	168	1344	168	1344	168	1344	
Properties Retained (%)									
Tensile strength	104.9	104.9	100	107.3	106.3	103.1	106.3	106.3	ASTM D638
Flexural strength	102.8	101.4	109.7	104.2	105.2	101.7	110.3	105.2	ASTM D638
Elongation	106.5	80.6	77.4	77.4	107.9	96.6	103.4	94.4	ASTM D790
Impact strength	95.6	84.9	76.5	70.1	78.7	94.9	67.5	70.6	ASTM D638
Dart impact (peak energy)	102.1	104.3	104.3	85.1	90	90	73.3	86.7	ASTM D3763
Dart impact (total energy)	102.1	104.3	104.3	85.1	91.3	91.3	63	87	ASTM D3763
Heat deflection temperature	100	98.8	97.5	100	105.9	107.4	105.9	108.8	ASTM D648
Vicat softening point	100	98.2	98.2	98.2	99	99	100	99	ASTM D1525
Δa Color	1.47	2.34	2.6	2.26	−1.7	−0.8	0.4	−0.6	ASTM D2244
Δb Color	−2.39	1.99	−3.75	6.93	6.3	5.1	7.1	10.5	ASTM D2244
ΔL Color	−7.35	−2.11	−16.34	−3.16	−9.3	−1.5	−14.5	−3	ASTM D2244

Table 4.7 Effects of Gamma Radiation Sterilization on Ineos Lustran® ABS 248 and 743 Material[5] (*Test Method: ASTM D256*)

Material	**Lustran® ABS 248**				**Lustran® ABS 743**			
Sterilization Conditions								
Radiation dose (Mrad)	1.5	2.5	3.5	5	1.5	2.5	3.5	5
Properties Retained (%)								
Notched Izod impact	90	90	90	90	90	90	90	90

Table 4.8 Effects of Electron Beam Radiation Sterilization on Ineos Lustran® ABS 248 and 743 Material[5] (*Test Method: ASTM D256*)

Material	**Lustran® ABS 248**				**Lustran® ABS 743**			
Sterilization Conditions								
Radiation dose (Mrad)	1.5	2.5	3.5	5	1.5	2.5	3.5	5
Properties Retained (%)								
Notched Izod impact	100	97	95	90	100	98	96	94

Table 4.9 Ethylene Oxide (EtO) Sterilization Effects Using HCFC Carrier Gas on Dow Chemical Magnum 2642[3]

Postexposure Conditioning						
Weeks	Unexposed	1	8	1	8	
Properties						**Test Method**
Tensile yield (MPa)	39	32	37	31	37	ASTM D638
Elongation (%)	102	72	95	54	91	ASTM D638
Izod impact (J/m)	192	192	176	181	176	ASTM D256
Peak energy (J)	30	29	24	29	28	ASTM D3763

Note: Carrier gas, HCFC.

Table 4.10 Ethylene Oxide Sterilization Effects Using Pure EtO Carrier Gas on Dow Chemical Magnum 2642[3]

Sterilization Conditions						
Cycles	Unexposed	1	3	1	3	
Properties						**Test Method**
Tensile yield (MPa)	39	36	36	36	36	ASTM D638
Elongation (%)	102	86	87	77	82	ASTM D638
Izod impact (J/m)	192	176	176	176	187	ASTM D256
Peak energy (J)	30	28	24	29	26	ASTM D3763

Note: Carrier gas, ethylene oxide.

Table 4.11 Effects of Ethylene Oxide Sterilization on Dow Low-Gloss ABS[2]

Sterilization Conditions							
Cycles	1	1	1	5	5	5	
Postexposure Conditioning at 21 °C							
Storage in dark, time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	103.9	100.4	103.1	97.8	101.2	99.9	ASTM D638
Tensile strength at yield	99.9	98.3	101.1	98.1	99.2	98.5	ASTM D638
Elongation at break	74.7	45.3	56	26.7	24	17.3	ASTM D638
Dart impact (total energy)	52.9	56.9	65.7	53.9	45.1	59.8	ASTM D3763
Notched Izod impact	116	120	108	136	128	120	ASTM D3763

Note: (1) Preexposure conditioning: time: 8 h, 37.8 °C, RH: 60%. (2) Exposure conditions: 49 °C, 60% RH, 8 h, 12% EtO/88% Freon. (3) Postexposure conditions: Evacuation at 127 mmHg, aeration at 32.2 °C for ≥16 h.

Table 4.12 Effects of Ethylene Oxide Sterilization on Dow High-Gloss ABS[2]

Sterilization Conditions							
Cycles	1	1	1	5	5	5	
Postexposure Conditioning at 21 °C							
Storage in dark, time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	103.4	105	105	105.5	106.1	107.3	ASTM D638
Tensile strength at yield	103.3	106	107	105.1	107.5	108.5	ASTM D638
Elongation at break	71.1	50	63.2	42.1	44.7	42.1	ASTM D638
Dart impact (total energy)	187.8	178	169.8	148.8	116.1	107.3	ASTM D3763
Notched Izod impact	95.3	90.6	87.5	92.2	84.4	81.3	ASTM D3763

Note: (1) Preexposure conditioning: 8 h, 37.8 °C, RH: 60%. (2) Exposure conditions: 49 °C, 60% RH, 8 h, 12% EtO/88% Freon. (3) Postexposure conditions: Evacuation at 127 mmHg, aeration at 32.2 °C for ≥16 h.

Table 4.13 Effects of Ethylene Oxide Sterilization on Dow Magnum 2642 ABS[10]

Sterilization Conditions									
Composition	12% EtO and 88% Freon				8.6% EtO and 91.4% HCFC-124				
Cycles	1	1	2	2	1	1	2	2	
Postexposure Conditioning at Ambient Conditions									
Storage, time (h)	168	1344	168	1344	168	1344	168	1344	
Properties Retained (%)									**Test Method**
Tensile strength at yield	100.7	100.8	100.5	95.2	97.2	91.4	100.3	95.9	ASTM D638
Elongation at break	90.9	127.3	81.8	72.7	100	109.1	127.3	100	ASTM D638
Tensile modulus	97.1	101.3	100.3	76.8	98.7	96.2	101.6	72.6	ASTM D638
Dart impact (total energy)	69	89.7	100	37.9	65.5	65.5	89.7	94.9	ASTM D3763
Notched Izod impact	92.3	102.6	72.4	53.8	87.2	82.1	69	79.3	ASTM D3763
ΔE color	0.26	0.41	0.16	0.48	0.24	0.76	0.41	0.61	

Note: (1) Preexposure conditioning: 18 h, 37.8 °C, RH: 60%. (2) Exposure conditions: 48.6 °C, 60% RH, 6 h. (3) Postexposure conditions: Aeration at 32.2 °C, 127 mmHg.

Table 4.14 Effects of Ethylene Oxide Sterilization on Dow Magnum 2642 ABS[10]

Sterilization Conditions				
Gas composition	12% EtO and 88% Freon		8.6% EtO and 91.4% HCFC-124	
Postexposure Conditions				
Aeration changes per hour	10	30	10	30
Temperature (°C)	32.2	54.4	32.2	54.4
Residual Ethylene Oxide (ppm)				
Little or no aeration	984	984	866	866
24 h Aeration	465	200	467	383
48 h Aeration	–	162	–	195
72 h Aeration	152	146	258	169
168 h Aeration	92	–	134	–

Note: (1) Preexposure conditioning: 18 h, 37.8 °C, 60% RH. (2) Exposure conditions: 48.6 °C, 60% RH, 6 h. (3) Postexposure conditions: Aeration at 32.2 °C, 127 mmHg.

Table 4.15 Effects of Ethylene Oxide Sterilization on Dow Magnum 9020 ABS[4]

Exposure Conditions			
Cycles	1	5	
Properties Retained (%)			**Test Method**
Tensile strength at yield	103.6	105.4	ASTM D638
Notched Izod impact	95.3	92.2	ASTM D256

Note: (1) Preexposure conditioning: 8 h, 37.8 °C, 60% RH. (2) Exposure conditions: 49 °C, 60% RH, ≥6 h, 12% EtO and 88% Freon. (3) Postexposure conditions: (1) Aeration at 32 °C, 127 mmHg, ≥16 h; (2) Storage in dark, 21 °C, 336 h, 50% RH.

is one of the highest gloss ABS resins with high-impact strength and medium flow.

INEOS Lustran ABS 248 is a high-gloss, medium impact ABS. Lustran ABS 743 is a high-impact ABS.

4.2 Methacrylate–Acrylonitrile–Butadiene–Styrene Copolymer

Methacrylate–acrylonitrile–butadiene–styrene (MABS) copolymer is similar to ABS except for the addition of an additional monomer, usually methyl methacrylate. MABS is an amorphous, clear, transparent material with the thermal and mechanical properties like ABS. The transparency is achieved by matching the refractive indices of the matrix resin (the transparent acrylate-acrylonitrile-styrene polymer) with the polybutadiene rubber impact modifier. MABS has the highest impact resistance of all the styrenic plastics.

Manufacturers and trade names include: Samsung Starex, BASF AG Terlux®.

Applications requiring sterilization include: Infusion sets, tubing, multiflow devices.

Data for MABS plastics are found in Table 4.18 and Fig. 4.19.

4.3 Polystyrene

Polystyrene is the simplest plastic based on styrene. Its structure is shown in Fig. 4.20. CAS Number: 9003-53-6.

4.3.1 General-Purpose or Crystal Polystyrene

Pure solid polystyrene is a colorless, hard plastic with limited flexibility. Polystyrene can be transparent

Table 4.16 The Effect of Ethylene Oxide Sterilization on the Properties of High-Gloss Magnum 2620 ABS[11]

Carrier Gas	Sterilization	Postexposure Time	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Instrumented Dart Impact Peak Energy (J)	Izod (J/m)
Control	Unexposed		41	51	2230	68	2450	29	246
Average standard deviation (%)			7	45	9	2	7	13	2
HCFC-124	One cycle	1 Week	43	29	2170	70	2450	31	235
		8 Weeks	43	31	2230	72	2690	27	230
	Three cycles	1 Week	43	14	2210	71	2470	29	235
		8 Weeks	45	22	2280	73	2590	29	235
Average standard deviation (%)			7	38	13	2	4	22	2
HCFC-124/22	One cycle	1 Week	43	28	2190	72	2520	27	235
		8 Weeks	44	20	2190	70	2570	26	240
	Three cycles	1 Week	43	22	2180	71	2480	28	240
		8 Weeks	44	21	2190	71	2570	24	240
Average standard deviation (%)			7	41	7	4	9	24	2
EtO	One cycle	1 Week	42	26	2210	73	2320	28	230
		8 Weeks	43	22	2180	70	2460	26	251
	Three cycles	1 Week	42	26	2190	73	2540	31	224
		8 Weeks	43	21	2210	69	2390	24	246

Table 4.17 The Effect of Ethylene Oxide Sterilization on the Properties of Low-Gloss Magnum 2642 ABS[7]

Carrier Gas	Sterilization	Postexposure Time	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Instrumented Dart Impact Peak Energy (J)	Izod (J/m)
Control	Unexposed		39	102	1990	56	2080	26	192
Average standard deviation (%)			1	20	7	3	5	13	3
HCFC-124	One cycle	1 Week	32	72	1790	55	2080	29	192
		8 Weeks	37	95	1880	56	2180	24(33%)	176
	Three cycles	1 Week	31	54	1880	56	2110	29	181
		8 Weeks	37	91	1940	55	2170	28	176
Average standard deviation (%)			1	27	9	4	5	13	3
HCFC-124/22	One cycle	1 Week	36	71	1860	57	2120	28	187
		8 Weeks	37	85	1820	55	2220	27	181
	Three cycles	1 Week	36	66	1870	55	2140	17(47%)	181
		8 Weeks	36	68	1810	55	2090	20(44%)	181
Average standard deviation (%)			1	25	5	4	9	14	3
EtO	One cycle	1 Week	36	86	1940	56	2080	28	176
		8 Weeks	36	87	1860	53	2040	24	176
	Three cycles	1 Week	36	77	1860	55	2190	29	176
		8 Weeks	36	82	1800	55	2040	26	187

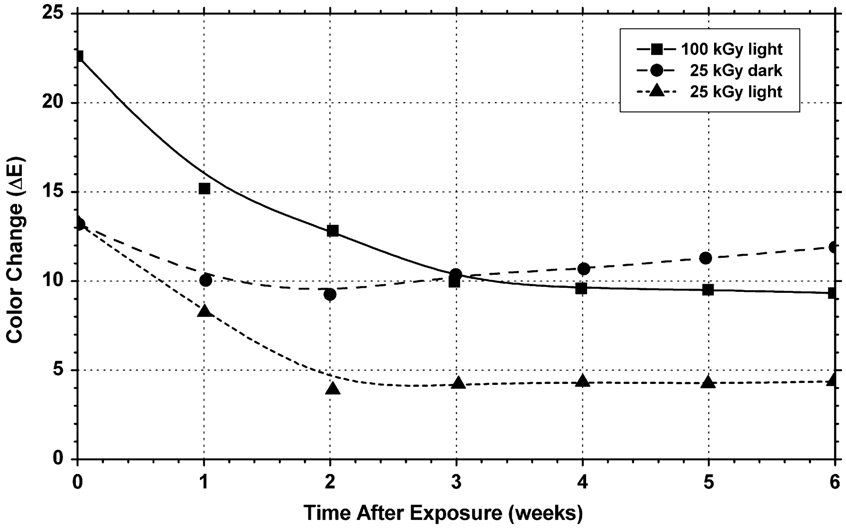


Figure 4.3 Color change (Δ*E*) of natural Dow Chemical Magnum™ 2642 after gamma sterilization.[6]

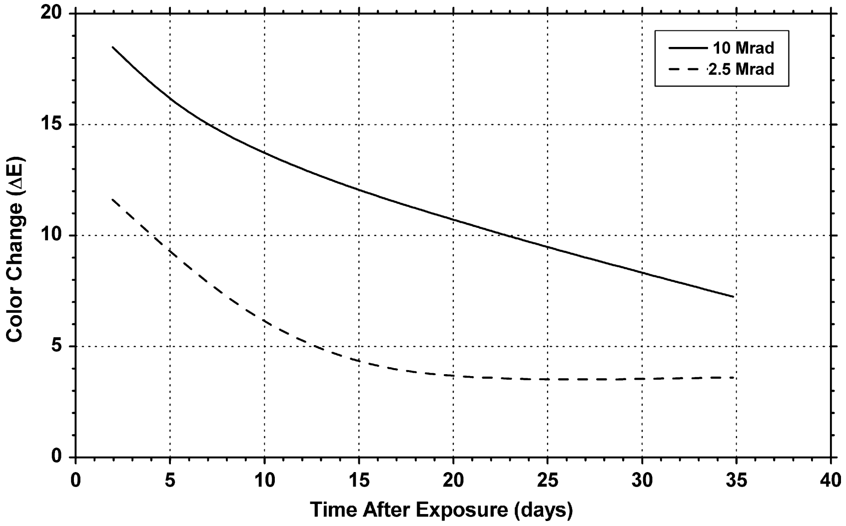


Figure 4.4 Post-gamma radiation exposure time versus Δ*E* color change of Dow Magnum™ 9020 ABS.[4]

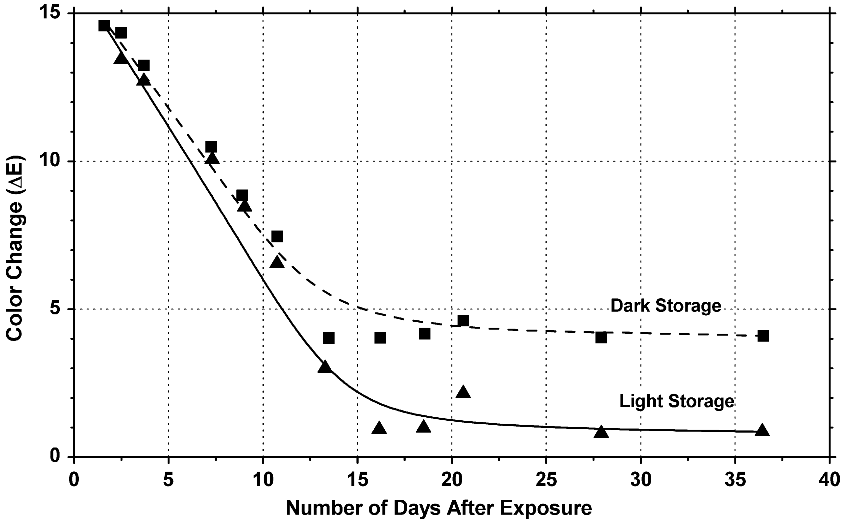


Figure 4.5 Color shift (Δ*E*) after 2.5 Mrad of gamma radiation for low-gloss Dow Magnum™ 2600 Series.[7]

Figure 4.6 Color shift (ΔE) after 2.5 Mrad of gamma radiation and storage in dark or light conditions for high-gloss Dow Magnum™ 2600 Series.[7]

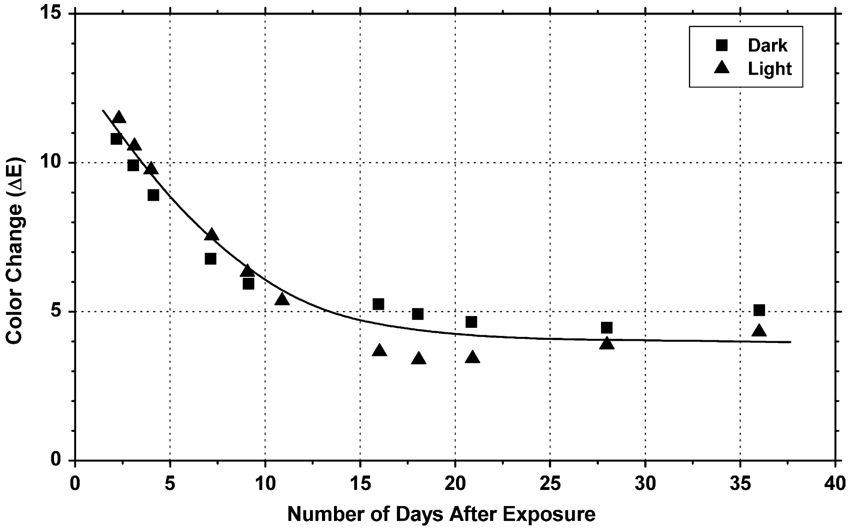


Figure 4.7 Color shift (ΔE) after 2.5 Mrad of gamma radiation for low-gloss natural and white Dow Magnum™ 2600 Series stored in light.[7]

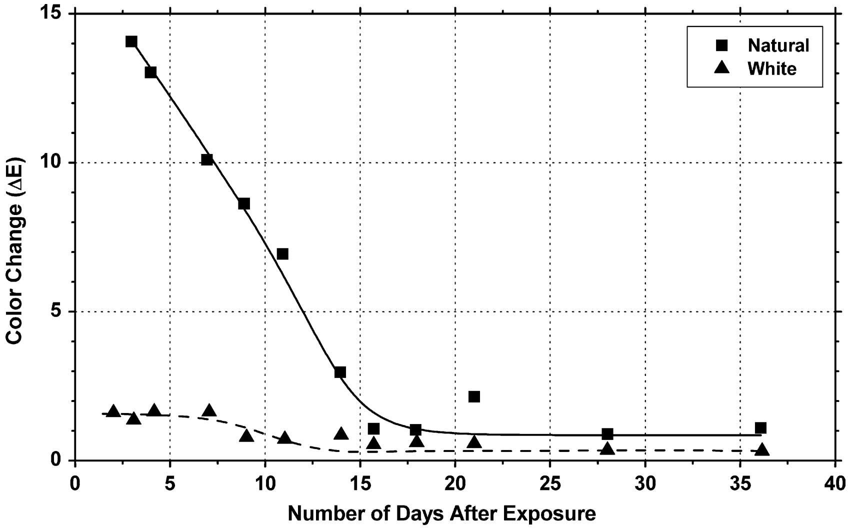
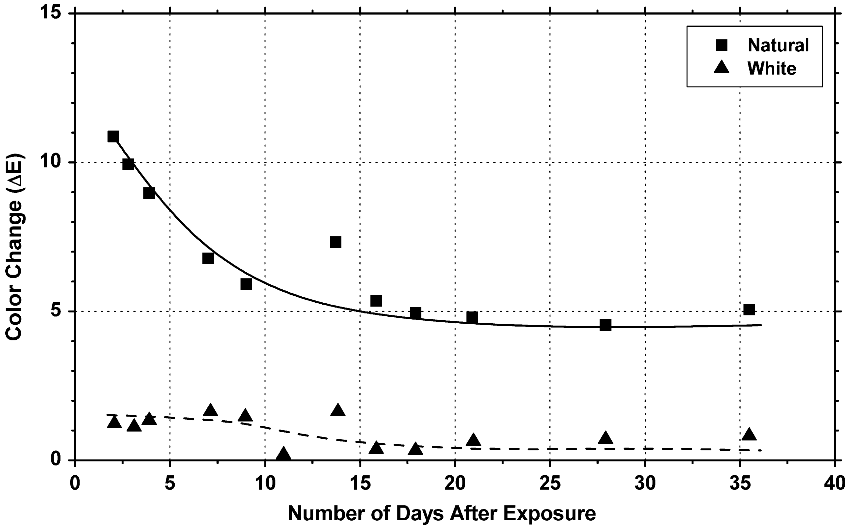


Figure 4.8 Color shift (ΔE) after 2.5 Mrad of gamma radiation for high-gloss natural and white Dow Magnum™ 2600 Series stored in light.[7]



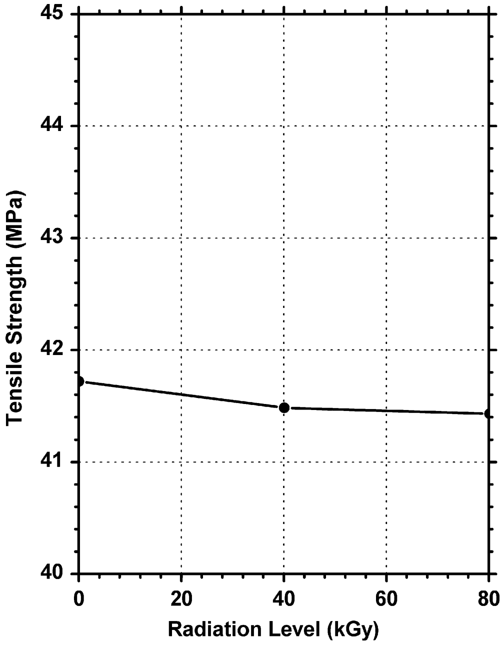


Figure 4.9 The effect of gamma radiation on the tensile strength of Sabic Innovative Plastics Cycolac MD ABS resins.[8]

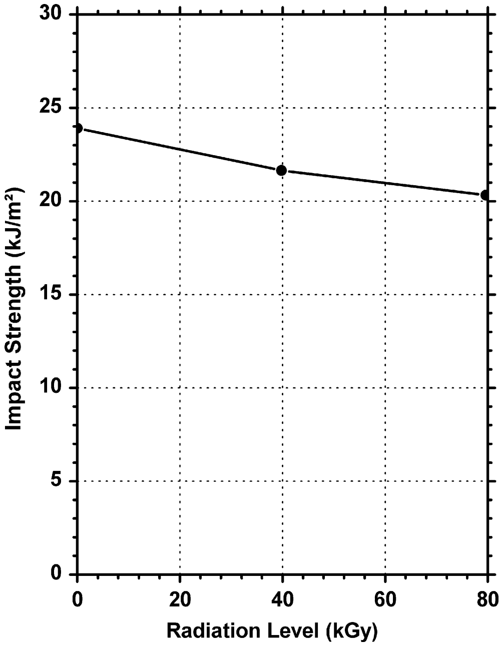


Figure 4.11 The effect of gamma radiation on the Izod notched impact strength of Sabic Innovative Plastics Cycolac MD ABS resins.[8]

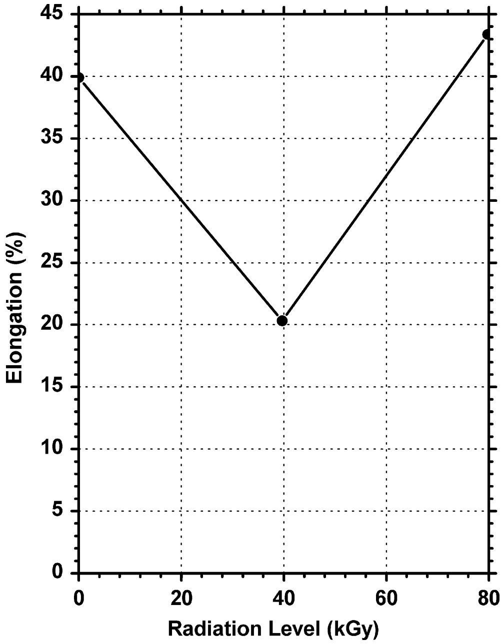


Figure 4.10 The effect of gamma radiation on the elongation of Sabic Innovative Plastics Cycolac MD ABS resins.[8]

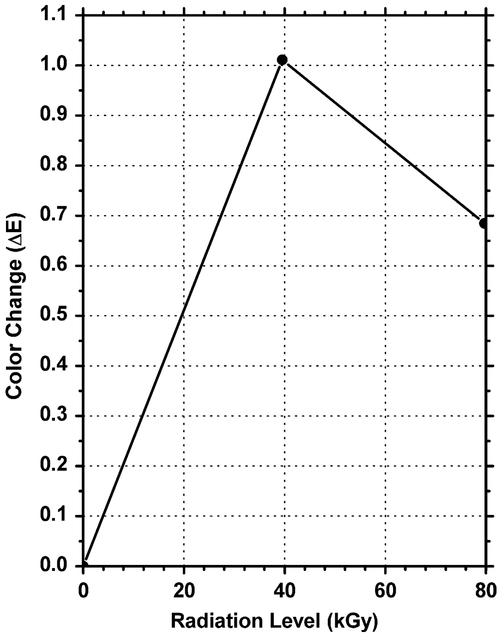


Figure 4.12 The effect of gamma radiation on color shift of Sabic Innovative Plastics Cycolac MD ABS resins.[8]

Figure 4.13 Beta radiation dose versus tensile strength of generic acrylonitrile–butadiene–styrene.[9]

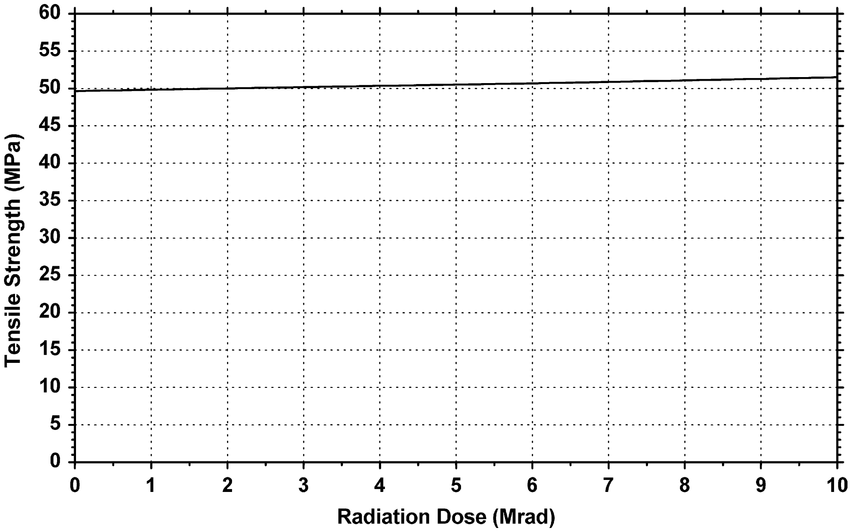


Figure 4.14 Beta radiation dose versus tensile modulus of generic acrylonitrile–butadiene–styrene.[9]

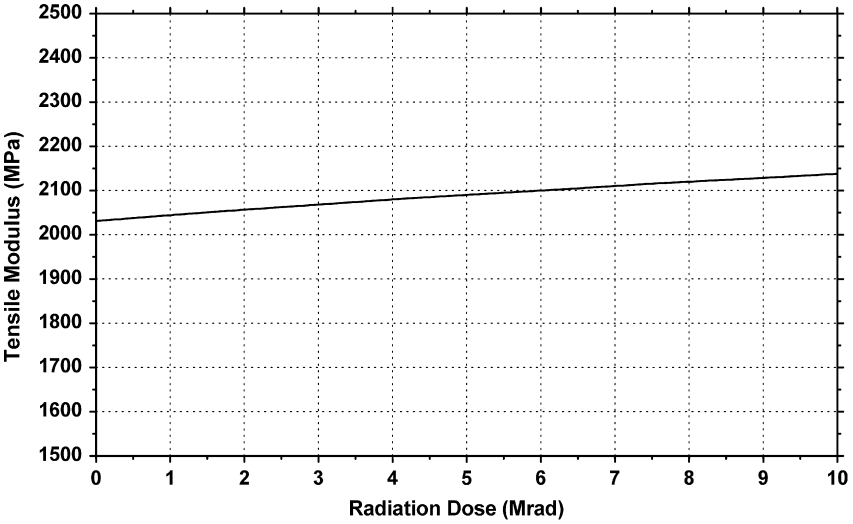
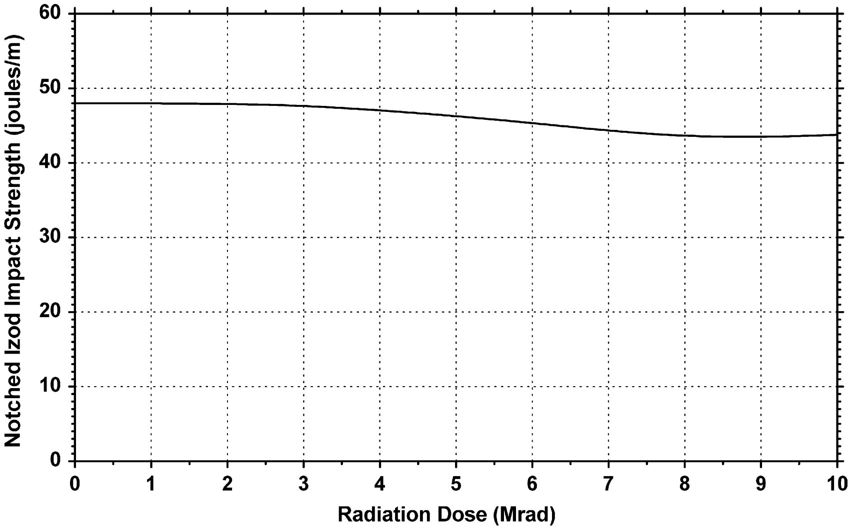


Figure 4.15 Beta radiation dose versus notched Izod impact strength of generic acrylonitrile–butadiene–styrene.[9]



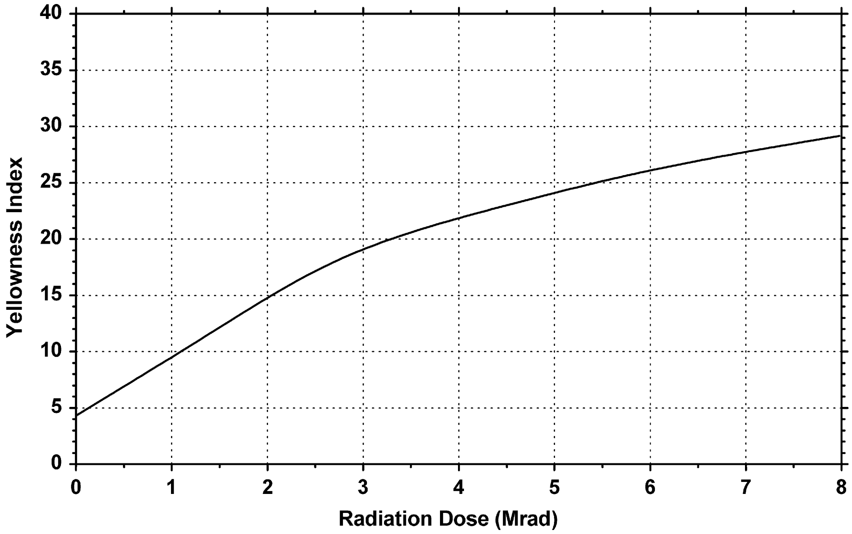


Figure 4.16 Beta radiation dose versus yellowness index of generic acrylonitrile–butadiene–styrene.[9]

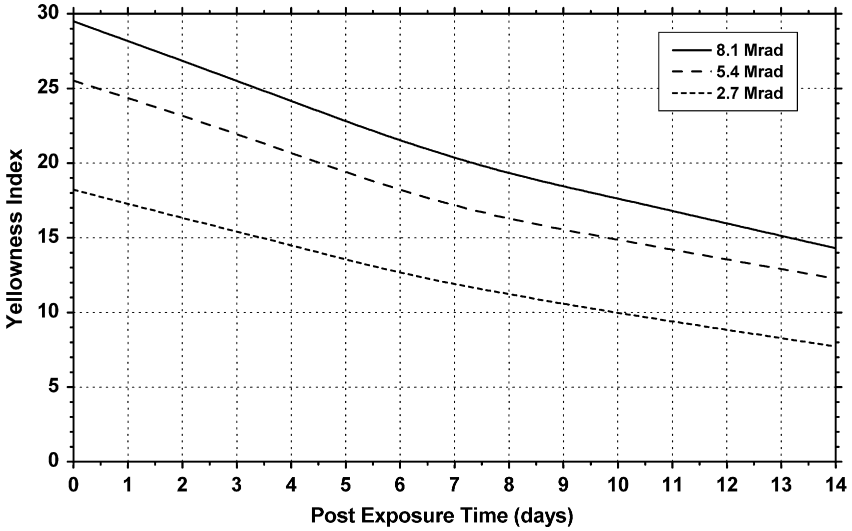


Figure 4.17 Post-beta radiation exposure time versus yellowness index of generic acrylonitrile–butadiene–styrene.[9]

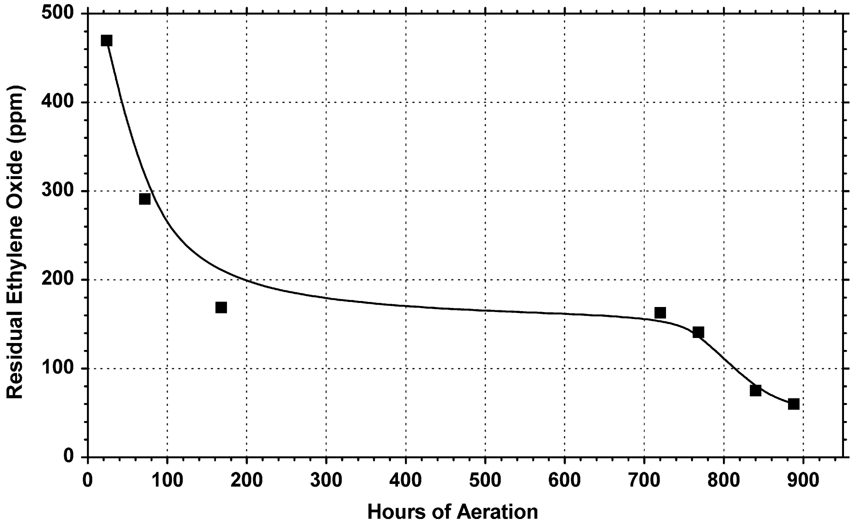
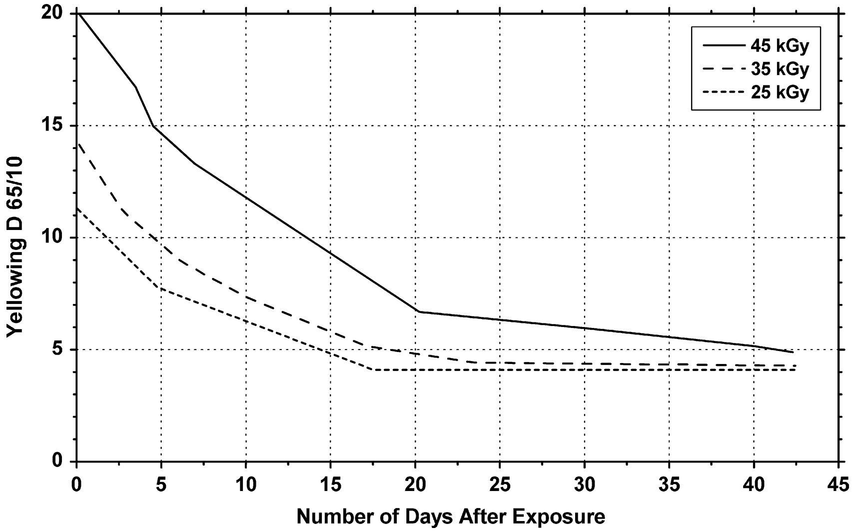


Figure 4.18 Ethylene oxide sterilization residuals versus hours of aeration of Dow Magnum 9020 ABS.[4] 1. Preexposure conditioning: 8 h, 37.8 °C, 60% RH. 2. Exposure conditions: 49 °C, 60% RH, $\geq$6 h, 12% EtO and 88% Freon. 3. Postexposure conditions: aeration at 32 °C, 127 mmHg.

Table 4.18 Physical Properties Before and After E-Beam Radiation of BASF Terlux® 2802 MABS[12]

	E-beam Energy (Mrad)	Terlux® 2802
Tensile yield strength (MPa)	Unexposed	49
	25	48
	50	48
Tensile break strain (%)	Unexposed	14
	25	15
	50	17
Flatwise impact at 23 °C; total energy (J)	Unexposed	4.6
	25	3.8
	50	3.2

Figure 4.19 The reduction in post-gamma sterilization yellowing in BASF Terlux® 2808 TR exposed to daylight.



or can be made in various colors. It is economical and is used for producing plastic model assembly kits, plastic cutlery, CD "jewel" cases, and many other objects where a fairly rigid, economical plastic is desired.

Polystyrene's most common use, however, is as expanded polystyrene. Expanded polystyrene is produced from a mixture of about 5—10% gaseous blowing agent (most commonly pentane or carbon dioxide) and 90—95% polystyrene by weight. The solid plastic beads are expanded into foam through the use of heat (usually steam). The heating is carried out in a large vessel holding 200—2000 l. An agitator is used to keep the beads from fusing together. The expanded beads are lighter than unexpanded beads so they are forced to the top of the vessel and removed. This expansion process lowers the density of the beads to 3% of their original value and yields a smooth-skinned, closed cell structure. Next, the pre-expanded beads are usually "aged" for at least 24 h in mesh storage silos. This allows air to diffuse into the beads, cooling them and making them harder. These expanded beads are excellent for detailed molding. Extruded polystyrene, which is different from expanded polystyrene, is commonly known by the trade name Styrofoam™. All these foams are not of interest in this book.

Three general forms of polystyrene are:

- General purpose or crystal (PS or GPPS)
- High impact (HIPS)
- Syndiotactic (SPS).

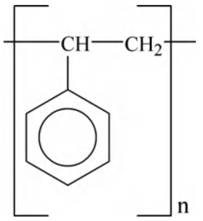


Figure 4.20 Chemical structure of polystyrene.

Each of these is discussed in a separate subsection of this chapter.

Manufacturers and trade names: BASF Polystyrene and Polystyrol, Dow Chemical Trycite™, and Styron Styron™.

Sterile applications and uses:

- General purpose: Diagnostic instruments and disposable laboratory ware, petri dishes, tissue culture components, flasks, and pipettes.
- Oriented: Oriented polystyrene films can be printed and laminated to foams for food service plates and trays offering improved aesthetics. The films can also be used as a laminate to polystyrene sheet for a high-gloss shine. Bakery, convenience food items.
- Syndiotactic: Personal care packaging
- High impact: Laboratory ware and other medical devices.

Polystyrene is not recommended for steam and autoclave sterilization. Its low heat distortion temperature will cause the parts to warp and disfigure. Polystyrene can be sterilized with ethylene oxide.

Ethylene oxide (EtO) resistance: Styron resins retain their properties after exposure to one normal ethylene oxide sterilization cycle. Excessive or multiple exposures to EtO sterilization are not recommended because EtO can cause embrittlement and stress cracking of the polymer.[13]

Gamma and electron beam resistance: Polystyrene is very stable to gamma radiation and electron beam due to its high aromatic content. Color changes are seen after e-beam sterilization.[3]

UV light sterilization resistance: Styron is resistant to sterilization by UV light. This technology is based on a short wavelength of 254 nm during which the part-to-lamp distance is controlled.[13]

Data for polystyrene plastics are found in Tables 4.19–4.35 and Figs 4.21–4.31.

Table 4.19 The Effect of Gamma Radiation Sterilization on General-Purpose Polystyrene[2]

Sterilization Conditions							
Radiation dose (Mrad)	2.5	2.5	2.5	10	10	10	
Postexposure Conditioning							
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	99.7	100.4	98.1	96	97.4	96	ASTM D638
Tensile strength at yield	99.7	100.4	98.1	96	97.4	96	ASTM D638
Elongation at break	100	100	100	100	100	100	ASTM D638
Izod impact strength	100	100	125	75	75	125	ASTM D256
Dart impact (total energy)	150	66.7	77.8	827.8	72.2	44.4	ASTM D3763

Note: (1) Source Cobalt-60. (2) Postexposure conditioning: 21 °C, stored in dark.

Table 4.20 Gamma Radiation Sterilization Effects on Dow Chemical Styron 666D GPPS[3]

Sterilization Conditions						
Radiation dose (Mrad)	Unexposed	2.5	2.5	10	10	
Postexposure Conditioning						
Weeks	–	1	8	1	8	
Properties						**Test Method**
Tensile yield (MPa)	46	46	46	45	46	ASTM D638
Elongation (%)	2	2	2	2	2	ASTM D638
Izod impact (J/m)	27	27	21	21	21	ASTM D256
Peak energy (J)	1	1	1	1	1	ASTM D3763

Table 4.21 Gamma Radiation Sterilization Effects on Dow Chemical Styron 666D GPPS[1]

Sterilization Conditions					
Radiation dose (Mrad)	2.5	2.5	10	10	
Postexposure Conditioning					
Aging time (h)	168	1344	168	1344	
Properties Retained (%)					**Test Method**
Tensile strength at yield	100	100	97.8	100	ASTM D638
Flexural strength	102.2	102.2	100	101.1	ASTM D790
Elongation	100	100	100	100	ASTM D638
Impact strength	128.6	100	100	100	ASTM D256
Dart impact (peak energy)	100	100	100	100	ASTM D3763
Dart impact (total energy)	100	100	100	100	ASTM D3763
Heat deflection temperature	97.4	98.7	100	101.3	ASTM D648
Vicat softening point	101	100	101	100	ASTM D1525
Yellowness index	0.9	0.2	3.4	2.2	ASTM D1925
Light transmission retained (%)	100	109.9	97.8	109.9	
Haze after exposure (%)	4.1	2.08	2.77	0.74	

Table 4.22 Ethylene Oxide (EtO) Sterilization Effects on Dow Chemical Styron 666D GPPS[3]

Postexposure Conditioning				
Weeks	Unexposed	1	8	
Properties				**Test Method**
Tensile yield (MPa)	46	45	46	ASTM D638
Elongation (%)	2	2	2	ASTM D638
Izod impact (J/m)	21	21	21	ASTM D256
Peak energy (J)	1	1	1	ASTM D3763

4.3.2 High-Heat Crystal Polystyrene

High-heat crystal polystyrene incorporates thermal stabilizers into polystyrene.

4.3.3 Syndiotactic Polystyrene

Syndiotactic polystyrene (SPS) is a semicrystalline polymer synthesized from styrene monomer using a single-site catalyst such as metallocene. Because of its semicrystalline nature, SPS products exhibit performance attributes that are significantly different from those of amorphous styrenic materials. See Section 2.7.3 for an explanation of the structural differences of syndiotactic versus atactic polymer structures.

Dow Plastics had made Questra SPS but has since discontinued these products in 2004. Xarec® SPS, which is made by Idemitsu and is distributed by PTS, is a successor product to Questra. Dow Chemical has redirected all new customer inquiries to Idemitsu and also transferred all U.L. ratings from Questra to the Idemitsu Xarec® file. Idemitsu Kosan invented SPS resin back in 1985. Several companies, including RTP Company, compound plastic formulations based on SPS.

4.3.4 High-Impact Polystyrene

One of the most important plastics is high-impact polystyrene or HIPS. This is a polystyrene matrix that is imbedded with an impact modifier, which is basically a rubber-like polymer such as polybutadiene. This is shown in Fig. 4.25. High-impact grades typically contain in the range of 6–12% elastomers and medium-impact grades contain about 2–5%.

4.4 SAN Copolymer

Styrene and acrylonitrile monomers can be copolymerized to form a random, amorphous copolymer

Table 4.23 Electron Beam Sterilization Effects on Dow Chemical Styron 666D GPPS[1]

Sterilization Conditions					
Radiation dose (Mrad)	2.5	2.5	10	10	
Postexposure Conditioning					
Aging time (h)	168	1344	168	1344	
Properties Retained (%)					**Test Method**
Modulus	101.8	96.6	104	90.2	ASTM D638
Modulus	101.8	104.2	101.8	103.6	ASTM D638
Tensile strength	97.8	100	97.8	100	ASTM D638
Flexural strength	95.7	102.2	96.7	102.2	ASTM D790
Elongation	100	100	100	100	ASTM D638
Impact strength	100	100	100	100	ASTM D256
Dart impact (peak energy)	100	100	100	100	ASTM D3763
Dart impact (total energy)	100	200	100	100	ASTM D3763
Heat deflection temperature	97.4	98.7	105.3	109.2	ASTM D648
Vicat softening point	99	100	101	100	ASTM D1525
Yellowness index	0	−0.4	1.5	0.8	ASTM D1925
Light transmission	98.9	109.9	97.8	109.9	
Haze after exposure (%)	2.19	1.99	3.54	1.95	

Table 4.24 Ethylene Oxide (EtO) Sterilization Effects using HCFC-124 Carrier Gas on Dow Chemical Styron 666D GPPS[10]

Sterilization Conditions									
Gas composition	12% EtO and 88% Freon				8.6% EtO and 91.4% HCFC-124				
Number of cycles	1	1	2	2	1	1	2	2	
Postexposure Conditioning									
Time (h)	168	1344	168	1344	168	1344	168	1344	
Properties Retained (%)									**Test Method**
Tensile strength at yield	95.8	92.2	89.5	82.7	93.1	73	101.6	80.2	ASTM D638
Elongation	100	100	100	100	100	100	200	100	ASTM D638
Tensile modulus	92.4	98.1	88	93.8	85.6	85.4	90.1	85.8	ASTM D638
Dart impact (peak energy)	77.8	55.6	55.6	66.7	66.7	100	77.8	111.1	ASTM D3763
Dart impact (total energy)	100	90.9	90.9	90.9	81.8	127.3	90.9	127.3	ASTM D3763
Yellowness index	0.93	0.8	1.06	1.03	1.06	0.95	0.97	1.21	
Light transmission	90	91	90	90	91	90	89	90	
Haze after exposure	4.98	5.84	7.4	7	2.15	4.6	10.39	8.73	

Note: (1) Preexposure Conditioning: 60% RH, 37.8 °C, 18 h. (2) Sterilization conditions: 60% RH, 48.9 °C, 6 h. (3) Postexposure conditioning: Aeration, 127 mmHg, 32.2 °C.

Table 4.25 Ethylene Oxide (EtO) Residuals Poststerilization using HCFC-124 Carrier Gas on Dow Chemical Styron 666D GPPS[10]

Sterilization Conditions				
Gas composition	12% EtO and 88% Freon		8.6% EtO and 91.4% HCFC-124	
Postexposure Conditioning				
Aeration air changes/h	10	30	10	30
Temperature (°C)	32.2	54.4	32.2	54.4
Residuals (ppm)				
Little or no aeration	1002	1002	1006	1006
24 h Aeration	429	171	356	312
48 h Aeration	–	112	–	290
72 h Aeration	129	105	176	119
168 h Aeration	77	–	108	–

Note: (1) Preexposure conditioning: 60% RH, 37.8 °C, 18 h. (2) Sterilization conditions: 60% RH, 48.9 °C, 6 h. (3) Postexposure conditioning: aeration.

that has good weatherability, stress crack resistance, and barrier properties. The copolymer is called styrene–acrylonitrile or SAN. The SAN copolymer generally contains 70–80% styrene and 20–30% acrylonitrile. It is a simple random copolymer. This monomer combination provides higher strength, rigidity, and chemical resistance than polystyrene, but it is not quite as clear as crystal polystyrene and its appearance tends to discolor more quickly. The general structure is shown in Fig. 4.32. Its CAS number is 9003-54-7.

Manufacturers and trade names: BASF Luran®, Dow Chemical Tyril™ Resins.

Sterile applications and uses: Urine containers, vacuum bottles, nebulizer housings, specimen holders, diagnostic components, fluid handling devices, and flat plate dialyzers.

Regulatory status: SAN is rated USP XXIII Class VI. Lustran® 31 is in chemical compliance with 21CFR 181.32 and meets USP Class VI test requirements. Lustran® Sparkle is in compliance with 21CFR 181.32.

Gamma sterilization: This does not significantly affect the tested physical properties of SAN. Samples of Tyril™ 1000B were exposed to gamma radiation (Cobalt-60) of 2.5 Mrad and 10 Mrad and showed no significant changes in physical properties.[3] However, color is affected by radiation but the discoloration diminished with time, and after 4 weeks, the SAN samples exposed to 2.5 Mrad of radiation appear close to their original color, while the 100 kGy sample maintained the yellow hue.[3]

Ethylene oxide sterilization: SAN maintains its impact strength, both Izod and instrumented dart, after ethylene oxide sterilization with both HCFC-124 carrier gas and pure EtO carrier gas. However, after exposure to EtO, the SAN samples showed some surface crazing. In a previous study,[10] five repeated sterilization cycles cause some embrittlement. The embrittlement is seen as a loss of tensile elongation at break and a decrease in instrumented dart impact energy. After multiple EtO cycles, the embrittlement appears to compound with time. The elongation and instrumented dart impact strengths at 6 months and 1 year were significantly less than what was observed at 2-weeks poststerilization. Silver streaks, or crazes along the flow lines, were noted after five EtO cycles. This is indicative of stress cracking of the polymer with excessive exposure to ethylene oxide.[2]

Steam sterilization: SAN distorts in steam sterilization and it is, therefore, not recommended.

Data for SAN plastics are found in Tables 4.36–4.43 and Figs 4.33–4.38.

Table 4.26 The Effect of EtO Sterilization on Several Properties of General-Purpose STYRON* 666D Polystyrene[11]

Carrier Gas	Sterilization	Postexposure Time	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Instrumented Dart Impact Peak Energy (J)	Izod (J/m)
Control	Unexposed		44	2	3120	83	3440	1.0	27
Average standard deviation (%)			2	7	7	6	6	30	0
HCFC-124	One cycle	1 Week	43	2	2990	80	3410	1.1	n/a
		8 Weeks	46	2	3120	75	3520	0.9	21
	Three cycles	1 Week	44	1	3230	86	3510	0.9	n/a
		8 Weeks	45	2	3320	78	3620	1.0	27
Average standard deviation (%)			5	13	7	14	4	34	0
HCFC-124/22	One cycle	1 Week	38	1	3180	75	3450	0.7	21
		8 Weeks	37	1	3010	72	3570	1.0	21
	Three cycles	1 Week	44	2	3080	75	3400	1.0	27
		8 Weeks	43	2	3080	76	3570	0.7	21
Average standard deviation (%)			5	10	5	7	4	28	0
EtO	One cycle	1 Week	44	2(19)	3040	85	3450	0.8	21
		8 Weeks	44	2	3010	82	3440	1.3	21
	Three cycles	1 Week	44	2	3050	81	3490	0.8	27
		8 Weeks	43	1	3070	76	3380	0.9	27

Note: n/a, not applicable.

Table 4.27 Physical Properties and Yellowness Indices of Ineos Nova High-Heat Crystal Polystyrene Post-Gamma Sterilization[15]

Sterilization Conditions								
Radiation dose (Mrad)	Unexposed	2.5	5	2.5	5	2.5	5	
Postexposure Conditioning								
Time, months	–	3	3	12	12	24	24	
Properties								**Test Method**
Tensile strength at yield (psi)	7700	7800	7800	7700	7700	7900	7900	ASTM D638
Tensile elongation (%)	3.3	3.4	2.8	5.2	5.6	–	–	ASTM D638
Yellowness index	−1.5	11.0	22.2	12.3	21.7	13.7	23.7	ASTM D1925

Table 4.28 Physical Properties and Yellowness Index of High-Heat Crystal Polystyrene[15]

Sterilization Conditions										
Radiation dose (Mrad)	0	2.5	5.0	0	2.5	5.0	0	2.5	5.0	
Postexposure Conditioning										
Time	3 Months			1 Year			2 Years			
Properties Retained										**Test Method**
Tensile strength, yield (psi)	7700	7800	7800	7800	7700	7700	7900	7900	7900	ASTM D638
Tensile elongation (%)	3.3	3.4	2.8	4.9	5.2	5.6	–	–	–	ASTM D638
Yellowness index	−1.5	11.0	22.2	−1.4	12.3	21.7	−1.1	13.7	23.7	ASTM D1925

Table 4.29 Physical Properties of Dow Plastics Questra 2730 (Discontinued) Post-Autoclave Sterilization[16]

Sterilization Cycles	**0**	**10**	**50**	**100**	**250**	**750**	**1000**	
Tensile strength at break (MPa)	106	102	98	96	97	93	95	95
Tensile modulus (MPa)	7590	7590	7390	8010	8150	7760	7340	7670
Elongation at break (%)	3.2	2.2	1.8	1.8	1.8	1.8	1.8	1.7
Dart impact (peak energy) (J)	7	6	6	5	6	5	5	5
Color (ΔE)	0.00	0.51	0.76	0.67	1.81	2.56	3.49	4.56

Table 4.30 Physical Properties and Yellowness Indices of Ineos Nova High-Impact Polystyrene[15]

Sterilization Conditions										
Radiation dose (Mrad)	0	2.5	5.0	0	2.5	5.0	0	2.5	5.0	
Postexposure Conditioning										
Time	3 Months			1 Year			2 Years			
Properties Retained										**Test Method**
Tensile strength, yield (psi)	3300	3400	3400	3400	3400	3400	3300	3300	3400	ASTM D638
Tensile elongation (%)	57	58	57	58	58	52	52	51	49	ASTM D638
Notched Izod impact strength (ft-lbs/in)	2.3	2.1	2.0	2.2	2.1	2.2	2.3	2.3	2.2	ASTM D256
Yellowness index	2.6	9.1	14.5	2.3	10.3	16.1	1.7	12.0	16.3	ASTM D1925

Table 4.31 The Effect of Gamma Radiation Sterilization on Impact Polystyrene[2]

Sterilization Conditions							
Radiation dose (Mrad)	2.5	2.5	2.5	10	10	10	
Postexposure Conditioning							
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	99.3	99.8	101.9	99.3	100.6	100.3	ASTM D638
Tensile strength at yield	101.4	101.6	102.8	105.5	108.3	108.8	ASTM D638
Elongation at break	85.5	90.9	89.1	67.3	63.6	61.8	ASTM D638
Dart impact (total energy)	102	66.7	61.4	63.4	61.4	47.1	ASTM 3763
Notched Izod impact strength	93.3	93.3	93.3	73.3	73.3	73.3	ASTM D256

Note: (1) Sterilization conditions: Source: Cobalt-60. (2) Postexposure conditions: 21 °C, storage in dark.

Table 4.32 The Effect of Gamma Radiation Sterilization on Dow Styron 478 Impact Polystyrene[1]

Sterilization Conditions					
Radiation dose (Mrad)	2.5	2.5	10	10	
Postexposure Conditioning					
Time (h)	168	1344	168	1344	
Properties Retained (%)					**Test Method**
Tensile strength at yield	100	104.3	100	104.3	ASTM D638
Flexural strength	104.2	97.9	108.3	100	ASTM D790
Elongation at break	78.4	86.3	84.3	78.4	ASTM D638
Impact strength	100	96.1	87.5	87.5	ASTM D256
Dart impact (peak energy)	81.3	81.3	87.5	87.5	ASTM 3763
Dart impact (total energy)	81.3	81.3	87.5	87.5	ASTM 3763
Heat deflection temperature	101.2	101.8	101.8	103.1	ASTM D648
Vicat softening point	100.5	100.5	100.9	100.5	ASTM D1525
Δ*a* Color	−2.39	−2.08	−2.22	−5.19	ASTM D2244
Δ*b* Color	−6.82	3.69	4.95	8.46	ASTM D2244
Δ*L* Color	84.16	−0.88	−0.74	−3.25	ASTM D2244

Table 4.33 The Effect of Electron Beam Radiation Sterilization on Impact Polystyrene[1]

Sterilization Conditions					
Radiation dose (Mrad)	2.5	2.5	10	10	
Postexposure Conditioning					
Time (h)	168	1344	168	1344	
Properties Retained (%)					**Test Method**
Tensile strength at yield	100	100	104.3	104.3	ASTM D638
Flexural strength	100	97.9	106.3	102.1	ASTM D790
Elongation at break	86.3	74.5	72.5	68.6	ASTM D638
Impact strength	91.4	96.1	83.6	87.5	ASTM D256
Dart impact (peak energy)	100	87.5	93.8	68.8	ASTM 3763
Dart impact (total energy)	100	87.5	93.8	68.8	ASTM 3763
Heat deflection temperature	103.1	102.5	110.4	108	ASTM D648
Vicat softening point	100.9	100.5	100.9	100.9	ASTM D1525
Δa Color	−3.97	−2.35	−1.9	−2.74	ASTM D2244
Δb Color	11.64	2.18	3.75	5.27	ASTM D2244
ΔL Color	−2.33	−1.28	−0.6	−1.05	ASTM D2244

4.5 Styrene−Butadiene Copolymers

Styrenic block copolymer, or SBC, is a commercially important thermoplastic elastomer. The polymer is made of three separate polymeric blocks (see Section 2.2 for an explanation of block copolymers). At one end is a hard polystyrene block, in the middle a long polybutadiene (or other elastomeric) block, and followed by a second hard block of polystyrene. These blocks are immiscible, so they form discrete domains of polystyrene within a polybutadiene matrix. The separate domains are chemically connected. This is shown in Fig. 4.39, where one might notice that this looks a lot like high-impact polystyrene, except that the continuous phase and hard discrete phase are switched in SBC and the domains are connected. One additional property of interest is that some SBCs blend well with general-purpose polystyrene (GPSS), allowing customization of properties.

Styrene−butadiene copolymers (SBC) are crystal clear, combining high transparency with impact strength. They are often blended or mixed with polystyrene.

Manufacturers and trade names: Chevron Phillips K-Resin®, BASF Styrolux®.

Sterile applications: Rigid packaging, syringes, tubing, and respiratory Yankauers.

Gamma radiation resistance: K-Resin exhibits good resistance to gamma radiation. Slight yellowing, which tends to clear after exposure to daylight, can be seen. The benzene rings in these materials protect the structure from a breakdown. K-resin, which also contains polybutadiene, is protected by the aid of the aromatic group, which absorbs the high-energy radiation and dissipates it without material destruction.[19]

Ethylene oxide (EtO) resistance: Injection-molded K-Resin parts were ethylene oxide sterilized and the physical properties suffered no deterioration as a result of the EtO sterilization.[20]

Regulatory status: K-Resins qualify as USP Class VI-50 materials.[21]

Data for SBC plastics are found in Tables 4.44−4.53 and Fig. 4.40.

Table 4.34 The Effect of EtO Sterilization on Several Properties of STYRON* 478 High-Impact Polystyrene[11]

Carrier Gas	Sterilization	Postexposure Time	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Instrumented Dart Impact Peak Energy (J)	Izod (J/m)
Control	Unexposed		23	47	2210	46	2290	10	107
Average standard deviation (%)			6	18	10	4	6	33	0
HCFC-124	One cycle	1 Week	23	28	2000	46	2360	7	n/a
		8 Weeks	23	22	2.080	46	2350	6	107
	Three cycles	1 Week	22	29	2080	49	2360	6	n/a
		8 Weeks	23	18	2090	46	2400	5	101
Average standard deviation (%)			5	27	10	2	3	33	5
HCFC-124/22	One cycle	1 Week	23	20	2050	46	2380	7	n/a
		8 Weeks	23	17	1980	46	2410	6	112
	Three cycles	1 Week	23	21	2030	46	2360	5	107
		8 Weeks	23	12	2150	46	2360	6	117
Average standard deviation (%)			5	28	10	2	4	25	0
EtO	One cycle	1 Week	23	33	2110	47	2310	6	107
		8 Weeks	22	34	2050	46	2350	7	112
	Three cycles	1 Week	22	35	2100	46	2270	5	101
		8 Weeks	23	17	1990	45	2320	7	112

Note: n/a, not applicable.

Table 4.35 The Effect of Ethylene Oxide Sterilization on Dow Natural-Impact Polystyrene[2]

Sterilization Conditions							
Number of cycles	1	1	1	5	5	5	
Postexposure Conditioning (3)							
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	86.7	85.9	87.5	81.8	75.4	76.5	ASTM D638
Tensile strength at yield	98.5	100.2	101.4	98.5	99.6	100.9	ASTM D638
Elongation at break	60	52.7	52.7	45.5	30.9	30.9	ASTM D638
Dart impact (total energy)	70.6	62.1	69.9	80.4	68.6	68.6	ASTM D3763
Notched Izod impact strength	100	100	93.3	100	86.7	93.3	ASTM D256

Note: (1) Preexposure conditioning: 60% RH, 37.8 °C, 8 h. (2) Sterilization conditions: 60% RH, 49 °C, ≥6 h, 12% EtO and 88% Freon. (3) Postexposure conditioning: (1) evacuation, 127 mmHg; (2) aeration, 32.2 °C, ≥16 h; (3) storage in dark, 21 °C.

Figure 4.21 Post-gamma radiation exposure time versus yellowness index of Dow GPPS.[2]

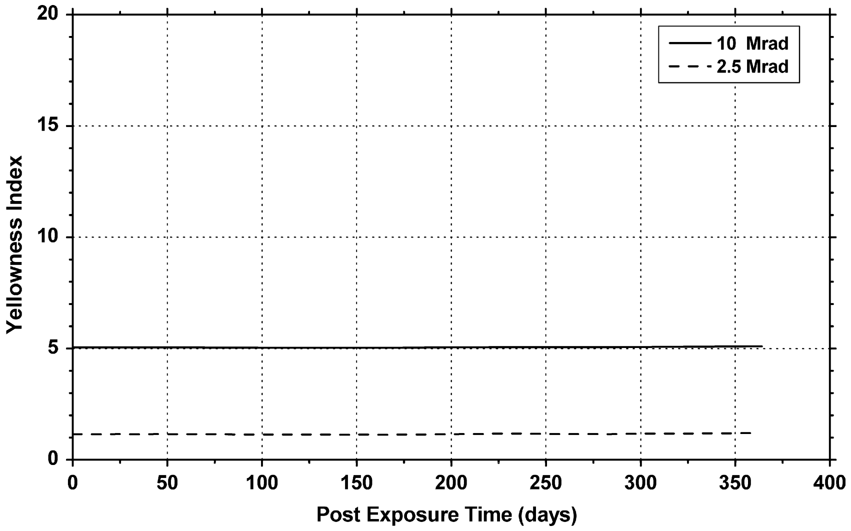
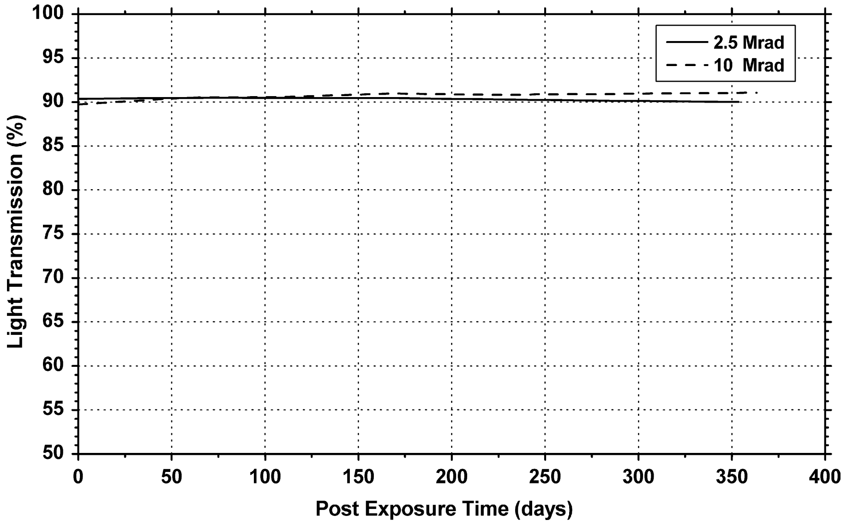


Figure 4.22 Post-gamma radiation exposure time versus percent light transmission of general-purpose polystyrene.[2]



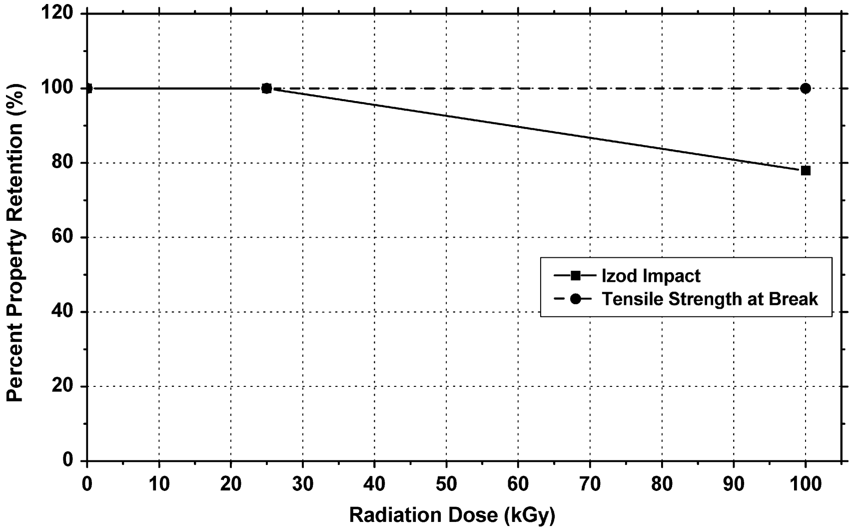


Figure 4.23 Effect of gamma radiation on some properties of general-purpose polystyrene.[14]

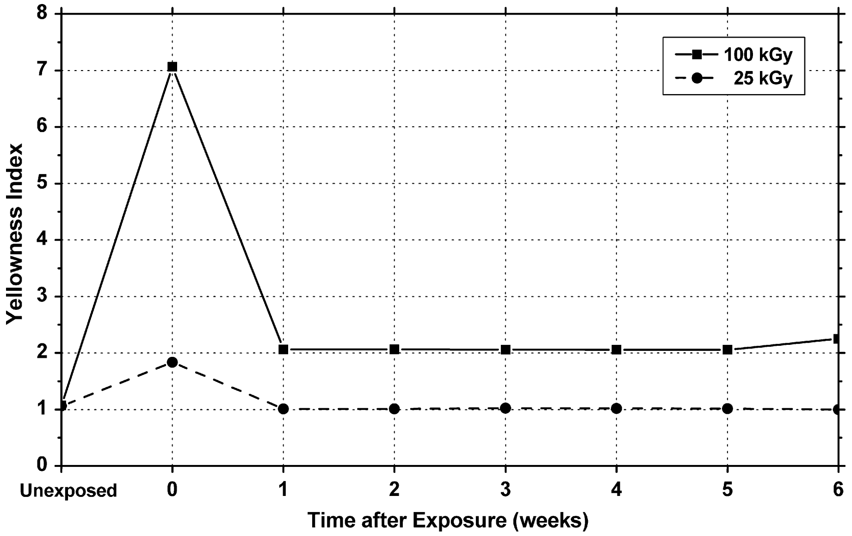


Figure 4.24 Yellowness index of general-purpose polystyrene after gamma sterilization.[14]

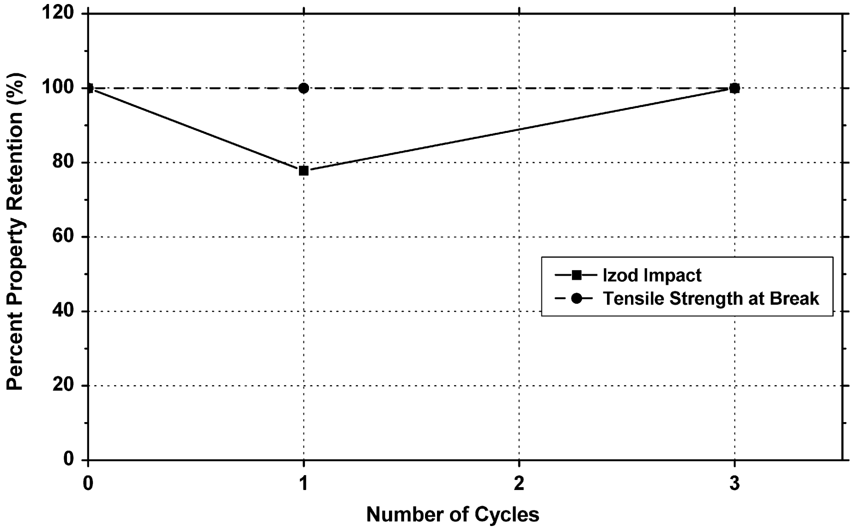


Figure 4.25 Effect of EtO sterilization on some properties of general-purpose polystyrene.[14]

Figure 4.26 Tensile strength of SPS versus autoclave sterilization cycles.[17]

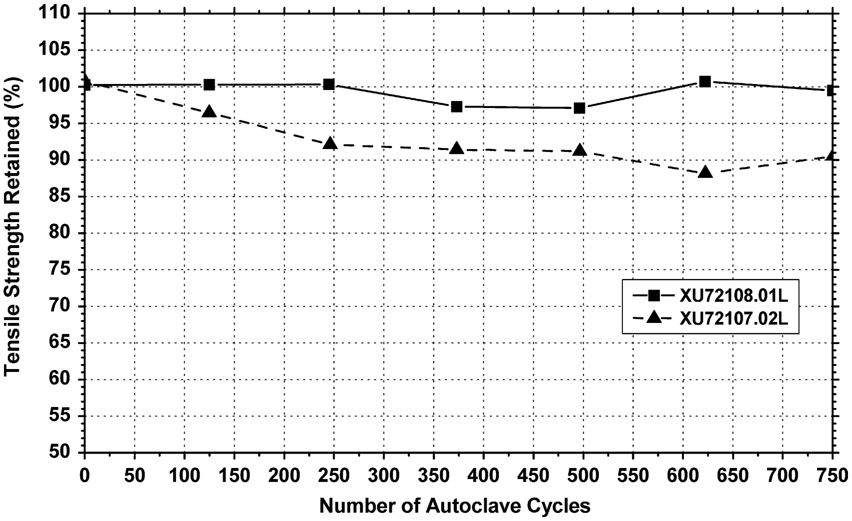
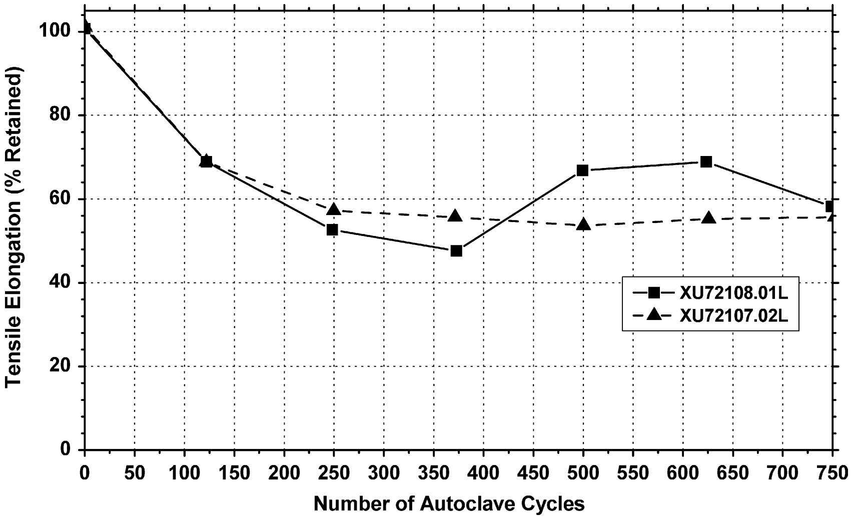


Figure 4.27 Elongation of SPS versus autoclave sterilization cycles.[17]



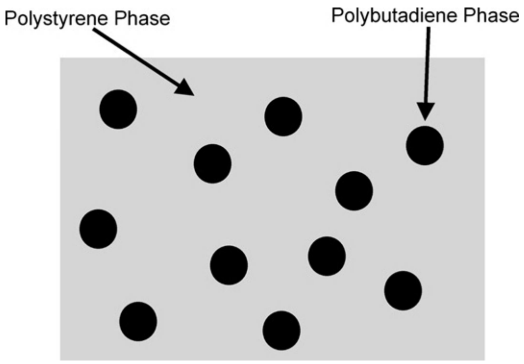


Figure 4.28 The structure of high-impact polystyrene.

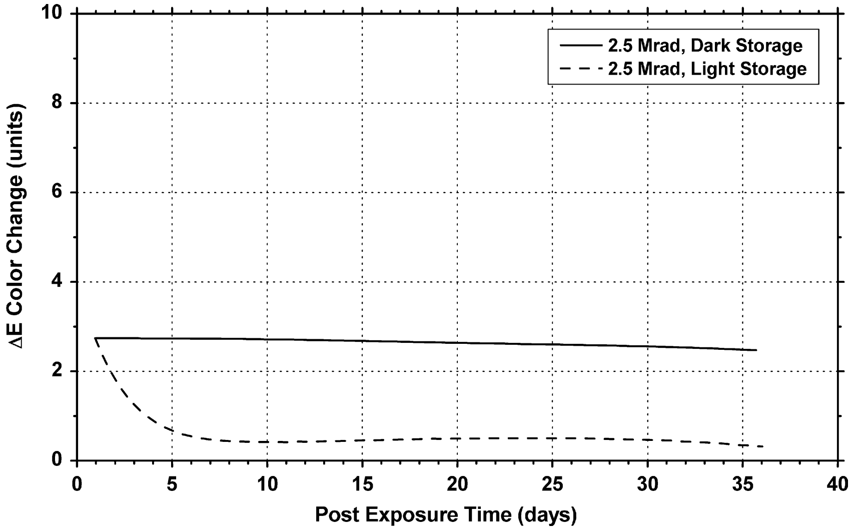


Figure 4.29 Post-gamma radiation exposure time versus Δ*E* color change of impact polystyrene.[4]

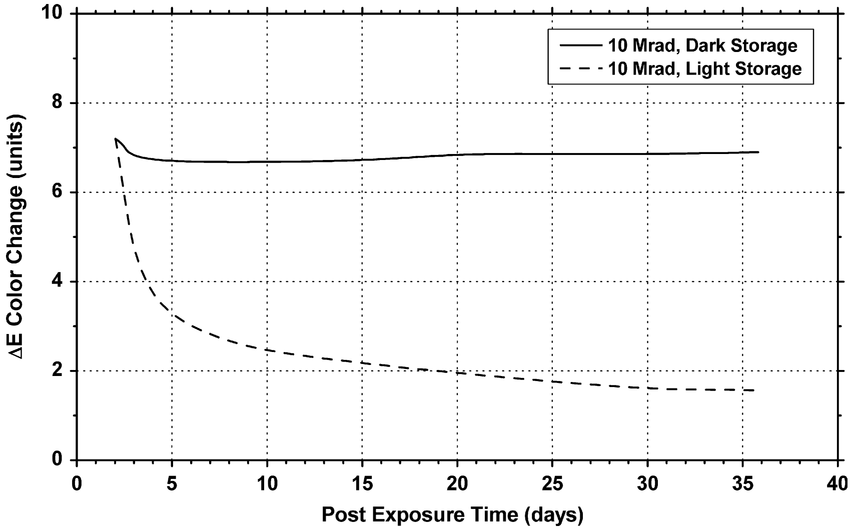


Figure 4.30 Post-gamma radiation exposure time versus Δ*E* color change of impact polystyrene.[4]

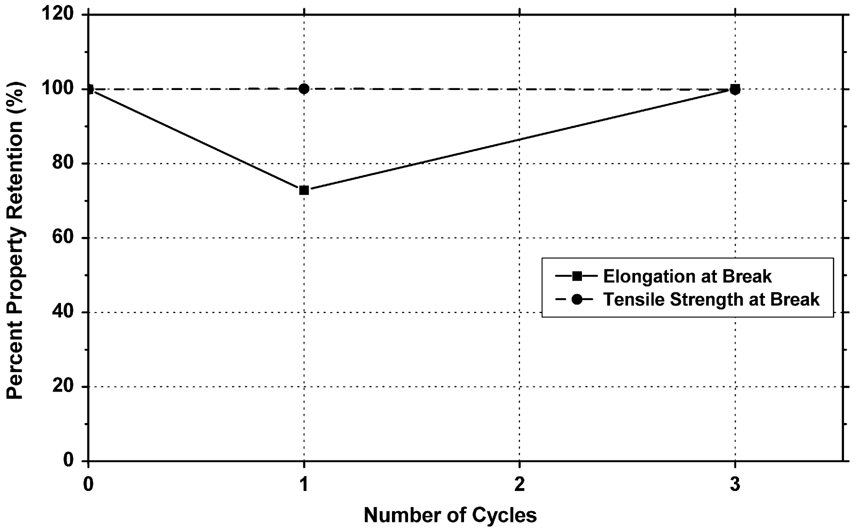


Figure 4.31 Effect of EtO sterilization on some properties of high-impact polystyrene.[14]

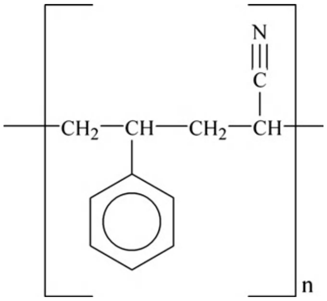


Figure 4.32 Chemical structure of styrene–acrylonitrile.

Table 4.36 Gamma Radiation Sterilization Effects of Dow Plastics Tyril™ 1000B[3]

Sterilization Conditions						
Radiation dose (Mrad)	Unexposed	2.5	2.5	10	10	
Postexposure Conditioning						
Time (weeks)	–	1	8	1	8	
Properties						**Test Method**
Tensile yield (MPa)	73	72	70	72	72	ASTM D638
Elongation (%)	3	3	2	3	2	ASTM D638
Izod impact (J/m)	16	16	21	16	16	ASTM D256
Peak energy (J)	1	1	1	1	1	ASTM D3763

Table 4.37 Effect of Gamma Radiation Sterilization on Styrene–Acrylonitrile Copolymer[2]

Sterilization Conditions							
Radiation dose (Mrad)	2.5	2.5	2.5	10	10	10	
Postexposure Conditioning							
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	100	98.9	94.3	98	98.8	95.1	ASTM D638
Tensile strength at yield	100	98.9	94.3	98	98.8	95.1	ASTM D638
Elongation at break	66.7	66.7	66.7	66.7	66.7	66.7	ASTM D638
Dart impact (peak energy)	94.1	76.5	58.8	123.5	76.5	58.8	ASTM D3763
Notched Izod impact	66.7	166.7	100	166.7	100	166.7	ASTM D256

Note: (1) Exposure conditions: source cobalt 60. (2) Postexposure conditions: storage in dark, 21 °C.

Table 4.38 Effect of Gamma Radiation Sterilization on Bayer Lustran® SAN 31 Styrene–Acrylonitrile Copolymer[5]

Sterilization Conditions					
Radiation dose (Mrad)	1.5	2.5	3.5	5	
Properties Retained (%)					**Test Method**
Flexural strength	99	99	92	93	ASTM D790

Table 4.39 Effect of Electron Beam Radiation Sterilization on Bayer Lustran® SAN 31 Styrene–Acrylonitrile Copolymer[5]

Sterilization Conditions					
Radiation dose (Mrad)	1.5	2.5	3.5	5	
Properties Retained (%)					**Test Method**
Flexural strength	102	102	99	93	ASTM D790

Table 4.40 Ethylene Oxide (EtO) Sterilization Effects Using HCFC Carrier Gas on Dow Plastics Tyril™ 1000B[3]

Sterilization Conditions						
Cycles	–	1	1	3	3	
Postexposure Conditioning						
Time (weeks)	–	1	8	1	8	
Properties						**Test Method**
Tensile yield (MPa)	73	51	51	50	49	ASTM D638
Elongation (%)	3	2	2	1	1	ASTM D638
Izod impact (J/m)	16	11	16	11	16	ASTM D256
Peak energy (J)	1	1	1	1	1	ASTM D3763

Table 4.41 Ethylene Oxide (EtO) Sterilization Effects Using Pure EtO Carrier Gas on Dow Plastics Tyril™ 1000B[3]

Sterilization Conditions						
Cycles	–	1	1	3	3	
Postexposure Conditioning						
Time (weeks)	–	1	8	1	8	
Properties						**Test Method**
Tensile yield (MPa)	73	64	42	48	46	ASTM D638
Elongation (%)	3	2	1	1	2	ASTM D638
Izod impact (J/m)	16	11	16	16	16	ASTM D256
Peak energy (J)	1	1	1	1	1	ASTM D3763

Table 4.42 Effect of Ethylene Oxide (EtO) Sterilization on Dow Transparent SAN Copolymer[5]

Sterilization Conditions							
Number of cycles	1	1	1	5	5	5	
Postexposure Conditions							
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	95	78.8	81.1	77.7	64.5	79.1	ASTM D638
Tensile strength at yield	95	78.8	81.1	77.7	64.5	79.1	ASTM D638
Elongation at break	66.7	66.7	66.7	66.7	33.3	66.7	ASTM D638
Dart impact (total energy)	158.8	158.8	76.5	94.1	41.2	52.9	ASTM D3763
Notched Izod impact	133.3	100	133.3	66.7	133.3	100	ASTM D256

Note: (1) Preexposure conditioning: 37.8 °C, 60% RH, 8 h. (2) Exposure conditions: 49 °C, 60% RH, 12% EtO and 88% Freon. (3) Postexposure conditions: (1) evacuation 127 mmHg; (2) aeration, 32.2 °C, $\geq$ 16 h; (3) storage in dark, 21 °C, time in table.

Table 4.43 The Changes in Ethylene Oxide Sterilization and Their Effect on Properties of Styrene–Acrylonitrile[11]

Carrier Gas	Sterilization	Postexposure Time	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Instrumented Dart Impact Peak Energy (J)	Izod (J/m)
Control	Unexposed		73	2	3560	119	3880	1.1	11
Average standard deviation (%)			8	10	9	22	5	40	33
HCFC-124	One cycle	1 Week	51	2	3390	93	3910	1.0	11 (50%)
		8 Weeks	51	2	3400	118	4030	0.6	16
	Three cycles	1 Week	50	1	3550	109	3970	0.9	11
		8 Weeks	49	1	3380	108	4050	0.8	16
Average standard deviation (%)			3	18	11	25	3	28	33
HCFC-124/22	One cycle	1 Week	46	1	3400	71	3820	1.0	21
		8 Weeks	44	1	3430	79	3930	0.9	21
	Three cycles	1 Week	50	1	3430	89	3920	1.1	16
		8 Weeks	47	1	3440	79	3940	0.9	27
Average standard deviation (%)			18	17	6	23	8	34	33
EtO	One cycle	1 Week	64	2	3440	117	3830	0.8	16
		8 Weeks	42	1	3370	59	3740	0.8	16
	Three cycles	1 Week	48	1	3560	109	3800	0.6	16
		8 Weeks	46	2	3380	107	3750	1.0	16

Figure 4.33 Yellowness index versus time post-gamma sterilization for Dow Plastics Tyril™ 1000B.[3]

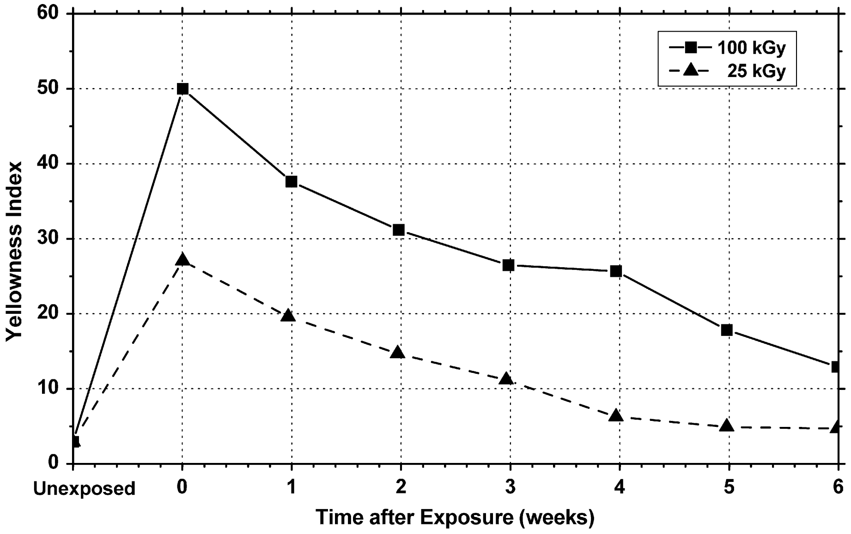


Figure 4.34 Gamma radiation doses versus tensile modulus retained of Bayer Lustran® SAN.[5]

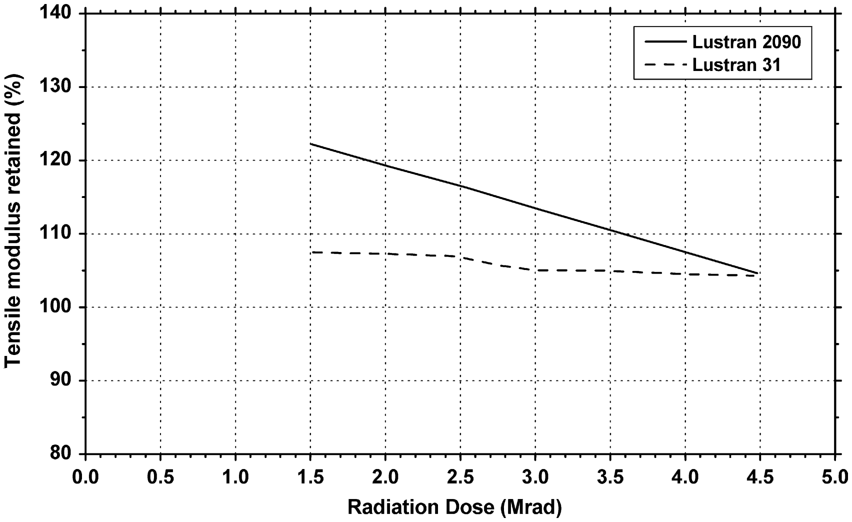
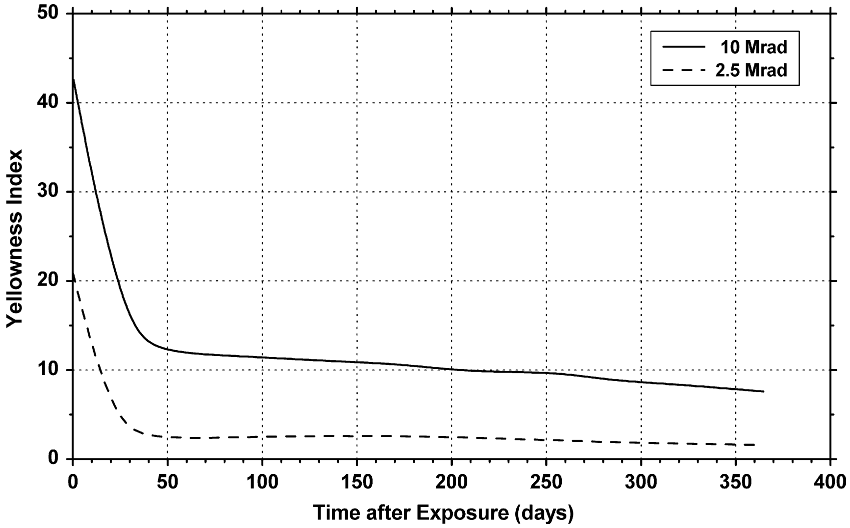


Figure 4.35 Post-gamma radiation exposure time versus yellowness index of styrene–acrylonitrile copolymer.[2]



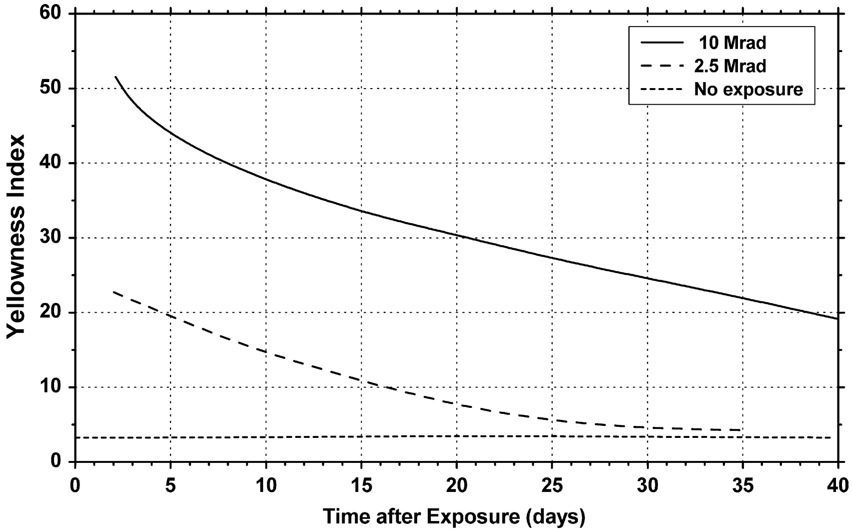


Figure 4.36 Post-gamma radiation exposure time versus yellowness index of Dow Tyril™ 1000B SAN.[4]

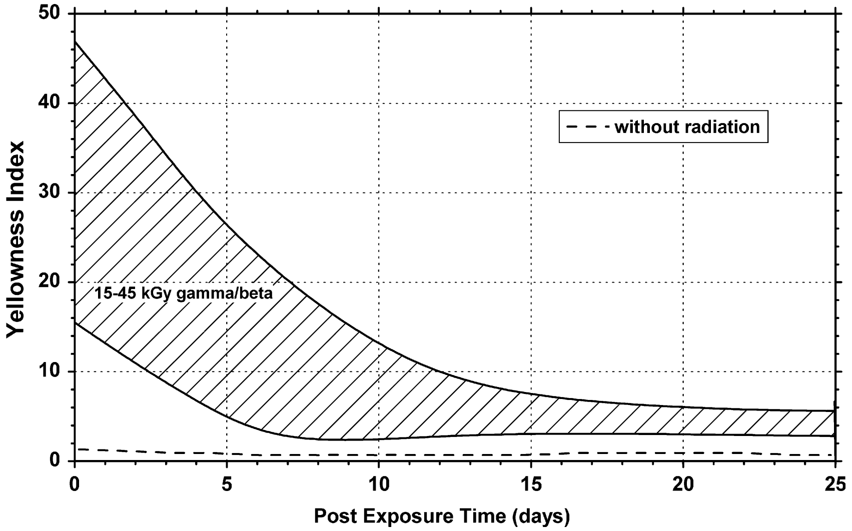


Figure 4.37 Yellowness index of Luran® HD-20 SAN resin after gamma exposure.[18]

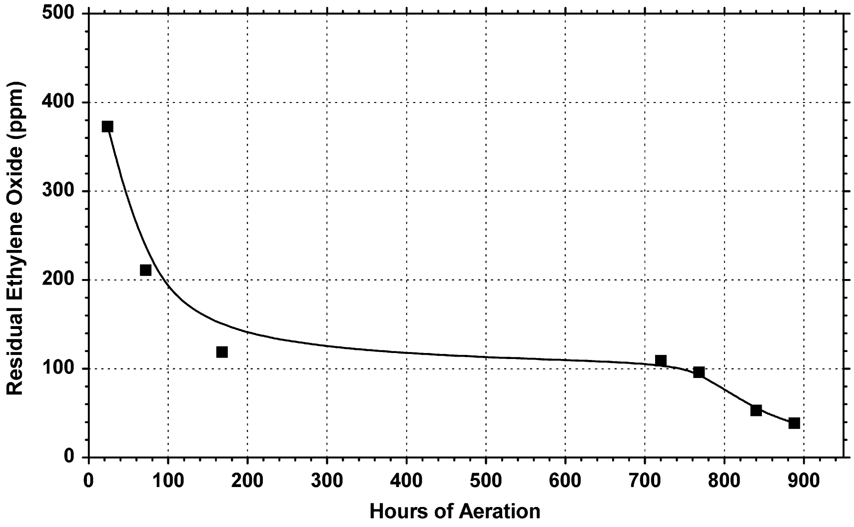


Figure 4.38 Effect of aging on the ethylene oxide residuals following sterilization of Dow Tyril™ SAN copolymer.[4]

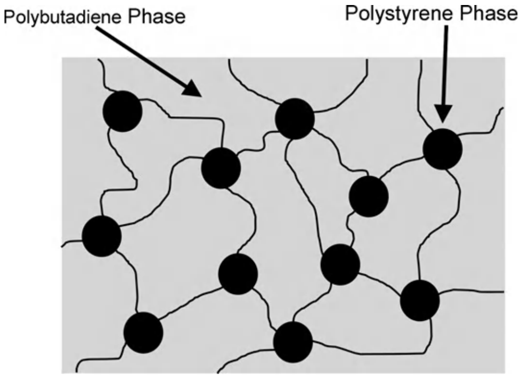


Figure 4.39 The "microscopic" structure of styrenic block copolymers.

Table 4.44 Effect of Gamma Radiation Sterilization on Chevron Phillips K-Resin® Styrene–Butadiene Copolymer[20]

Product	**KR01**		**KR03**		**KR01**			**KR03**		
Sterilization Conditions										
Radiation dose	2.6	5.1	2.6	5.1	10	20	30	10	20	30
Properties Retained (%)										
Modulus	97.2	96.3	100.4	100	100.4	98.7	99.6	100	101.2	102
Tensile strength	102.5	102.5	97	97	103.7	104.9	109.8	100	101.4	100
Elongation	107.7	107.7	100	91.7	116.7	133.3	116.7	86.6	85.8	66.1
Impact strength	100	100	120	120	100	100	100	100	100	100
Heat deflection temperature	101.8	103	100.6	100.6	106.2	104.9	108	106.3	102.5	107
Vicat softening point	101.5	101.5	99	99.5	104	102.5	101	103	101.5	102
Melt flow rate	89.4	71.2	85.7	74.6	25.3	2.5	0.5	31.9	8.3	0

Table 4.45 The Effect of Gamma Irradiation on the Properties of Chevron Phillips K-Resin® Styrene–Butadiene Copolymer[22]

Property	KR03				60/40 KR03/GPPS			
Actual radiation level (Mrad)	0.0	3.5	6.0	10.0	0.0	3.5	6.0	10.0
Flow rate (g/10 min)	8.4	4.7	1.9	0.5	10.7	8.4	6.0	2.5
Tensile strength at yield (MPa)	29	29	29	29	37	38	38	37
Tensile strength at break (MPa)	20	20	20	19	24	25	25	26
Elongation at yield (%)	2.0	2.0	2.0	1.8	1.6	1.7	1.8	1.6
Elongation at break (%)	230	240	230	200	16	18	18	13
Tensile modulus (MPa)	2006	2103	2117	2944	3020	4351	3440	4847
Flexural yield (MPa)	41	41	41	41	56	56	57	57
Flexural modulus (MPa)	1641	1662	1669	1675	2337	2344	2358	2372
Notched, Izod impact (1/8") (J/m)	15.7	15.7	15.7	15.7	11.8	11.8	11.8	11.8
Unnotched, Izod impact (1/8") (J/m)	NB	NB	NB	NB	86.6	86.6	90.6	82.7
Dynatup impact (J)	29	26	27	37	2	1	2	2
Failure mode	Ductile	Ductile	Ductile	Ductile	Brittle	Brittle	Brittle	Brittle
Vicat softening point (°C)	84	89	84	85	93	93	93	93
Heat deflection temperature at 1.8 MPa (°C)	61	62	63	60	73	72	73	73
Shore D hardness	67	67	67	67	76	76	76	76
Light transmission (%)	93	93	92	93	87	87	86	87
Haze (%)	6.4	5.9	5.9	6.0	4.0	4.0	4.4	3.6
Hunter color – *a*	−1.2	−1.7	−2.1	−2.7	−0.6	−1.5	−2.0	−2.7
Hunter color – *b*	3.1	4.5	5.7	7.2	5.9	8.0	9.4	11.1
Hunter color – −*b*	−4.4	−4.1	−4.0	−3.8	−18.0	−16.5	−14.7	−13.5

Note: NB, no break.

Table 4.46 The Effect of Aging 1 Year after Gamma Irradiation on the Properties of Chevron Phillips K-Resin® Styrene−Butadiene Copolymer[22]

Property	**KR03**				**60/40 KR03/GPPS**			
Actual radiation level (Mrad)	0.0	3.5	6.0	10.0	0.0	3.5	6.0	10.0
Flow rate (g/10 min)	8.2	3.0	4.6	0.34	9.7	5.8	8.1	1.6
Tensile strength at yield (MPa)	30.0	30.0	29.6	30.3	37.9	38.0	37.6	38.3
Tensile strength at break (MPa)	19.0	19.3	19.0	19.0	25.5	25.5	25.5	25.9
Elongation at yield (%)	2.3	2.4	2.3	2.3	2.1	2.1	2.1	2.0
Elongation at break (%)	150	208	198	172	22	24	16	21
Tensile modulus (MPa)	1669	1964	1692	1788	2350	2269	2336	2073
Flexural yield (MPa)	43.4	44.1	44.1	44.1	58.3	60.0	59.0	59.0
Flexural modulus (MPa)	1791	1798	1813	1801	2522	2563	2548	2517
Notched, Izod impact (1/8") (J/m)	16.5	12.2	14.2	14.2	10.6	11.8	11.0	10.6
Unnotched, Izod impact (1/8") (J/m)	NB	NB	NB	NB	86.6	82.7	86.6	90.6
Dynatup impact (J)	6.0	7.8	13.7	11.4	1.5	1.6	1.6	1.8
Failure mode	Both	Both	Ductile	Both	Brittle	Brittle	Brittle	Brittle
Vicat softening point (°C)	85	86	86	86	94	94	93	94
Heat deflection temperature at 1.8 MPa (°C)	67	67	65	67	75	75	76	75
Shore D hardness	65	66	64	64	73	72	73	72
Light transmission (%)	92	92	92	92	87	87	87	87
Haze (%)	6.9	7.0	7.0	7.4	4.6	4.6	4.5	3.9
Hunter color − *a*	−1.3	−2.1	−1.5	−2.7	−0.7	−2.1	−1.5	−2.8
Hunter color − *b*	1.8	4.7	3.1	6.4	4.3	8.5	6.8	10.5
Hunter color − −*b*	−4.9	−4.0	−4.4	−3.7	−18.8	−14.4	−16.1	−13.6

Note: NB, no break.

Table 4.47 The Effect of Aging 2 Years after Gamma Irradiation on the Properties of Chevron Phillips K-Resin® Styrene−Butadiene Copolymer[22]

Property	**KR03**				**60/40 KR03/GPPS**			
Actual radiation level (Mrad)	0.0	2.5	5.0	7.5	0.0	2.5	5.0	7.5
Flow rate (g/10 min)	0.0	3.5	6.0	10.0	0.0	3.5	6.0	10.0
Tensile strength at yield (MPa)	8.3	1.4	4.0	0.2	10.5	3.5	8.0	0.4
Tensile strength at break (MPa)	30	30	30	30	38	38	38	38
Elongation at yield (%)	18	18	18	18	26	25	25	26
Elongation at break (%)	2.1	2.1	2.1	2.1	1.9	1.9	1.9	1.9
Tensile modulus (MPa)	242	226	228	225	203	20	20	20
Flexural yield (MPa)	1805	2	1814	1784	2352	2365	2345	2357
Flexural modulus (MPa)	43	44	44	44	58	60	59	59
Notched, Izod impact (1/8") (J/m)	1783	1783	3036	1787	2539	2558	2549	2447
Unnotched, Izod impact (1/8") (J/m)	7.9	9.4	8.7	12.2	9.8	15.7	18.9	18.1
Dynatup impact (J)	—	—	—	—	—	—	—	—
Failure mode	3	18	11	14	3	2	2	2
Vicat softening point (°C)	Brittle	Both	Both	Ductile	Brittle	Brittle	Brittle	Brittle
Heat deflection temperature at 1.8 MPa (°C)	84	85	85	85	94	94	94	94
Shore D hardness	68	69	68	70	77	78	77	78
Light transmission (%)	64	64	64	65	74	74	74	73
Haze (%)	91	91	91	90	85	86	85	85
Hunter color − *a*	6.7	7.0	7.5	6.8	4.8	4.0	4.3	4.6
Hunter color − *b*	−1.1	−2.0	−1.7	−2.6	−0.6	−2.1	−1.5	−2.6
Hunter color − −*b*	1.7	4.6	3.7	6.4	4.3	8.8	7.3	10.1

Note: NB, no break.

Table 4.48 The Effect of Aging 1 Year after Electron Beam Sterilization on the Properties of Chevron Phillips K-Resin® Styrene–Butadiene Copolymer[22]

Property	**KR03**				**60/40 KR03/GPPS**			
Actual radiation level (Mrad)	0.0	2.5	5.0	7.5	0.0	2.5	5.0	7.5
Flow rate (g/10 min)	5.2	5.3	2.1	0.1	9.7	8.1	5.2	2.'1
Tensile strength at yield (MPa)	30.0	28.6	30.0	30.0	37.9	37.6	37.9	38.3
Tensile strength at break (MPa)	19.0	18.3	18.6	19.0	25.5	25.5	26.2	25.5
Elongation at yield (%)	2.3	2.1	2.0	2.1	2.1	1.9	1.9	2.0
Elongation at break (%)	150	194	160	231	22	22	15	21
Tensile modulus (MPa)	1669	1745	1809	2	2350	2430	2353	2365
Flexural yield (MPa)	43	43	44	44	58	58	59	60
Flexural modulus (MPa)	1791	1777	1799	1797	2522	2473	2508	2547
Notched, Izod impact (1/8") (J/m)	16.5	16.5	16.5	16.1	10.6	8.7	10.2	10.2
Unnotched, Izod impact (1/8") (J/m)	NB	NB	NB	NB	86.6	90.6	90.6	102.4
Dynatup impact (J)	6.0	3.8	9.2	6.6	1.5	1.5	1.7	1.7
Failure mode	Both	Brittle	Both	Both	Brittle	Brittle	Brittle	Brittle
Vicat softening point (°C)	85	86	86	87	94	94	94	95
Heat deflection temperature at 1.8 MPa (°C)	67	67	68	68	75	75	75	76
Shore D hardness	65	64	64	64	73	73	73	72
Light transmission (%)	92	92	93	92	87	87	87	87
Haze (%)	6.9	8.0	7.5	8.0	4.6	4.3	4.7	4.2
Hunter color – *a*	−1.3	−1.5	−1.8	−1.9	−0.7	−1.4	−1.8	−1.8
Hunter color – *b*	1.8	2.8	3.7	3.7	4.3	6.4	7.3	7.6
Hunter color – −*b*	−4.9	−4.8	−4.3	−4.3	−13.8	−16.7	−15.1	−15.5

Note: NB, no break.

Table 4.49 The Effect of E-Beam Radiation on the Properties of Chevron Phillips K-Resin® Styrene–Butadiene Copolymer[22]

Property	**KR03**				**60/40 KR03/GPPS**			
Actual radiation level (Mrad)	0	2.5	5	7.5	0	2.5	5	7.5
Flow rate (g/10 min)	8.4	5.1	2	0.6	10.7	8.6	5.9	42
Tensile strength at yield (MPa)	29	28	28	29	37	37	37	37
Tensile strength at break (MPa)	20	19	19	19	24	24	24	24
Elongation at yield (%)	2	2	1.9	1.7	1.6	1.8	1.9	16
Elongation at break (%)	232	234	223	232	17	28	21	20
Tensile modulus (MPa)	2006	2041	2703	2503	3020	3896	3385	3206
Flexural yield (MPa)	41	40	40	40	56	56	56	57
Flexural modulus (MPa)	1641	1634	1634	1641	2337	2317	2337	2324
Notched, Izod impact (1/8") (J/m)	15.7	15.7	15.7	15.7	11.8	11.8	11.8	11.8
Unnotched, Izod impact (1/8") (J/m)	NB	NB	NB	NB	866	87	98	94
Dynatup impact (J)	28.7	28.4	37.7	31.5	1.9	2.0	2.6	1.9
Failure mode	Ductile	Ductile	Ductile	Ductile	Brittle	Brittle	Brittle	Brittle
Vicat softening point (°C)	84	79	80	81	93	93	93	93
Heat deflection temperature at 1.8 MPa (°C)	61	59	69	61	73	74	73	73
Shore D hardness	67	67	68	68	76	77	76	76
Light transmission (%)	93	92	92	92	87	87	88	87
Haze (%)	64	5.6	6.6	5.5	41	4.2	3.6	3.4
Hunter color − *a*	−12	−1.6	−1.8	−1.8	−0.6	−1.3	−1.6	−1.8
Hunter color − *b*	3.1	4.1	4.6	4.6	5.9	7.4	8	8.5
Hunter color − −*b*	−4.4	−4.5	−4.6	−4.5	−18	−16.5	−15.8	−16.3

Note: NB, no break.

Table 4.50 The Effect of Aging 2 Years after Electron Beam Sterilization on the Properties of Chevron Phillips K-Resin® Styrene–Butadiene Copolymer[22]

Property	**KR03**				**60/40 KR03/GPPS**			
Actual radiation level (Mrad)	0.0	2.5	5.0	7.5	0.0	2.5	5.0	7.5
Flow rate (g/10 min)	8.3	4.1	1.2	NF	10.5	8.7	5.0	0.6
Tensile strength at yield (MPa)	30.3	30.3	30.3	30.3	37.9	37.2	37.6	37.6
Tensile strength at break (MPa)	17.9	18.6	17.9	18.6	25.5	24.1	25.2	25.2
Elongation at yield (%)	2.1	2.1	2.1	2.1	1.9	1.9	1.9	1.9
Elongation at break (%)	242	250	232	244	203	21	20	20
Tensile modulus (MPa)	1805	1808	1814	1806	235	1580	2359	2349
Flexural yield (MPa)	43	45	44	45	58	59	61	61
Flexural modulus (MPa)	1783	1790	1805	1824	2539	2491	2515	2519
Notched, Izod impact (1/8") (J/m)	7.9	19.3	17.3	10.2	9.8	8.3	17.7	16.5
Unnotched, Izod impact (1/8") (J/m)	–	–	–	–	–	–	–	–
Dynatup impact (J)	2.7	24.3	13.7	16.3	2.6	2.4	2.3	2.4
Failure mode	Brittle	Ductile	Both	Both	Brittle	Brittle	Brittle	Brittle
Vicat softening point (°C)	84	85	85	86	94	94	94	94
Heat deflection temperature at 1.8 MPa (°C)	68	68	69	69	77	77	78	78
Shore D hardness	64	65	64	65	74	74	73	73
Light transmission (%)	91	91	91	91	85	85	86	86
Haze (%)	6.7	8.9	7.8	6.7	4.8	5.1	3.8	4.4
Hunter color – *a*	−1.1	−1.3	−1.6	−1.6	−0.6	−1.3	−1.5	−1.7
Hunter color – *b*	1.7	2.7	3.6	3.5	4.3	6.6	5.8	7.6
Hunter color – −*b*	−4.8	−4.4	−4.5	−4.5	−18.6	−17.1	−15.7	−15.6

Note: NF, no flow.

Table 4.51 The Effect of Ethylene Oxide Sterilization on the Properties of Chevron Phillips K-Resin® Styrene−Butadiene Copolymer[22]

Property	**KR03**				**60/40 KR03/GPPS**			
Sterilization cycles	0	1	3	5	0	1	3	5
Flow rate (g/10 min)	8.4	8.4	8.0	8.0	10.7	10.6	11.0	10.7
Tensile strength at yield (MPa)	29	29	29	30	37	36	37	36
Tensile strength at break (MPa)	20	19	20	17	24	20	23	23
Elongation at yield (%)	2.0	1.6	2.0	1.9	1.6	1.8	1.8	1.8
Elongation at break (%)	232	238	196	113	17	25	18	14
Tensile modulus (MPa)	2006	2544	1979	2427	3020	3565	2744	2523
Flexural yield (MPa)	41	41	42	42	56	57	57	57
Flexural modulus (MPa)	1641	1662	1696	1703	2337	2324	2372	2351
Notched, Izod impact (1/8") (J/m)	15.7	15.7	15.7	19.7	11.8	11.8	11.8	11.8
Unnotched, Izod impact (1/8") (J/m)	NB	NB	NB	NB	86.6	86.6	98.4	98.4
Dynatup impact (J)	29	28	23	21	2	2	2	2
Failure mode	Ductile	Ductile	Ductile	Ductile	Brittle	Brittle	Brittle	Brittle
Vicat softening point (°C)	183	185	185	186	199	199	199	199
Heat deflection temperature at 1.8 MPa (°C)	142	142	147	153	163	163	171	163
Shore D hardness	67	68	68	68	76	76	76	76
Light transmission (%)	93	93	92	92	87	87	87	87
Haze (%)	6.4	5.3	5.3	6.2	4.1	3.7	4.3	4.1
Hunter color − *a*	−1.2	−1.1	−1.2	−1.1	−0.6	−0.6	−0.5	−0.6
Hunter color − *b*	3.1	3.4	3.1	3.2	5.9	5.7	5.6	5.8
Hunter color − −*b*	−4.4	−4.7	−4.6	−4.5	−18.0	−17.9	−18.1	−17.6

Note: NB, no break.

Table 4.52 The Effect of Aging 1 Year after EtO Sterilization on the Properties of Chevron Phillips K-Resin® Styrene−Butadiene Copolymer[22]

Property	**KR03**				**60/40 KR03/GPPS**			
Sterilization cycles	0	1	3	5	0	1	3	5
Flow rate (g/10 min)	8.2	8.0	7.7	7.8	9.7	10.2	9.8	9.9
Tensile strength at yield (MPa)	30	30	30	30	38	38	37	38
Tensile strength at break (MPa)	19	18	19	18	26	26	26	26
Elongation at yield (%)	2.3	2.1	2.3	2.3	2.1	2.1	2.2	2.0
Elongation at break (%)	150	254	150	91	22	19	19	21
Tensile modulus (MPa)	1669	1747	1804	1753	2350	2369	2372	2375
Flexural yield (MPa)	43	44	44	45	58	59	59	59
Flexural modulus (MPa)	1791	1807	1814	1820	2522	2534	2518	2532
Notched, Izod impact (1/8") (J/m)	16.5	15.0	16.5	17.3	10.2	11.0	11.8	10.2
Unnotched, Izod impact (1/8") (J/m)	NB	NB	NB	NB	86.6	98.4	90.6	98.4
Dynatup impact (J)	6	4	4	4	1	2	2	2
Failure mode	Both	Brittle	Brittle	Brittle	Brittle	Brittle	Brittle	Brittle
Vicat softening point (°C)	85	86	86	86	94	93	93	94
Heat deflection temperature at 1.8 MPa (°C)	67	70	70	73	75	76	78	80
Shore D hardness	65	64	65	65	73	73	73	73
Light transmission (%)	92	92	93	93	87	87	87	87
Haze (%)	6.9	7.7	7.0	7.1	4.6	4.9	4,7	4.4
Hunter color − *a*	−1.3	−1.3	−1.3	−1.2	−0.7	−3.6	−0.6	−0.5
Hunter color − *b*	1.8	1.6	1.8	1.8	4.3	4.1	4.3	4.2
Hunter color − −*b*	−4.9	−5.0	−4.9	−4.7	−18.8	−18.0	−18.5	−19.0

Note: NB, no break.

Table 4.53 The Effect of Aging 2 Years after EtO Sterilization on the Properties of Chevron Phillips K-Resin® Styrene−Butadiene Copolymer[22]

Property	**KR03**				**60/40 KR03/GPPS**			
Sterilization cycles	0	1	3	5	0	1	3	5
Flow rate (g/10 min)	8.3	7.8	7.9	7.8	10.5	10.3	9.9	10.8
Tensile strength at yield (MPa)	30	30	30	30	38	38	37	38
Tensile strength at break (MPa)	18	18	18	18	26	25	25	25
Elongation at yield (%)	2.1	2.1	2.1	2.1	1.9	1.9	1.9	1.9
Elongation at break (%)	242	234	223	231	203	19	22	22
Tensile modulus (MPa)	1805	1824	1811	1814	2352	2356	2369	2380
Flexural yield (MPa)	43	44	44	44	58	60	60	59
Flexural modulus (MPa)	1783	1809	1789	1812	2539	2525	1782	2515
Notched, Izod impact (1/8") (J/m)	7.9	9.4	7.5	9.8	9.8	15.7	16.9	14.2
Unnotched, Izod impact (1/8") (J/m)								
Dynatup impact (J)	3	14	15	5	3	2	3	3
Failure mode	Brittle	Both	Both	Brittle	Brittle	Brittle	Brittle	Brittle
Vicat softening point (°C)	84	84	85	85	94	94	94	94
Heat deflection temperature at 1.8 MPa (°C)	68	70	71	73	77	78	80	80
Shore D hardness	64	65	65	65	74	74	73	73
Light transmission (%)	91	91	91	91	85	86	86	86
Haze (%)	6.7	6.7	7.3	7.2	4.8	4.5	4.1	3.9
Hunter color − *a*	−1.1	−1.1	−1.2	−1.2	−0.6	−0.6	−0.5	−0.6
Hunter color − *b*	1.7	1.8	1.8	1.8	4.3	4.4	4.4	4.3
Hunter color − −*b*	−4.8	−4.8	−4.9	−4.8	−18.6	−18.4	−18.5	−18.7

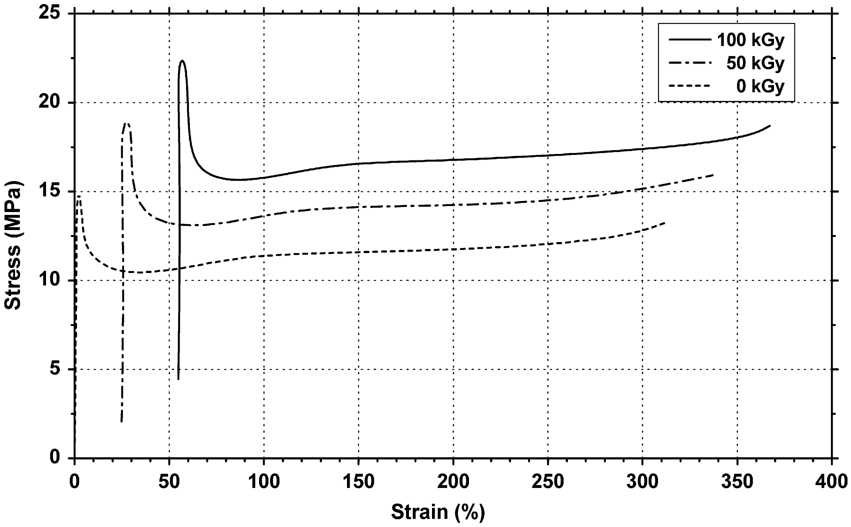


Figure 4.40 Tensile stress–strain curves of BASF Styrolux® for various levels of radiation.

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5 Polyesters

Polyesters are formed by a condensation reaction that is very similar to the reaction used to make polyamide or nylons. A diacid and dialcohol are reacted to form the polyester with the elimination of water as shown in Fig. 5.1. The monomers of each polyester are described in each plastic section.

While the actual commercial route to making the polyesters may be more involved, the end result is the same polymeric structure. The diacid is usually aromatic. Polyester resins can be formulated to be brittle and hard, tough and resilient, or soft and flexible. In combination with reinforcements such as glass fibers, they offer outstanding strength, a high strength-to-weight ratio, chemical resistance, and other excellent mechanical properties. The three dominant materials in this plastics family are polycarbonate (PC), polyethylene terephthalate (PET), and polybutylene terephthalate (PBT). Thermoplastic polyesters are similar in properties to Nylon 6 and Nylon 66 but have lower water absorption and higher dimensional stability than the nylons.

Polyesters generally can be sterilized with ethylene oxide. Due to their low hydrolytic stability (i.e. the polymer chains can be cleaved by hydrolysis) and low glass transition temperatures, steam and higher heat autoclave sterilizations are not recommended. All polyesters based on terephthalic acid contain aromatic groups and hence can be sterilized with gamma and electron beam (e-beam) radiation.

5.1 Liquid Crystalline Polymers

Liquid crystalline polymers (LCPs) are a relatively unique class of partially crystalline aromatic polyesters based on 4-hydroxybenzoic acid and related monomers shown in Fig. 5.2. Liquid crystal polymers are capable of forming regions of highly ordered structure while in the liquid phase. However, the degree of order is somewhat less than that of a regular solid crystal. Typically, LCPs have outstanding mechanical properties at high temperatures, excellent chemical resistance, inherent flame retardancy, and good weatherability. Liquid crystal polymers come in a variety of forms from sinterable high temperature to injection moldable compounds.

LCPs are exceptionally inert. They resist stress cracking in the presence of most chemicals at elevated temperatures, including aromatic or halogenated hydrocarbons, strong acids, bases, ketones, and other aggressive industrial substances. Hydrolytic stability in boiling water is excellent. Environments that deteriorate these polymers are high-temperature steam, concentrated sulfuric acid, and boiling caustic materials.

As an example, the structure of Ticona Vectra® A950 LCP is shown in Fig. 5.3.

Manufacturers and trade names: Eastman Thermx®, DuPont Engineering Polymers Zenite®, Ticona Vectran™ and Vectra®, Solvay Advanced Polymers Xydar®, Sumitomo Sumikasuper®, and Toray Siveras®.

Sterile applications and uses: Sterilizable trays, dental tools and surgical instruments, surgical device control cables, surgical tubing, cannulae, and films. High barrier retort: pouches, closures, trays, and lids.

Gamma radiation resistance: Vectra® LCPs have excellent resistance to gamma radiation.

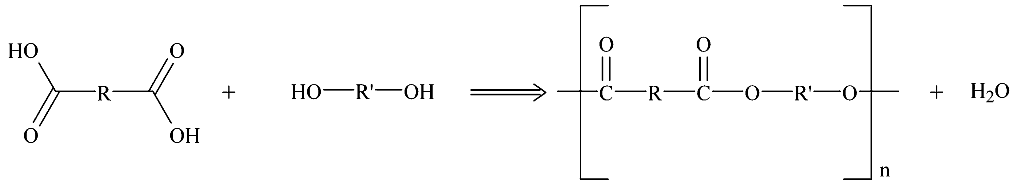
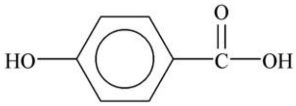


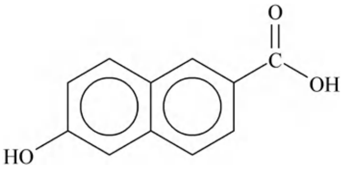
Figure 5.1 Chemical structure of polyester.

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00005-8

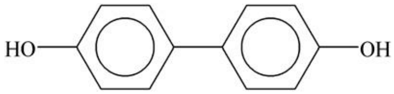
Figure 5.2 Chemical structures of monomers used to make liquid crystalline polymer polyesters.



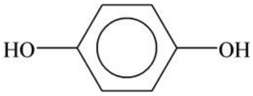
HBA
4-hydroxybenzoic acid



HNA
6-hydroxynaphthalene-2-carboxylic acid

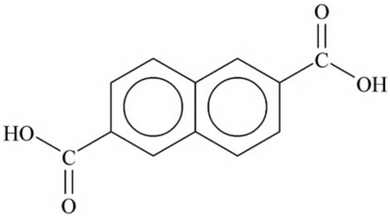


BP
4-(4-hydroxyphenyl)phenol

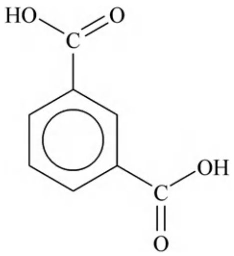


HQ
benzene-1,4-diol
(hydroquinone)

TA
benzene-1,4-dicarboxylic acid
(terephthalic acid)



NDA
Naphthalene-2,6-dicarboxylic acid



IA
benzene-1,3-dicarboxylic acid
(isophthalic acid)

Steam sterilization resistance: Vectra® LCP has good resistance to hydrolysis. Prolonged exposure to hot water and steam at high temperatures (121 °C, 2 bar up to 1000 h) leads to hydrolytic degradation however. The glass-fiber reinforced grades exhibit a more severe decline in mechanical properties, as do many other glass-fiber reinforced polymers, owing to capillary action at the glass-fiber/polymer interface (wick effect). Vectra® A625 has particularly good resistance to hydrolysis. Under selected test conditions, virtually no change in tensile strength or elastic modulus occurred after 1000 h.

Regulatory status: Many Vectra® grades are compliant with Food and Drug Administration (FDA) regulations for food contact, specifically Food Contact Substance Notification (FCN #103) and are listed in the FDA Drug and Device Master Files. Many also meet United States Pharmacopoeia (USP) Class VI requirements. Some grades of Vectra® LCP have been found to meet the requirements of ISO

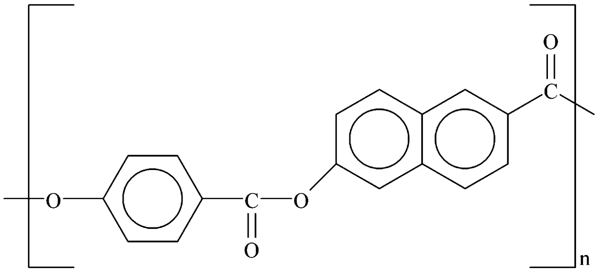


Figure 5.3 Chemical structure of Ticona Vectra® A950 LCP.

10993 biocompatibility tests (Tables 5.1 and 5.2) (Figs 5.4–5.7).

Table 5.2 Effect of 500 Mrad Exposure from Cobalt-60 Gamma Radiation on Ticona Vectra® A950 and B950 Liquid Crystal Polymer[2]

	Vectra Grade	
Physical Property	**A950**	**B950**
Tensile strength	97.1	100.0
Tensile modulus	100.0	100.0
Elongation	81.3	100.0
Flexural strength	100.0	100.0
Flexural modulus	100.0	100.0
Heat deflection temperature (at 1.8 MPa)	94.2	95.2

5.2 Polybutylene Terephthalate

PBT is semicrystalline, white or off-white polyester similar in both composition and properties to PET. It has somewhat lower strength and stiffness than PET, is a little softer, but has higher impact strength and similar chemical resistance. As it crystallizes more rapidly than PET, it tends to be preferred for industrial scale molding. Its structure is shown in Fig. 5.8.

PBT performance properties include:

- High mechanical properties
- High thermal properties
- Good electrical properties
- Dimensional stability
- Excellent chemical resistance
- Flame retardancy.

PBT can be sterilized by gamma ray or dry heat, up to about 180 °C. Ultradur® HR (hydrolysis resistant) PBT.

Manufacturers and trade names: BASF Ultradur®, DuPont Crastin®, PolyOne Burgadur™, SABIC Innovative Plastics Enduran, and Ticona Celanex®.

Sterile applications and uses: Packaging, syringe pump component, dental instruments, miniature scalpel blade holders, melt blown for liquid filtration applications, and high-temperature caps (Tables 5.3–5.6).

5.3 Polycarbonate

Theoretically, polycarbonate is formed from the reaction of bis-phenol A and carbonic acid. The

Table 5.1 Effect of Cobalt-60 Gamma Radiation on Ticona Vectra® A950 Liquid Crystal Polymer[1]

Exposure Conditions					
Radiation dose (Mrad)	250	1000	2500	5000	
Properties Retained (%)					**Test Method**
Tensile strength	97	95	95	95	ASTM D638
Tensile modulus	100	100	106	106	ASTM D638
Elongation at break	81	81	79	79	ASTM D638
Flexural strength	101	102	102	102	ASTM D790
Flexural modulus	108	108	116	125	ASTM D790
Heat deflection temperature at 1.82 MPa	100	100	100	94	ASTM D648

Figure 5.4 Tensile strength retained versus immersion time in steam of Ticona Vectra® LCPs.[1]

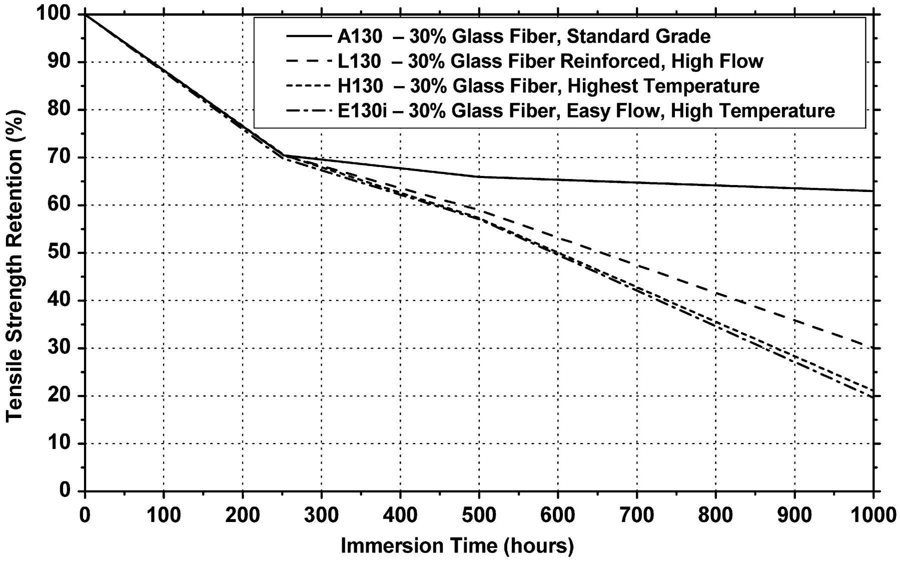


Figure 5.5 Tensile modulus retained versus immersion time in steam of Ticona Vectra® LCPs.[1]

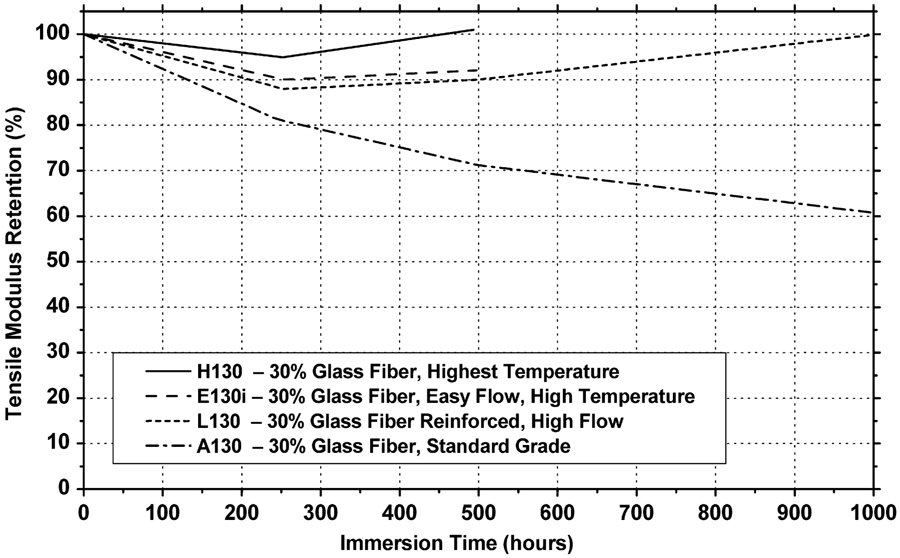
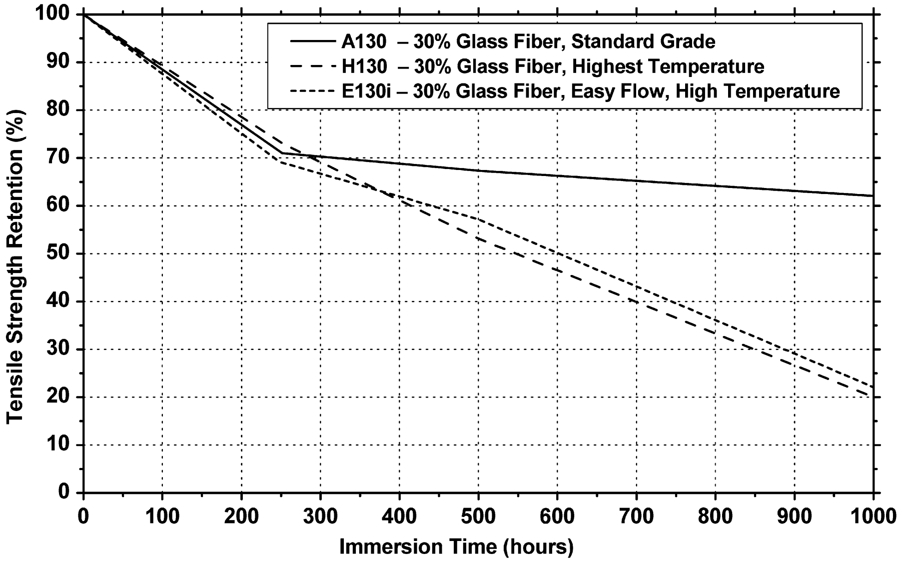


Figure 5.6 Tensile strength retained versus immersion time in hot water (120 °C, 2 bar) of Ticona Vectra® LCPs.[1]



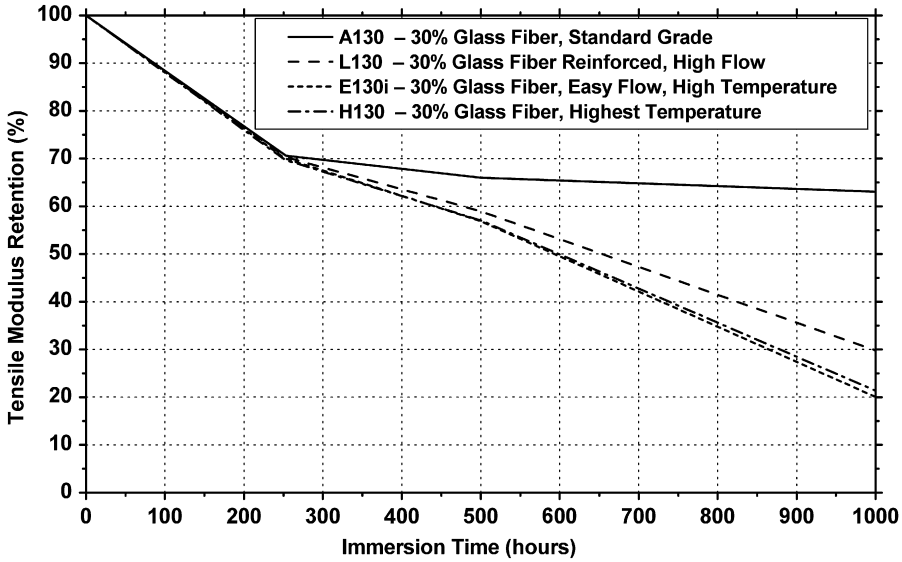


Figure 5.7 Tensile modulus retained versus immersion time in hot water (120 °C, 2 bar) of Ticona Vectra® LCPs.[1]

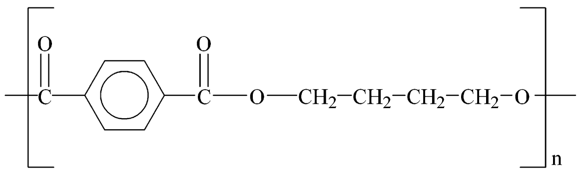


Figure 5.8 Chemical structure of polybutylene terephthalate polyester.

structures of these two monomers are given in Fig. 5.9.

Commercially, different routes are used (different monomers), but the polycarbonate polymer of the structure shown in Fig. 5.10 is the result.

Polycarbonate performance properties include:

- Very impact resistant and virtually unbreakable and remains tough at low temperatures
- “Clear as glass” clarity
- High heat resistance
- Dimensional stability
- Resistant to ultraviolet light, allowing exterior use
- Flame-retardant properties.

Polycarbonates can be sterilized by high-energy gamma and e-beam radiation but must be stabilized to prevent polymer degradation and discoloration.

Manufacturers and trade names: Bayer MaterialScience Makrolon® and Dow Calibre™.

Sterile applications and uses: Medical apparatus (sterilizable); packaging: milk bottles, baby bottles, food containers; medical: dialyzers, artery cannulas, stopcocks, syringes, and centrifugal force separators.

Gamma radiation resistance: Polycarbonate (PC) is much more resistant to gamma irradiation than most polymers. The primary effect of gamma irradiation on PC is chain scission (chain breakage). Fortunately, the high chain stiffness of PC makes it very difficult for the two ends of the chain to move apart. Therefore, many of the broken chains will recombine. In addition, the aromatic nature of the PC gives it other opportunities to absorb the energy from the gamma photon, rather than just breaking the polymer chain. From a retention of mechanical properties point of view, PC has always been considered one of the most resistant materials for gamma irradiation.[6] Makrolon® has a high resistance to the effects of high-energy radiation. Its resistance depends on the ambient conditions and the radiation dosage applied. Assuming that 28 kGy (2.8 Mrad) of energy is required to sterilize Makrolon®, the resin can be sterilized 10—20 times before any appreciable reduction in mechanical strength occurs.

Polycarbonate does, however, become progressively more yellow with each sterilization. Makrolon® grades Rx-2430, Rx-2530 and Rx-1805 contain a special stabilizer that makes them less susceptible to color changes caused by high-energy radiation than standard Makrolon® grades.[7]

Ethylene oxide (EtO) resistance: The properties of Lexan HP and HPS resins are unchanged to 50

Table 5.3 BASF Ultradur® Hydrolysis Resistance Comparison at 110 °C/100% RH for 10 days[3]

Properties	B 4300 G6 Standard PBT	B 300 G6 HR High Flow, HR	B 4043 G6 HR High Flow, Impact Modified, HR, Sodium Hydroxide Resistant	B 4330 G6 HR Impact Modified, Exceptional Sodium Hydroxide Resistance, HR
Tensile strength DAM (MPa)	145	139	117	110
Tensile strength after conditioning (MPa)	30	116	104	100
% Retention	21	83	89	91
Tensile elongation DAM (%)	2.8	3.2	3.9	5
Tensile elongation after conditioning (%)	0.4	2.6	2.9	3.1
% Retention	14	81	74	62
Charpy impact DAM (kJ/m^2)	72	74	78	75
Charpy impact after conditioning (kJ/m^2)	7.4	45	58	60
% Retention	10	61	74	80

Note: PBT, polybutylene terephthalate; HR, hydrolysis resistant; DAM, Dry as Molded.

Table 5.4 Effect of Gamma Radiation Sterilization (2.5 Mrad) on Sabic Valox HP and HP260 Polybutylene Terephthalate[4]

Properties Retained (%)	
Tensile strength at break	117
Elongation at break	103
Notched Izod impact strength	110

ethylene oxide sterilization cycles.[8] For Makrolon® polycarbonates, suitable sterilization processes are those which use ethylene oxide, either undiluted or mixed with carbon dioxide or inert gases in the ratio 10−20% ethylene oxide/90 to 80% remainder. The temperature during sterilization should not exceed 65 °C. Tests have shown that repeated sterilization can cause slight brittleness combined with crack formation. The impact strength of test specimens treated with pure ethylene oxide at 55 °C for 50 cycles of 6 h each is unchanged in comparison with the starting level despite slight crack formation.[7]

Steam resistance: After one to three autoclave cycles (Hi-Vac at 132 °C), Lexan HP and HPS resins have limited utility.[8] Calibre 2071 offers superior hydrolytic stability in those applications that use steam sterilization or autoclave.[9] Makrolon DP 1-1262 and Makrolon Rx-1805 can be sterilized by employing superheated steam (121 °C).[10,11] To prevent deformation of the molded parts, the sterilization temperature should not exceed 125 °C. Care must also be taken to ensure that Makrolon® parts are not damaged by substances added to the boiler feed water, such as alkaline corrosion inhibitors and that the article is positioned in such a way that no condensation can accumulate inside it. As a rule, it is possible to sterilize molded parts made of Makrolon® many times before gradual chemical

Table 5.5 Effect of Ethylene Oxide (EtO) Sterilization on Residual Molecule Content of Sabic Valox Polybutylene Terephthalate after Aeration with Fan[5]

Material	**Valox HP210**			**Valox HP260**		
Residuals (ppm)	**Ethylene Oxide**	**Ethylene Chlorohydrin**	**Ethylene Glycol**	**Ethylene Oxide**	**Ethylene Chlorohydrin**	**Ethylene Glycol**
24-h aeration	37	<1	<4	33	<1	<4
168-h aeration	8	–	–	12	–	–
336-h aeration	5	–	<4	5	–	<4

Note: (1) Preexposure conditioning: vacuum 660–711 mmHg; RH: 45–60%; dwell time: 15 min. (2) Sterilization conditions: 5 h, 100% EtO. (3) Postexposure conditioning: mechanical aeration with fan, 49 °C.

Table 5.6 Effect of Ethylene Oxide (EtO) Sterilization on Residual Molecule Content of Sabic Valox Polybutylene Terephthalate after Aeration[5]

Material	**Valox HP210**			**Valox HP260**		
Residuals (ppm)	**Ethylene Oxide**	**Ethylene Chlorohydrin**	**Ethylene Glycol**	**Ethylene Oxide**	**Ethylene Chlorohydrin**	**Ethylene Glycol**
24-h aeration	100	<1	35	111	<1	52
168-h aeration	53	–	–	73	–	–
336-h aeration	5	–	28	62	–	25

Note: (1). Preexposure conditioning: vacuum 660–711 mmHg; RH: 45–60%; dwell time: 15 min. (2) Sterilization conditions: 5 h, 100% EtO. (3) Postexposure conditioning: mechanical aeration (ambient), 49 °C.

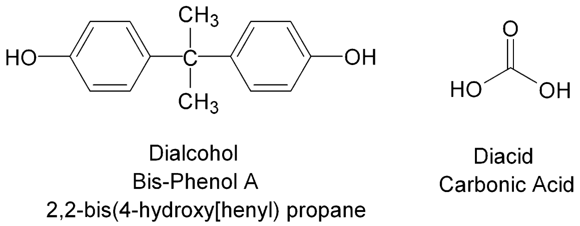


Figure 5.9 Chemical structures of monomers used to make polycarbonate polyester.

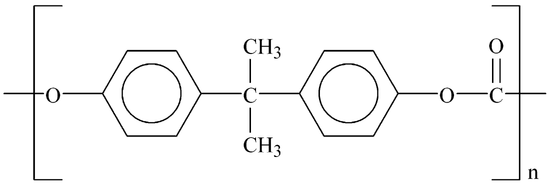


Figure 5.10 Chemical structure of polycarbonate polyester.

decomposition reduces the mechanical strength to a level where it is no longer adequate for certain applications. Sterilization tests on test specimens have shown that even after 100 cycles of 30 min each at 120–125 °C, the part still retains comparatively good impact strength. This also generally applies even if the material exhibits hairline cracks and the molded part appears slightly milky as a result of the high stresses imposed on the material by repeated sterilization.[7]

Sterilization with peracetic acid: Makrolon® can be sterilized with 2% concentration peracetic acid without suffering damage (appropriate safety precautions must be observed when handling peracetic acid!).[7]

Sterilization with hot air: Sterilization with hot air plays only a minor role for molded parts in Makrolon® since temperatures of 180–200 °C are generally used to save time. No problems are to be expected with molded parts in Makrolon® up to a hot air temperature of 135 °C.

Regulatory status: Many polycarbonates are FDA approved for medical supplies. Sabic Plastics Lexan HP grades maintain FDA and USP Class VI Compliance. Dow Plastics Calibre 2061, Calibre 2071, and Calibre MegaRad 2081 are USP Class VI and ISO 10993 tested. Makrolon DP 1-1262 and Makrolon Rx-1805 have been tested in accordance with the FDA-modified ISO 10993-1 and USP Class VI and fulfills the test criteria for a body contact period of up to 30 days (Tables 5.7–5.37) (Fig. 5.11–5.25).[10,11]

5.4 Polyethylene Terephthalate

PET polyester is the most common thermoplastic polyester and is often called just "polyester." This often causes confusion with the other polyesters in this chapter. PET exists both as an amorphous (transparent) and as a semicrystalline (opaque and white) thermoplastic material. The semicrystalline PET has good strength, ductility, stiffness, and hardness. The amorphous PET has better ductility but less stiffness and hardness. It absorbs very little water. Its structure is shown in Fig. 5.26.

Manufacturers and trade names: DuPont Teijin Films™, Mylar®, and Melinex® and Mitsubishi Polyester Film Hostaphan®.

Table 5.7 Effect of 2.5 Mrad Gamma Radiation Sterilization on Dow Polycarbonate after Dark Postexposure Conditioning[12]

Postexposure Conditioning							
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	100.8	97.3	93.7	101.1	97.7	97.6	ASTM D638
Tensile strength at yield	98.3	98.2	99.1	97.1	97.3	97.3	ASTM D638
Elongation at break	103.3	95.9	86.2	104.9	100	100	ASTM D638
Dart impact (total energy)	99.7	93.7	83.9	94.6	90.4	87	ASTM D3763
Notched Izod impact strength	99.4	105	98.8	72	95	91.9	ASTM D256

Table 5.8 Effect of Gamma Radiation Sterilization on Bayer and Sabic Plastics Polycarbonates

Material Name	**Lexan HP**	**Lexan HPS**
Material note	Transparent, medical grade	Gamma radiation stabilized, transparent, medical grade
Properties Retained (%)		
Tensile strength at break	9191	
Elongation at break	98	98
Notched Izod impact strength	94	94

Table 5.9 Effect of 2.5 Mrad Gamma Radiation Sterilization on the Yellowness Index of Sabic Plastics Lexan Polycarbonate[4]

Material Name	**Lexan HPS 1125**		**Lexan HPS 1136**		**Lexan HPS 1124**		**Lexan HP 1125**	
Material note	Gamma radiation stabilized, transparent, medical grade, tinted						Transparent, medical grade, tinted	
Postexposure Conditioning								
Time (h)	0	336	0	336	0	336	0	336
Properties Retained (%)								
Yellowness index 10	6	10	6	10	6	22	15	

Note: (1). Postexposure conditioning: mechanical aeration (ambient), 49 °C.

Table 5.10 Effect of Gamma Radiation (Cobalt-60) Sterilization on Dow Polycarbonate after Light Post Exposure Conditioning[22]

Material Name	**Calibre 2060**		**Developmental material**		**Calibre 2061**		**Developmental Material**		
Material Note	Transparent		Transparent		Transparent, Mold Release		Transparent		
Exposure Conditions									
Radiation dose (Mrad)	2.5	10	2.5	10	2.5	10	2.5	10	
Postexposure Conditioning									
Lighting type	Storage under fluorescent light				Storage in dark				
Properties Retained (%)									**Test Method**
Tensile strength at yield	8.9	97.7	100	98.9	98.9	97.7	98.9	97.9	ASTM D638
Notched Izod impact strength	96.3	88.8	98.6	104.2	99.4	72	101.4	97.2	ASTM D256

Note: (1) Sterilization: Source Cobalt 60. (2) Postexposure conditioning: 21 °C, 336 h, light condition indicated in table.

Applications and uses: Bottles for soft drinks and water, food trays for oven use, and roasting bags (Figs 5.27 and 5.28).

5.5 Polycyclohexylene-Dimethylene Terephthalate

Polycyclohexylene-dimethylene terephthalate (PCT) is high-temperature polyester that possesses the chemical resistance, processability, and dimensional stability of polyesters PET and PBT. However, the aliphatic cyclic ring shown in Fig. 5.29 imparts added heat resistance. This puts it between the common polyesters and the LCP polyesters described in the previous section. At this time, Ticona makes this plastic under the trade name Thermx®.

Manufacturers and trade ames: Eastman Eastar and Ticona Thermx®.

Sterile applications and uses: Rigid medical, blister packaging, laundry bags, and hospital bed pads.

Gamma sterilization: Eastman PCT polyesters can be sterilized by gamma radiation.[27]

Table 5.11 Effect of Gamma Radiation Sterilization on the Properties of Polycarbonate[13]

Material	Gamma Radiation Stabilized, Transparent		Transparent, General-Purpose Grade	
Exposure Conditions				
Radiation dose (Mrad)	3	5	3	5
Properties Retained (%)				
Tensile strength at yield	100	100	99	99
Flexural modulus	–	–	100	100
Notched Izod impact strength	–	–	96	96
Surface and Appearance				
Δ Yellowness index	16	30	30	50

Table 5.12 Effect of Gamma Radiation Sterilization on Dow Calibre MegaRad 2081-15-FC030105 Polycarbonate[14]

Sterilization Conditions					
Radiation dose (Mrad)	2.5	2.5	10	10	
Postexposure					
Aging time (h)	168	1344	168	1344	
Properties Retained (%)					**Test Method**
Tensile strength at yield	100	109.7	98.4	104.8	ASTM D638
Elongation	102.3	106.2	96.9	100.8	ASTM D638
Flexural strength	102	94	102	101	ASTM D790
Tensile modulus	108	96.6	105.9	101.3	ASTM D638
Flexural modulus	103.3	108.2	107.4	109.5	ASTM D790
Dart impact (total energy)	92.6	102.9	76.5	102.9	ASTM D3763
Dart impact (peak energy)	90.6	98.4	75	90.6	ASTM D3763
Notched Izod impact strength	105.1	101.5	97.8	98.7	ASTM D256
Heat deflection temperature	100	99.2	95.9	97.5	ASTM D648
Vicat softening point	100	98.7	97.3	97.3	–
Surface and Appearance					
Yellowness index	16.9	7	45.5	27.8	ASTM D1925
Haze (%)	0.72	–0.5	1.96	–0.85	–
Transparency retained (%)	96.97	121.21	96.97	116.67	–

Table 5.13 Effect of Gamma Radiation Sterilization on Dow Calibre Polycarbonate[14]

Material Name	Calibre MegaRad 2081-15-FC030006				Calibre MegaRad 2081-15-FC030116				
Sterilization Conditions									
Radiation dose (Mrad)	2.5		10		2.5		10		
Postexposure Conditioning									
Aging time (h)	168	1344	168	1344	168	1344	168	1344	
Surface and Appearance									**Test Method**
Yellowness index	11.56	8.13	41.86	8.6	6.22	0.52	43.72	12.27	ASTM D1925
Haze (%)	2.6	1.5	2	3.7	1.7	−1.3	0	−1.4	–
Transparency retained (%)	102.7	119.2	94.5	119.2	87.8	108	84	107	–

Table 5.14 Effect of Gamma Radiation Sterilization on the Color Properties for Dow Calibre 2061-15-FC850122 Polycarbonate[14]

Exposure Conditions					
Radiation dose (Mrad)	2.5		10		
Postexposure Conditioning					
Aging time (h)	168	1344	168	1344	
Surface and Appearance					**Test Method**
ΔL color	−0.7	−0.9	−1.8	−2.6	ASTM D2244
Δa color	−0.57	−0.22	−0.17	−1.09	ASTM D2244
Δb color	4.3	3.59	5.58	8.25	ASTM D2244

Table 5.15 Effect of Gamma Radiation Sterilization on Sabic Lexan 141 Polycarbonate[15]

Exposure Conditions			
Radiation dose (Mrad)	2.5	4	6
Properties Retained (%)			
Tensile strength	97.9	91.8	96.9
Elongation	61.3	83.8	81.1
Tensile modulus	97.2	97.2	105.6
Notched Izod impact strength	92.8	103	95.8
Melt flow rate	2600	2500	2520

Table 5.16 Effects of Gamma Radiation on Sabic LNP Thermocomp DF002 EM Mra Polycarbonate[10]

Exposure Conditions				
Type level	Unexposed	3.5 Mrad		
Time poststerilization		0 months	6 months	
Properties				**Test Method**
Izod impact (J/m)	147	139	147	ASTM D256
Tensile strength (MPa)	74.6	73.0	77.4	ASTM D638
Yellowness index	−4.68	16.5	–	
Δ*E** between exposed/unexposed	–	21.2	–	

Table 5.17 Effects of Gamma Radiation on Glass-filled Sabic LNP Thermocomp DF004 EM MR WT9-851 Polycarbonate[10]

Exposure Conditions				
Type level	Unexposed	3.5 Mrad		
Time poststerilization		0 months	6 months	
Properties				**Test method**
Izod impact (J/m)	138	132	135	ASTM D256
Tensile strength (MPa)	107	107	111	ASTM D638
Yellowness index	7.62	18.0	–	
Δ*E** between exposed/unexposed	–	10.3	–	

Table 5.18 Effects of Gamma Radiation on Glass-filled LNP Thermocomp DF008 EM MR WT9-007 Polycarbonate[10]

Exposure Conditions				
Type level	Unexposed	3.5 Mrad		
Time poststerilization		0 months	6 months	
Properties				**Test Method**
Izod impact (J/m)	29.9	31	31	ASTM D256
Tensile strength (MPa)	147	147	152	ASTM D638
Yellowness index	11.4	17.2	–	
ΔE^* between exposed/unexposed	–	5.82	–	

Table 5.19 Effects of Gamma Radiation on Carbon-filled Sabic LNP Thermocomp DC006 EM ER Polycarbonate[10]

Exposure Conditions				
Type level	Unexposed	3.5 Mrad		
Time poststerilization		0 months	6 months	
Properties				**Test Method**
Izod impact (J/m)	111	99.9	N/A	ASTM D256
Tensile strength (MPa)	180	182	186	ASTM D638

Table 5.20 Effect of Electron Beam Radiation Sterilization on Dow Calibre Polycarbonate[14]

Sterilization Conditions					
Radiation dose (Mrad)	2.5	2.5	10	10	
Postexposure Conditioning					
Aging time (h)	168	1344	168	1344	
Properties Retained (%)					**Test Method**
Tensile strength at yield	98.4	101.6	116.1	101.6	ASTM D638
Elongation	93.1	83.8	91.5	95.4	ASTM D638
Flexural strength	102	96	101	99	ASTM D790
Tensile modulus	101.3	98.7	117.7	103.8	ASTM D638
Flexural modulus	104.5	106.2	105.3	109.1	ASTM D790
Dart impact (total energy)	100	95.6	92.6	95.6	ASTM D3763
Dart impact (peak energy)	100	96.9	87.5	87.5	ASTM D3763
Notched Izod impact strength	103	92.2	101.5	99.3	ASTM D256
Heat deflection temperature	100	99.2	94.2	95	ASTM D648
Vicat softening point	98.7	98	97.3	98	–
Surface and Appearance					
Yellowness index	11.1	7.1	43.6	28.1	ASTM D1925
Haze (%)	0.98	−0.57	0.86	0.21	–
Transparency retained (%)	107.58	119.7	92.42	113.64	–

Table 5.21 Effect of Electron Beam Radiation Sterilization on Surface and Appearance Properties of Dow Calibre Polycarbonate[14]

Sterilization Conditions									
Radiation dose (Mrad)	2.5		10		2.5		10		
Postexposure Conditioning									
Aging time (h)	168	1344	168	1344	168	1344	168	1344	
	Surface and Appearance								**Test Method**
Yellowness index	11.54	8.71	11.12	8.84	3.75	0.73	36.67	20.91	ASTM D1925
Haze (%)	2.5	3.1	1.9	1.2	0.8	−0.6	−0.1	−1.4	—
Transparency retained (%)	106.8	117.8	106.8	119.2	97	108	82	104	—

Table 5.22 Effect of Electron Beam Radiation Sterilization on Bayer Makrolon® Polycarbonate[18]

Sterilization Conditions (%)		
Radiation dose (Mrad)	2.5	5
Properties Retained (%)		
Tensile strength	107.6	104.3
Tensile strength at yield	100	98.9
Elongation at break	96	96
Notched Izod impact strength	103.6	97.6
Heat deflection temperature	99.6	101.2

Table 5.23 Effect of Electron Beam Radiation Sterilization on Color Properties for Dow Calibre Polycarbonate[14]

Sterilization Conditions (%)					
Radiation dose (Mrad)	2.5		10		
Postexposure Conditioning					
Aging time (h)	168	1344	168	1344	
	Surface and Appearance				**Test Method**
ΔE color	−1.3	−0.7	−3.6	−2.5	ASTM D2244
ΔL color	−1.5	−0.88	−1.78	−1.36	ASTM D2244
Δa color	5.1	3.83	8.77	7.74	ASTM D2244

Table 5.24 Physical Properties before and after E-Beam Radiation of Bayer Makrolon® RX1805 PC[19]

Test and Units	**E-Beam Energy (Mrad)**	**Makrolon RX1805**
Tensile yield strength (MPa)	Unexposed	64
	25	63
	50	62
Tensile break strain (%)	Unexposed	146
	25	134
	50	147
Flatwise impact at 23 °C; total energy (J)	Unexposed	89
	25	95
	50	85

Table 5.25 Effect of Ethylene Oxide (EtO) Sterilization on Dow Polycarbonate after Dark Postexposure Conditioning[12]

Sterilization Conditions							
Cycles	1			5			
Postexposure Conditioning (3)							
Aging time (h)	336	4368	8760	336	4368	8760	
	Properties Retained (%)						**Test Method**
Tensile strength at break	102.9	98.2	93.5	78.8	76.4	75.8	ASTM D638
Tensile strength at yield	100	99.2	99	99.6	100	99.3	ASTM D638
Elongation at break	102.4	98.4	90.2	44.7	18.7	20.3	ASTM D638
Dart impact (total energy)	93.9	93.3	94.3	89.8	64.5	62.1	ASTM D3763
Notched Izod impact strength	98.8	98.1	102.5	101.2	102.5	101.2	ASTM D256

Note: (1) Preexposure conditioning: 60% RH, 37.8 °C, 8 h. (2) Sterilization conditions: ≥6 h, 12% EtO and 88% Freon, 49 °C, 60% RH. (3) Postexposure conditioning: (1) Evacuation 127 mmHg; (2) aeration, 32.2 °C, ≥16 h; and (3) storage in dark, 21 °C.

Table 5.26 Effect of Ethylene Oxide (EtO) Sterilization on Dow Calibre 2060-10 Polycarbonate after Ambient Postexposure Conditioning[12]

Sterilization Conditions									
Gas composition	12% EtO and 88% Freon				8.6% EtO and 91.4% HCFC-124				
Cycles	1	1	2	2	1	1	2	2	
Postexposure Conditioning (2)									
Aging time (h)	168	1344	168	1344	168	1344	168	1344	
	Properties Retained (%)								**Test Method**
Tensile strength at yield	99.4	95.5	99.8	95.7	97.1	97.7	99.9	95.4	ASTM D638
Elongation	87.8	84.9	65.5	48.2	85.6	89.9	91.4	91.4	ASTM D638
Tensile modulus	89	104.1	103.1	100.6	90.3	101.9	96.9	83.1	ASTM D638
Dart impact (total energy)	91.5	105.1	100	98.3	98.3	103.4	91.5	106.8	ASTM D3763
Dart impact (peak energy)	91.4	100	96.6	93.1	93.1	100	87.9	101.7	ASTM D3763
Surface and Appearance									
Yellowness index	1.61	1.33	1.52	1.43	1.77	1.48	1.58	1.66	
Haze %	3.07	3.12	6.25	5.23	1.99	2.93	4.27	6.44	
Transmittance %	88	88	87	88	88	88	88	87	

Note: (1) Preexposure conditioning: 60% RH, 37.8 °C, 18 h. (2) Sterilization conditions: 6 h, 49 °C, 60% RH, EtO mixture. (3) Postexposure conditioning: (1) aeration 127 mmHg, 32.2 °C, and (2) ambient conditions.

Table 5.27 Effect of Ethylene Oxide (EtO) Sterilization on Dow Calibre 2060-10 Polycarbonate after Aeration Postexposure Conditioning[21]

Postexposure Conditioning				
Aeration details	10 air changes per hour	30 air changes per hour	10 air changes per hour	30 air changes per hour
Temperature (°C)	32.2	54.4	32.2	54.4
Residuals, Ethylene Oxide (ppm)				
Little or no aeration	1011	1011	1249	1249
24-h Aeration	625	319	378	458
48-h Aeration	–	227	–	328
72-h Aeration	275	216	363	235
168-h Aeration	167	–	253	–

Table 5.28 Effect of Ethylene Oxide (EtO) Sterilization on Dow Calibre Polycarbonate after One and Five Exposure Cycles[22]

Material Name	**Calibre 2060**		**Transparent Developmental Resin**		
Sterilization Conditions					
Number of cycles	1	5	1	5	
Properties Retained (%)					**Test Method**
Tensile strength at yield	100	100	98.9	98.9	ASTM D638
Notched Izod impact strength	98.8	101.2	102.8	111.3	ASTM D256

Note: (1) Preexposure conditioning: 60% RH, 37.8 °C, 8 h. (2) Sterilization conditions: ≥6 h, 49 °C, 60% RH, 12% EtO and 88% Freon. (3) Postexposure conditioning: (1) evacuation 127 mmHg; 32.2 °C, (2) aeration, 32 °C, ≥16 h, and (3) 336-h storage in the dark, 21 °C, 50% RH.

Table 5.29 Effect of Ethylene Oxide (EtO) Sterilization on Residuals for Dow Calibre Polycarbonate[22]

Material Name	**Calibre 2060**	**Transparent Developmental Resin**
Residual EtO (ppm)		
25-h aeration	514	877
72-h aeration	335	449
168-h aeration	290	362
744-h aeration	202	270
792-h aeration	–	207
816-h aeration	99	–
840-h aeration	–	175
864-h aeration	97	–
888-h aeration	–	126

Note: (1) Preexposure conditioning: 60% RH, 37.8 °C, 8 h. (2) Sterilization conditions: ≥6 h, 49 °C, 60% RH, 12% EtO and 88% Freon. (3) Postexposure conditioning: (1) evacuation 127 mmHg; 32.2 °C, (2) aeration, 32 °C, hours in table.

Table 5.30 Effect of Ethylene Oxide (EtO) Sterilization on Bayer Makrolon Polycarbonate[13,23]

Material Name	**Makrolon FCR-2458**		**Bayer Makrolon 2608**		**Gamma Radiation Stabilized, Transparent**	
Sterilization Conditions						
Gas composition	12% EtO and 88% Freon		10% EtO and 90% CO_2		100% EtO	12% EtO and 88% Freon
Number of cycles	1	5	1	5	1	1
Temperature (°C)	48.9	48.9	48.9	48.9	48.9	54.4
Hours	6	6	10	10	4–6	4–6
Other	RH: 60%; pressure: 0.051 MPa		RH: 45%; pressure: 0.158 MPa			
Properties Retained (%)						
Tensile strength at break	95	85	102.9	103.9	100	100
Tensile strength at yield	100	100	102.2	101.1	–	–
Elongation at break	95.8	79.2	100	100	–	–
Flexural modulus	–	–	–	–	100	100
Notched Izod impact strength	97.4	95.4	97.4	95.5	100	99
Heat deflection temperature	99.2	97.7	–	–	–	–

Table 5.31 Effect of Ethylene Oxide (EtO) Sterilization (One Cycle) on Residuals for Bayer Makrolon 2608 Polycarbonate[23]

Residuals Determined (ppm)	**Ethylene Oxide**	**Ethylene Chlorohydrin**	**Ethylene Glycol**
24-h aeration	119	–	–
168-h aeration	19	0	0
336-h aeration	8	0	0

Table 5.32 Effect of Ethylene Oxide (EtO) Sterilization (Five Cycles) on Sabic Polycarbonate[24]

Properties Retained (%)	
Tensile strength at yield	112
Elongation at yield	107
Tensile modulus	103

Note: (1) Preexposure conditioning: vacuum 660–711 mmHg, 45–60% RH, 15 min. (2) Sterilization conditions: 5 h, 54.4 °C, 100% EtO.

Table 5.33 Effect of Ethylene Oxide (EtO) Sterilization on Residuals for Sabic Lexan Polycarbonate after Ambient Aeration Postexposure Conditioning[25]

Material Name	**Lexan 141**	**Lexan HP3**	**Lexan SP1310**	**Lexan 141**	**Lexan HP3**	**Lexan SP1310**
Material note	Transparent	Transparent, medical grade	Transparent, random copolymer	Transparent	Transparent, medical grade	Transparent, random copolymer
Residuals (ppm)						
Residuals determined	Ethylene chlorohydrin			Ethylene glycol		
336-h aeration	<3			<20	<24	<21

Note: (1) Preexposure conditioning: vacuum 660–711 mmHg, 45–60% RH, 15 min. (2) Sterilization conditions: 8 h, 51.7 °C, 100% EtO. (3) Postexposure conditioning: aeration, ambient conditions, 23 °C.

Table 5.34 Effect of Ethylene Oxide (EtO) Sterilization, 8-h Exposure, on Residuals for Sabic Lexan Polycarbonate after Aeration with Fan Postexposure Conditioning[25]

Material Name	**Lexan 141**	**Lexan HP3**	**Lexan SP1310**	**Lexan 141**	**Lexan HP3**	**Lexan SP1310**
Material note	Transparent	Transparent, medical grade	Transparent, random copolymer	Transparent	Transparent, medical grade	Transparent, random copolymer
Residuals (ppm)						
Residuals determined	Ethylene chlorohydrin			Ethylene glycol		
336-h aeration	<3			<25	<21	<23

Note: (1) Preexposure conditioning: vacuum 660–711 mmHg, 45–60% RH, 15 min. (2) Sterilization conditions: 8 h, 51.7 °C, 100% EtO. (3) Postexposure conditioning: aeration, with mechanical fan, 49 °C.

Table 5.35 Effect of Ethylene Oxide (EtO) Sterilization, 5-h Exposure, on Residuals for Sabic Lexan Polycarbonate after Aeration with Fan Post-exposure Conditioning[5]

	Residuals (ppm)					
Residuals Determined	**Ethylene Oxide**	**Ethylene Chlorohydrin**	**Ethylene Glycol**	**Ethylene Oxide**	**Ethylene Chlorohydrin**	**Ethylene Glycol**
24-h aeration	245	ND	21	177	ND	30
168-h aeration	78	–	–	54	–	–
336-h aeration	56	–	25	39	–	<4

Note: ND, none detected. (1) Preexposure conditioning: vacuum 660–711 mmHg, 45–60% RH, 15 min. (2) Sterilization conditions: 5 h, 100% EtO. (3) Postexposure conditioning: aeration, with mechanical fan, 49 °C.

Table 5.36 Effect of Ethylene Oxide (EtO) Sterilization, 5-h Exposure, on Sabic Lexan Polycarbonate after Ambient Aeration Postexposure Conditioning[5]

	Residuals (ppm)					
Residuals Determined	**Ethylene Oxide**	**Ethylene Chlorohydrin**	**Ethylene Glycol**	**Ethylene Oxide**	**Ethylene Chlorohydrin**	**Ethylene Glycol**
24-h aeration	332	ND	71	360	ND	76
168-h aeration	177	–	–	128	–	–
336-h aeration	49	–	33	111	–	31

Note: ND, none detected.

Table 5.37 The Effect of Ethylene Oxide Sterilization on the Properties of Polycarbonate[26]

Carrier Gas	Sterilization	Postexposure Time	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Instrumented Dart Impact Peak Energy (J)	Izod (J/m)
Control	Unexposed		62	145	2320	95	2520	75	822
Average standard deviation (%)			1	9	5	3	9	6	7
HCFC-124	One cycle	1 Week	62	142	2250	95	2450	75	769
		8 Weeks	61	145	2270	100	2600	73	785
	Three cycles	1 Week	62	137	2280	98	2560	68	779
		8 Weeks	62	125	2250	100	2590	68	790
Average standard deviation (%)			1	11	5	2	9	12	7
HCFC-124/22	One cycle	1 Week	62	142	2280	96	2500	77	763
		8 Weeks	62	131	2300	95	2520	68	833
	Three cycles	1 Week	62	137	2310	98	2540	70	790
		8 Weeks	63	148	2390	97	2590	69	795
Average standard deviation (%)			3	13	5	8	14	8	9
EtO	One cycle	1 Week	62	144	2300	98	2540	72	763
		8 Weeks	61	153	2190	94	2380	69	859
	Three cycles	1 Week	61	138	2280	100	2590	66	811
		8 Weeks	62	152	2230	93	2380	75	854

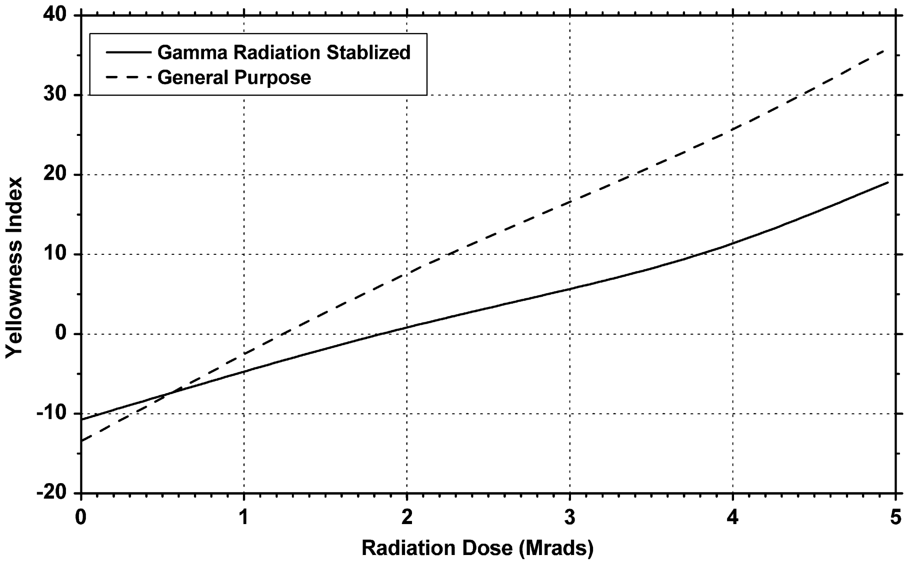


Figure 5.11 Gamma radiation dose versus yellowness index of polycarbonate.[13]

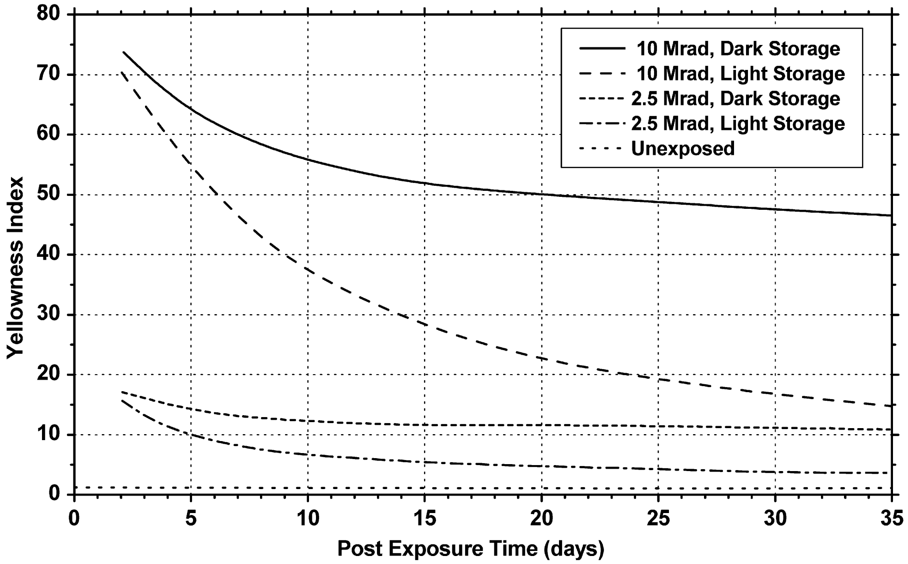


Figure 5.12 Post-gamma radiation exposure time versus yellowness index of Dow Calibre™ polycarbonate, 2.5 Mrad and 10 Mrad exposure, dark storage.[22]

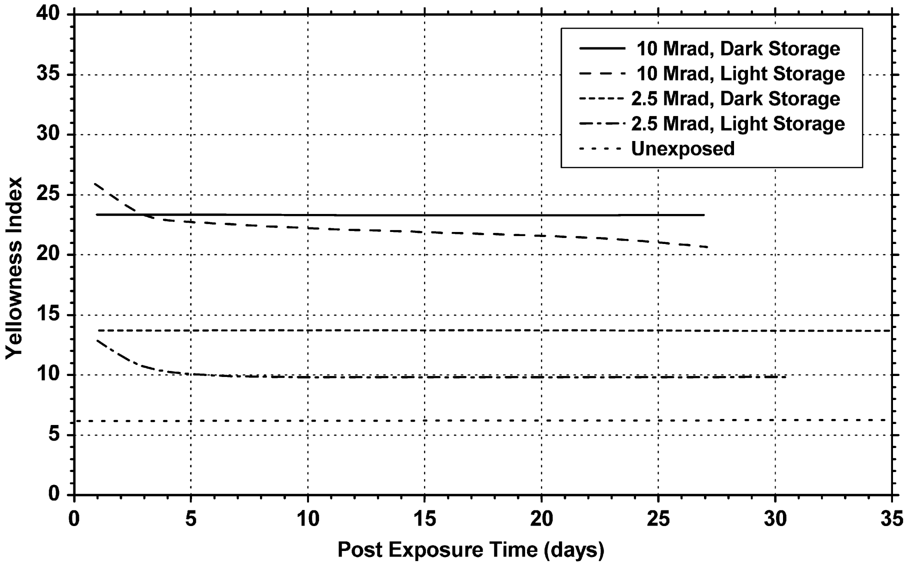


Figure 5.13 Post-gamma radiation exposure time versus yellowness index of Dow polycarbonate, 2.5 Mrad and 10 Mrad exposure, dark storage.[22]

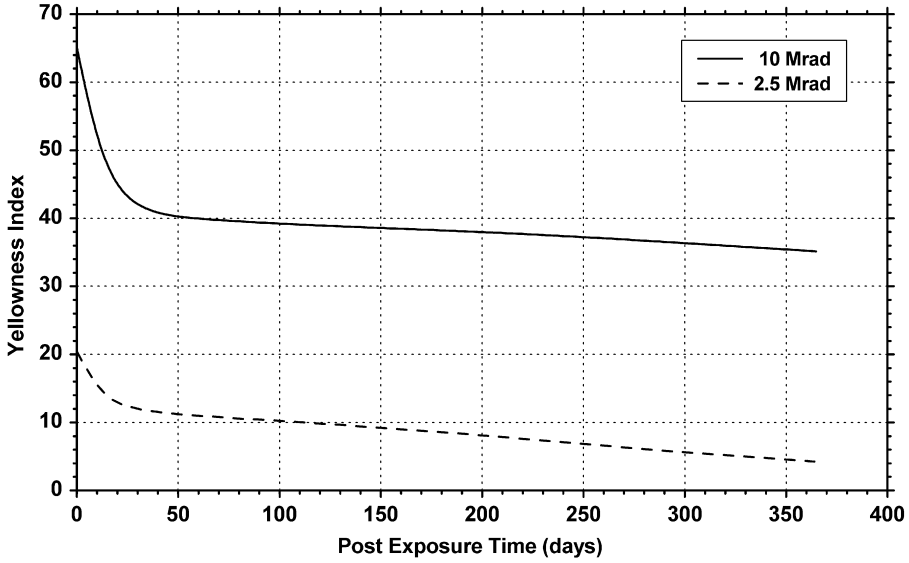


Figure 5.14 Post-gamma radiation exposure time versus yellowness index of Dow polycarbonate, 2.5 Mrad and 10 Mrad exposure.[12]

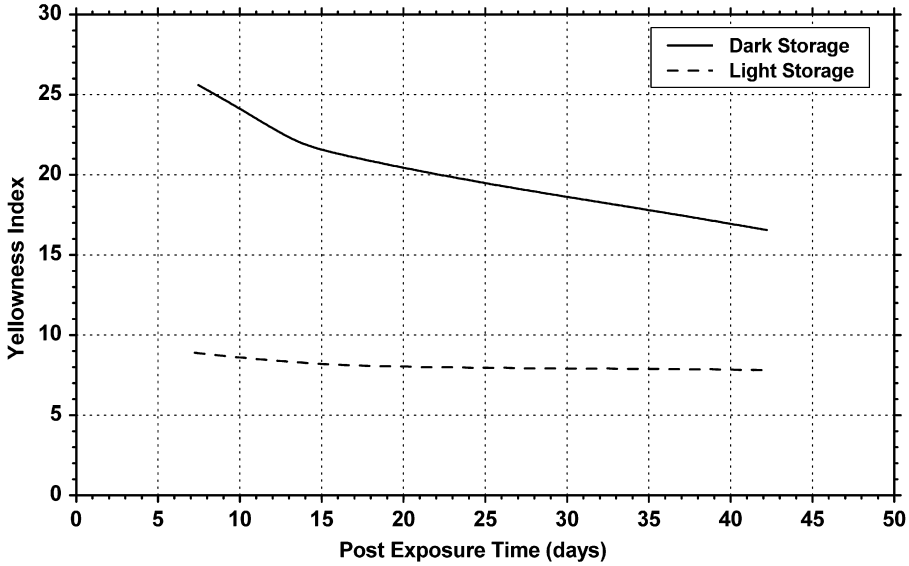


Figure 5.15 Post-gamma radiation exposure time versus yellowness index of Bayer Makrolon® polycarbonate, 3.5 Mrad exposure.[16]

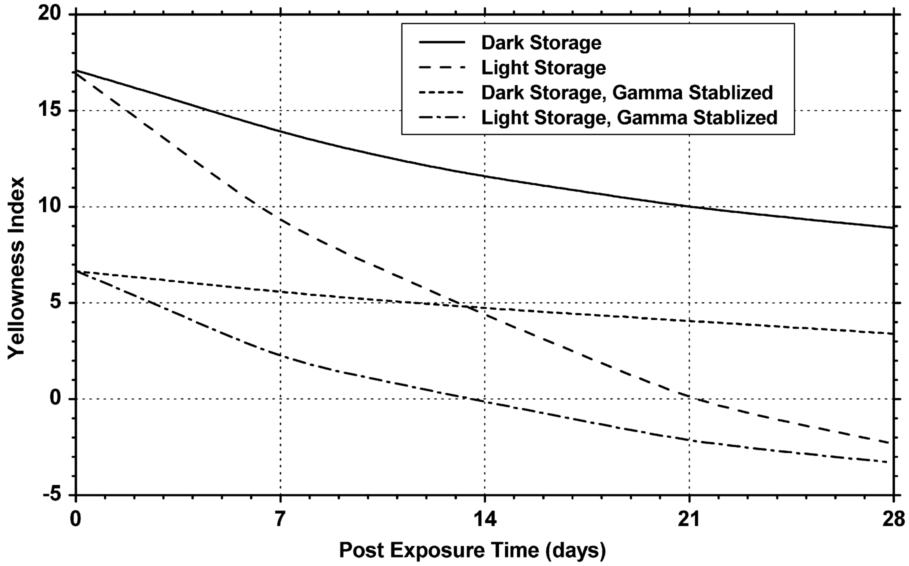


Figure 5.16 Post-gamma radiation exposure time versus yellowness index of polycarbonate, 3 Mrad exposure, light and dark storage.[13]

Figure 5.17 Post-gamma radiation exposure time versus yellowness index of polycarbonate, 5 Mrad exposure, light and dark storage.[13]

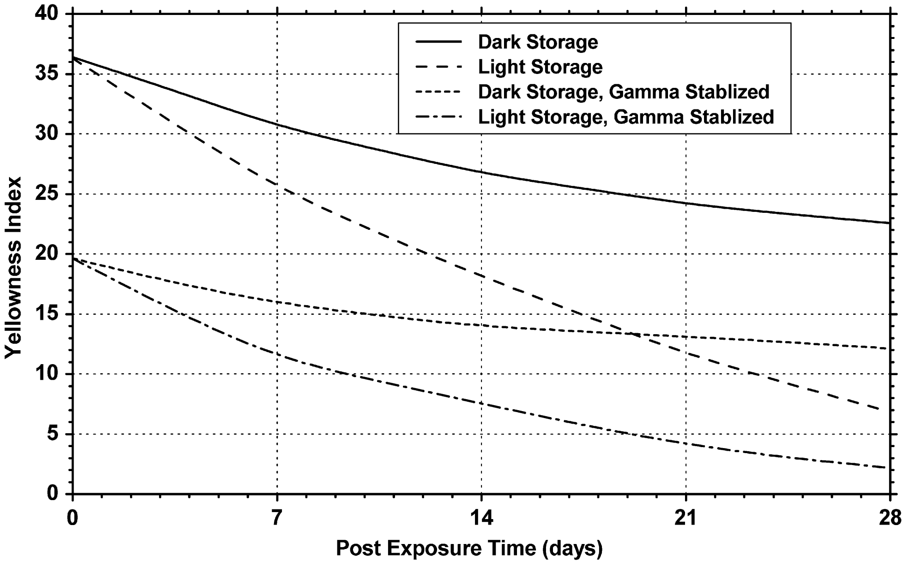


Figure 5.18 Post-gamma radiation exposure time versus percent light transmission of Dow polycarbonate, 2.5 Mrad and 10 Mrad exposure.[12]

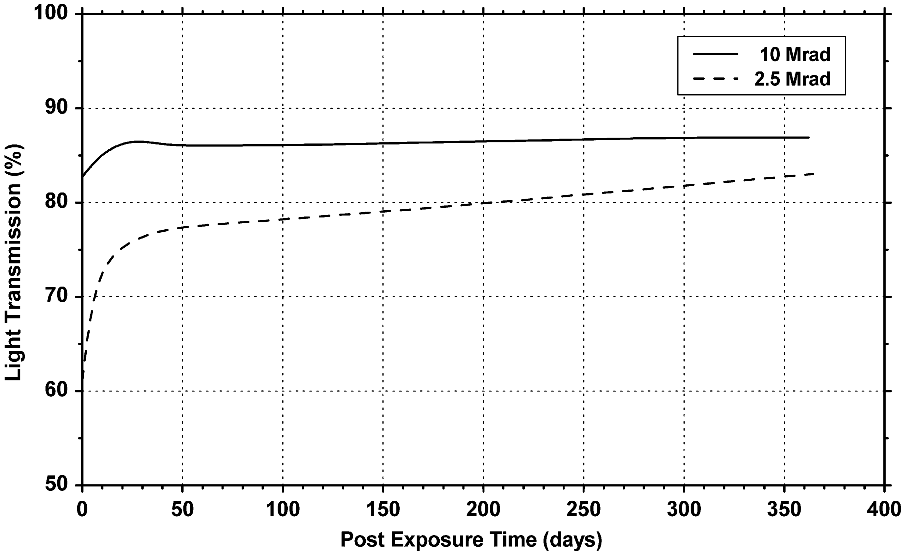
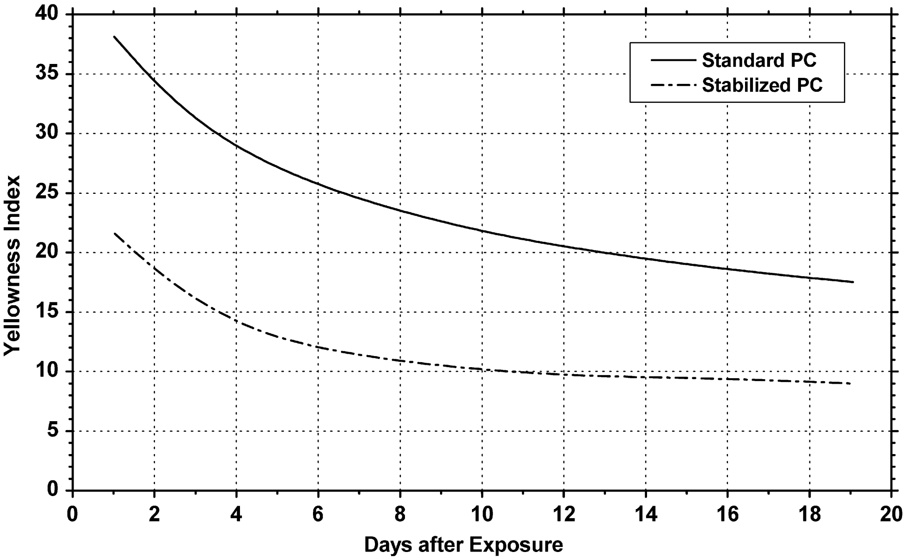


Figure 5.19 Comparison of standard and stabilized polycarbonate on the yellowness index of 100-mm-thick polycarbonate at 35 kGy dose of gamma radiation.[17]



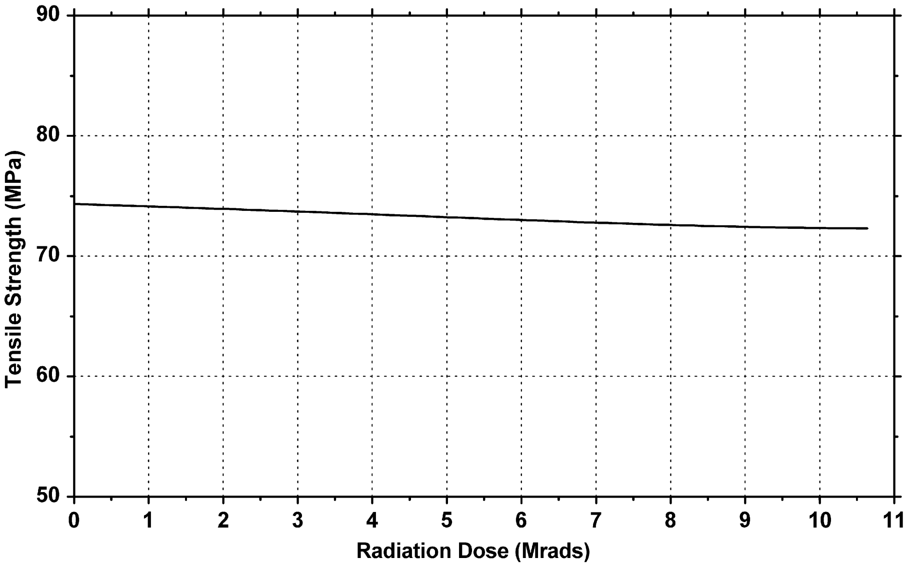


Figure 5.20 Beta radiation dose versus tensile strength of polycarbonate.[20]

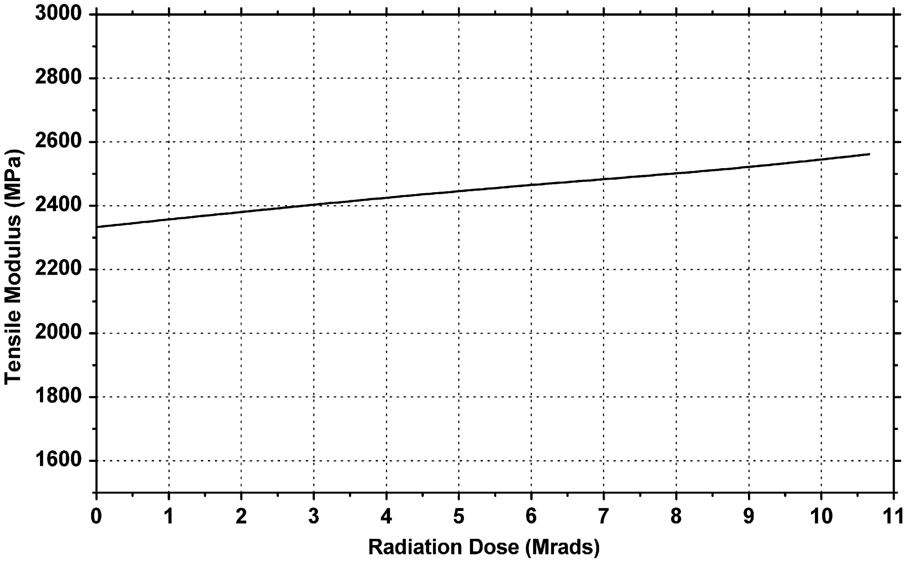


Figure 5.21 Beta radiation dose versus tensile modulus of polycarbonate.[20]

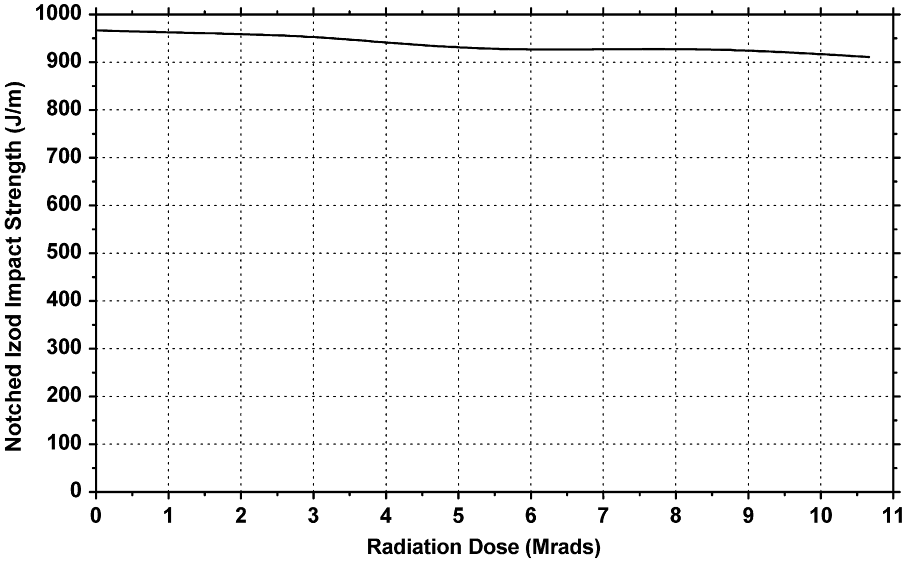


Figure 5.22 Beta radiation dose versus notched Izod impact strength of polycarbonate.[20]

Figure 5.23 Beta radiation dose versus yellowness index of polycarbonate.[20]

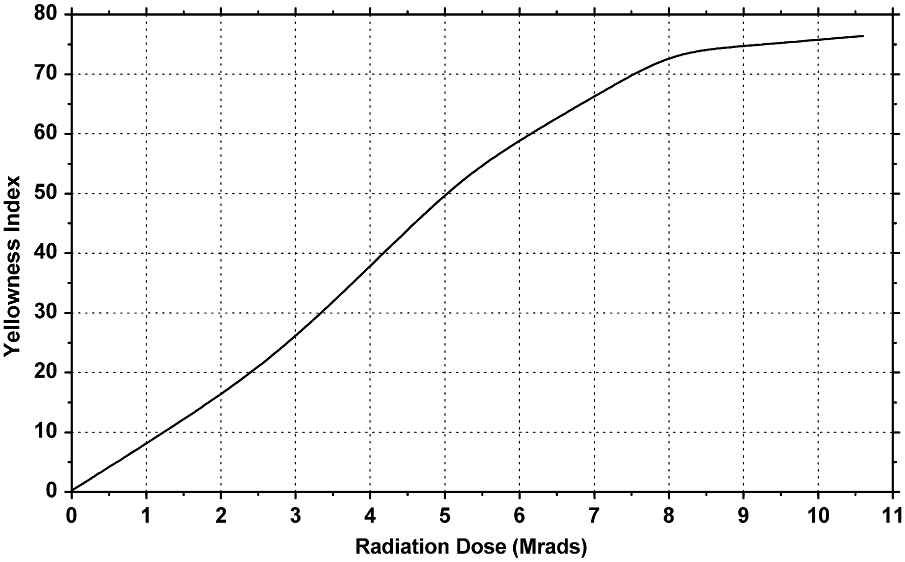


Figure 5.24 Post-beta radiation exposure time versus yellowness index of polycarbonate.[20]

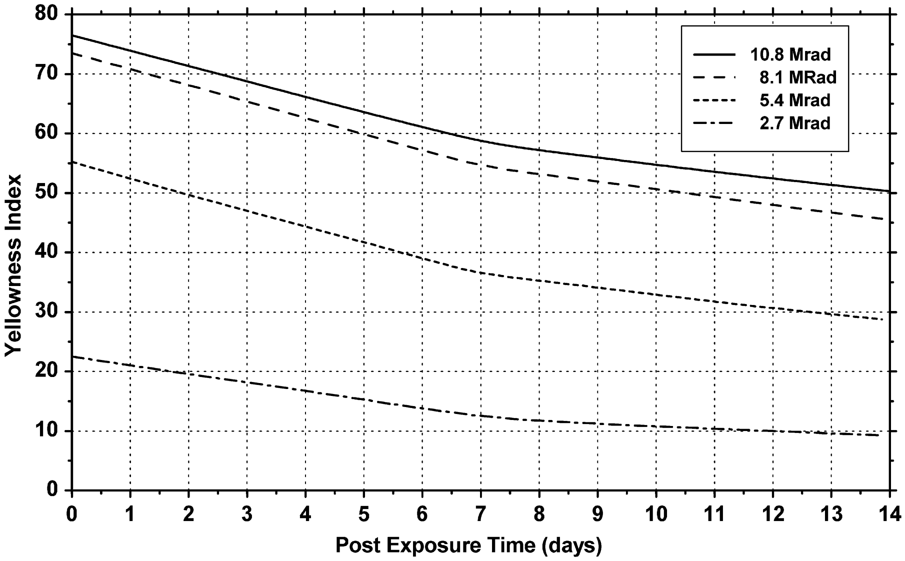
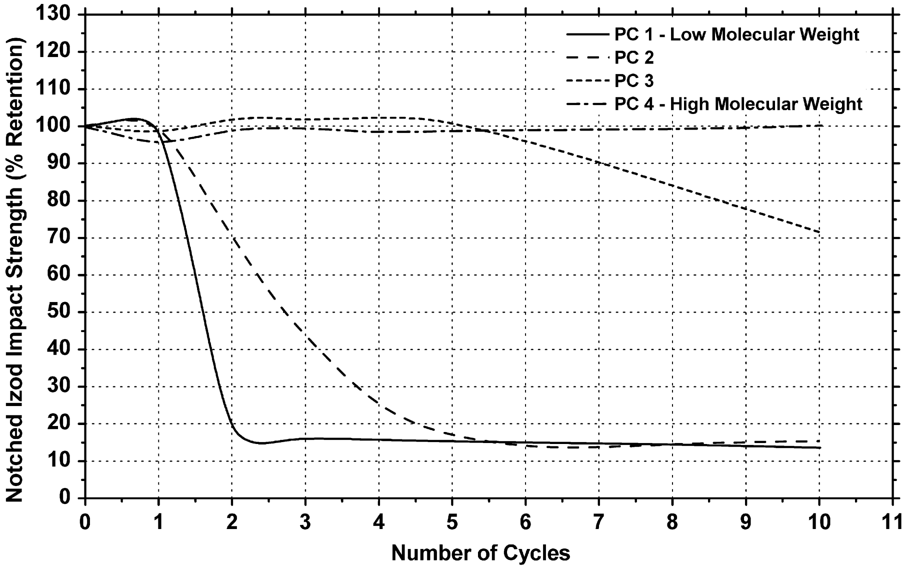


Figure 5.25 The effect of steam sterilization on the impact strength of polycarbonates.[17]



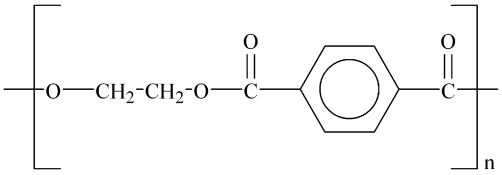


Figure 5.26 Chemical structure of polyethylene terephthalate polyester.

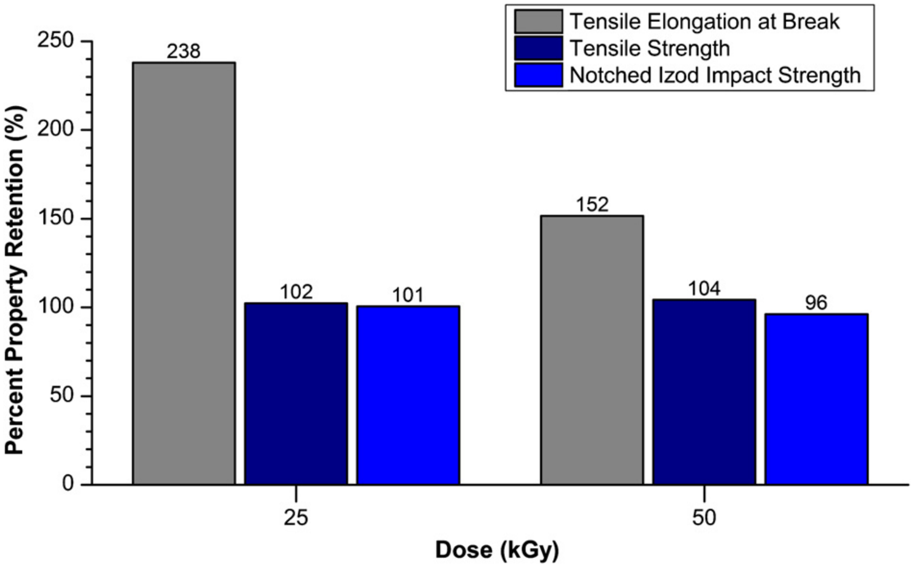


Figure 5.27 The effect of electron beam sterilization on the physical properties of polyethylene terephthalate.[17]

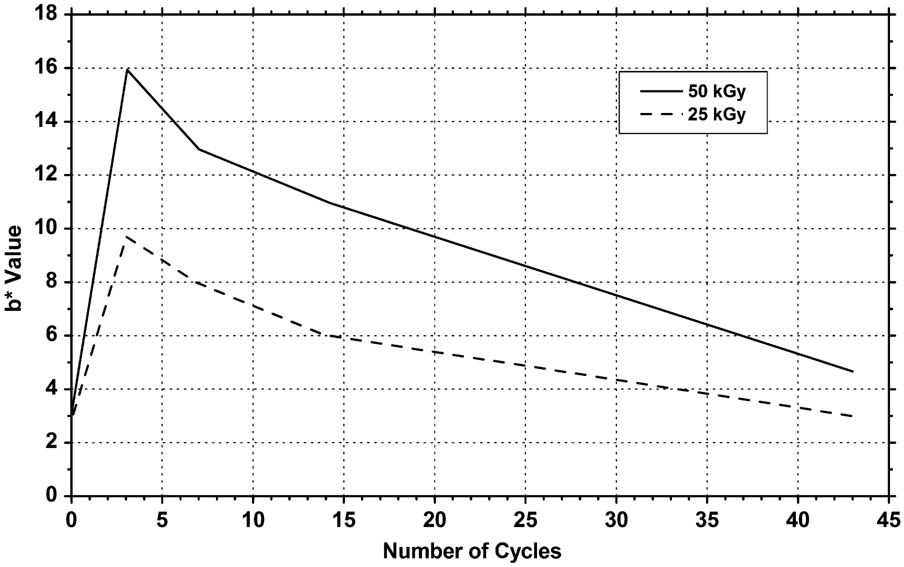


Figure 5.28 The effect of electron beam sterilization on the color of polyethylene terephthalate.[17]

Autoclave sterilization: Fabrics made from Eastman PCT polyesters have high hydrolytic stability and can tolerate both hot and moist environments making them ideal for laundry bags and hospital bed pads that need repeated autoclave sterilizations.[27]

5.6 Copolyesters

In addition to pure (homopolymer) PET, PET modified by copolymerization is also available. Copolyesters for medical and other applications are made from terephthalic acid or isophthalic polymerized with different ratios of ethylene glycol (EG) and

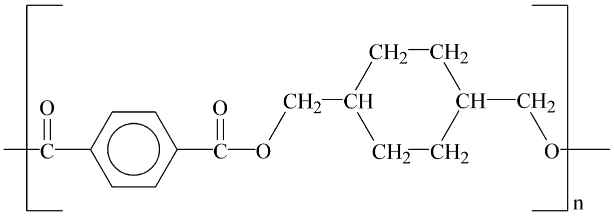


Figure 5.29 Chemical structure of polycyclohexylene-dimethylene terephthalate polyester.

1,4-cyclohexanedimethanol (CHDM). The structures of these monomers are shown in Fig. 5.30.

The three most common copolyesters are:

- Polyethylene Terephthalate Glycol-modified (PETG) made from TPA + EG + CHDM, but where EG content is greater than CHDM
- Poly Cyclohexylene dimethylene Terephtalate Glycol-modified (PCTG) made from TPA + CHDM + EG, but where CHDM content is greater than EG
- Polycyclohexylenedimethylene Terephthalate Alloy (PCTA) made from TPA + IPA (isophthalic acid) + CHDM.

Since CHDM is much larger (six additional carbon atoms) than the EG unit it replaces, it does not fit in with the neighboring polymer chains the way an EG unit would. This interferes with crystallinity and lowers the polymer's melting temperature. They yield properties such as excellent toughness and ductility, biocompatibility, clarity, sterilizability, chemical resistance, and solvent bondability. For example, Eastar Copolyester 6763 is a clear, amorphous PETG material. Because of its clarity, toughness, and good melt strength at processing temperatures, it is useful in a variety of processing techniques including film and sheet extrusion. Eastar Copolyester 6763 may be colored using color concentrates, dry colors, or liquid colorants.

Manufacturers: Eastman Chemical Eastar and SK Chemicals.

Sterile end uses: Blood therapy, drug delivery, Intravenous (IV) components, medical, surgical instruments, and packaging.

Suggested sterilization methods are:

Ethylene oxide (EtO) method: Efficiency is boosted by the use of moderately high temperature and humidity. Chamber gas can either be 100% EtO or 88% EtO/12% Freon. Typical cycle includes 18- to 24-h preconditioning [43 °C, 60% relative humidity (RH)], 8-h total cycle (with the average gas dwell of 3−4 h) all at 52 °C, and a 24-h aeration at 46−49 °C. Recommended sterilization conditions: minimize cycle time; maximum chamber temperature of 54 °C (maximum RH of 50%).

Gamma radiation method: These copolyesters are highly resistant to gamma radiation. Typical dose is 25−50 kGy (2.5−5 Mrad). Eastar™ Copolyester 6763 has been sterilized up to 95 kGy without any significant physical property loss.

E-beam radiation method: Typical dose is 25−50 kGy (2.5−5 Mrad). Eastar™ Copolyester 6763 has been sterilized up to 75 kGy without any significant physical property loss.

Chemical sterilization: PETG/PCTG is successfully sterilized by vapor hydrogen peroxide, and plasma without any significant changes in physical properties as long as proper processing conditions are used. If high humidity, high temperature, and/or long dwell times are used, increased physical aging will occur. This will cause brittleness in the package material and could lead to package integrity failure (Tables 5.38−5.44) (Figs 5.31−5.37).[28]

Figure 5.30 Monomers commonly used to make copolyesters.

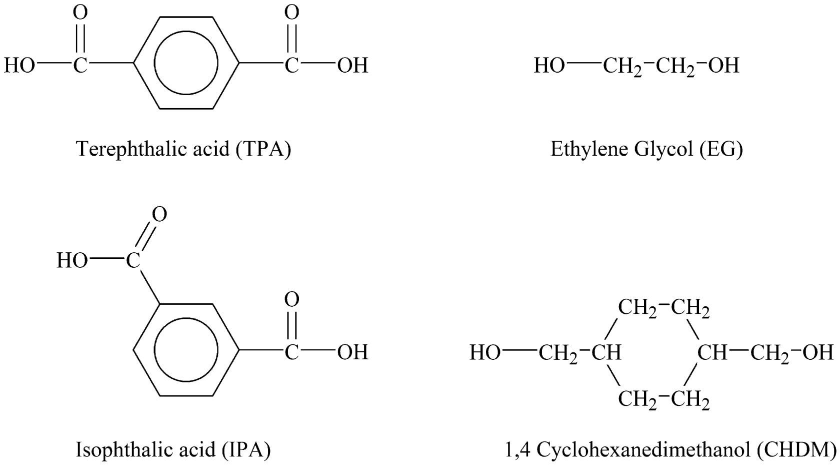


Table 5.38 Optical and Mechanical Properties of PETG Copolyesters before and after 50 kGy (5 Mrad) Gamma Sterilization[29]

Material Name	**MN058**		**MN100**		**MN005**	
Exposure Type	**Control**	**Exposed**	**Control**	**Exposed**	**Control**	**Exposed**
Radiation dose (Mrad)	–	5	–	5	–	5
Optical Properties						
Transmittance (%)	82	86	82	82	–	–
Yellowness index	1.0	3.2	−3.5	1.6	3.1	4.6
Mechanical Properties						
Elongation at break (%)	83	33	178	61	175	128
Notched Izod impact (J/m)	44	43	34	41	91	91

Table 5.39 Optical and Mechanical Properties of PCTG Copolyesters before and after 50 kGy (5 Mrad) Gamma Sterilization[29]

Material Name	**DN003**		**MC5100**	
Exposure type	**Control**	**Exposed**	**Control**	**Exposed**
Radiation dose (Mrad)	–	5	–	5
Optical Properties				
Transmittance (%)	9	86	89	–
Yellowness index	1.9	3.2	0.6	0.7
Mechanical Properties				
Elongation at break (%)	340	340	310	300
Notched Izod impact (J/m)	No break	No break	No break	No break

Table 5.40 Physical Properties before and after E-Beam Radiation of Eastman Specialty Plastics Copolyesters[19]

	E-beam Energy (Mrad)	**Eastar Polyester MN052**	**Eastar Copolyester MN211**	**Eastar Copolyester MN006**	**DuraStar Copolyester MN611**	**Eastalloy Copolyester/ PC Alloy DA003**
Tensile yield strength (MPa)	Unexposed	59	52	47	51	56
	25	61	52	47	51	56
	50	62	54	47	52	57
Tensile break strain (%)	Unexposed	117	71	312	271	150
	25	73	64	330	272	155
	50	99	38	340	288	139
Flatwise impact at 23 °C; total energy (J)	Unexposed	66	59	62	65	71
	25	63	57	62	66	74
	50	63	57	64	61	65

Table 5.41 *b** Color Measurements of Eastman Specialty Plastics and Competitive Resins after E-Beam Radiation at 50 kGy[19]

Days after E-beam Radiation	Eastar Polyester MN052	Eastar Copolyester MN211	Eastar Copolyester MN006	DuraStar Copolyester MN611	Eastalloy Copolyester/ PC Alloy DA003
Unexposed	2.8	0.3	0.4	0.0	-2.0
3	15.3	8.0	8.2	15.3	8.8
7	13.1	6.1	6.3	13.7	5.7
14	10.5	4.4	4.4	11.7	4.1
42	4.7	1.2	1.1	6.6	3.6

Table 5.42 Optical and Mechanical Properties of PETG Copolyesters before and after Ethylene Oxide (EtO) Sterilization[29]

Material Name	MN058		MN100	
Exposure Type	**Control**	**Exposed**	**Control**	**Exposed**
Optical Properties				
Transmittance (%)	83	83	81	82
Yellowness index	0.4	0.1	−2.7	−1.9
Mechanical Properties				
Elongation at break (%)	78	13	143	4.8
Notched Izod impact (J/m)	37	34	No break	No break

Table 5.43 Optical and Mechanical Properties of PCTG Copolyesters before and after Ethylene Oxide (EtO) Sterilization[29]

Material Name	DN003		MC500	
Exposure Type	**Control**	**Exposed**	**Control**	**Exposed**
Optical Properties				
Transmittance (%)	87	87		
Yellowness index	1.9	1.7	0.6	0.6
Mechanical Properties				
Elongation at break (%)	310	310	310	300
Notched Izod impact (J/m)	No break	No break	No break	No break

Table 5.44 Comparison of Selected Physical Properties of Sheets of Eastar PETG Copolyester 6763 before and after Low-Temperature Hydrogen Peroxide Gas Plasma Sterilization Process[30] (*aX26678-165-C, 25 mil thickness, produced at Eastman Chemical Co., ASP's Sterrad 100 SI GMP Sterilization System*)

Property (units)	Test Method	Control PETG 6763	PETG 6763 after LTHPGP
Haze (%)	ASTM D1003	92	94
Gloss at 45°, units	ASTM D2457/ D523	106	107
Gloss at 60°, units	ASTM D2457/ D523	161	161
Transparency (%)	ASTM D1746	80	81
Transmittance (%)	ASTM D1003	91	91
Tensile strength at yield, MD (MPa)	ASTM D882	49	50
Tensile strength at yield, TD (MPa)	ASTM D882	48	45
Tensile strength at break, MD (MPa)	ASTM D882	54	53
Tensile strength at yield, TD (MPa)	ASTM D882	48	45
Tensile strength at break, TD (MPa)	ASTM D882	52	51
Elongation at yield (%)	ASTM D882	4	4
Tensile modulus, MD, (MPa)	ASTM D882	1737	1674
Tensile modulus, TD, (MPa)	ASTM D882	1723	1741
Impact at 23 °C – maximum load (kN)	ASTM D3763	0.95	0.095
Impact at 23 °C – energy at maximum load (J)	ASTM D3763	7.3	7.
Impact at 23 °C – total energy (J)	ASTM D3763	8.7	8.4
Impact at −18 °C – maximum load (kN)	ASTM D3763	1.1	1.1
Impact at −18 °C – energy at maximum load (J)	ASTM D3763	7.3	7.8
Impact at −18 °C – total energy (J)	ASTM D3763	10.7	11.3
Color *L**	ASTM D2244	95.48	95.49
Color *a**	ASTM D2244	0.04	0.02
Color *b**	ASTM D2244	0.72	0.72
$Na_2S_2O_3$ residuals (ppm)	ASTM D2244	ND	279

Note: ND, none detected; MD, machine direction; TD, transverse direction.

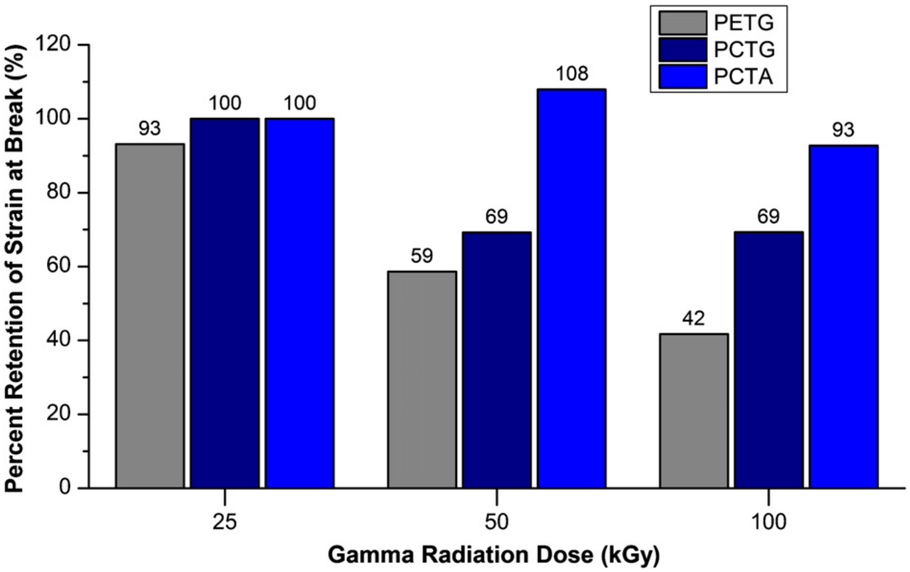


Figure 5.31 The effect of gamma sterilization on the retention of strain at break of three types of copolyesters after 1 day.[17]

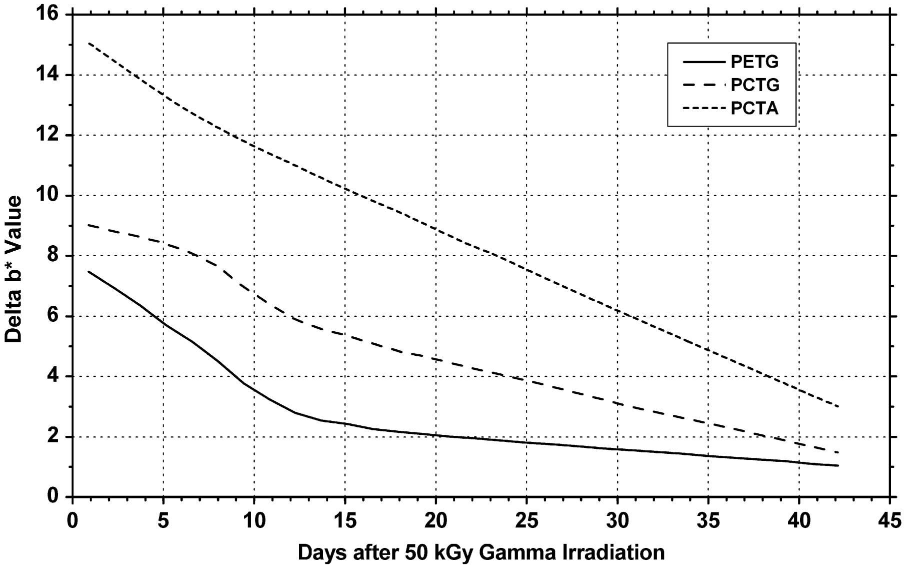


Figure 5.32 The effect of 50 kGy gamma sterilization on the color of three types of copolyesters.[17]

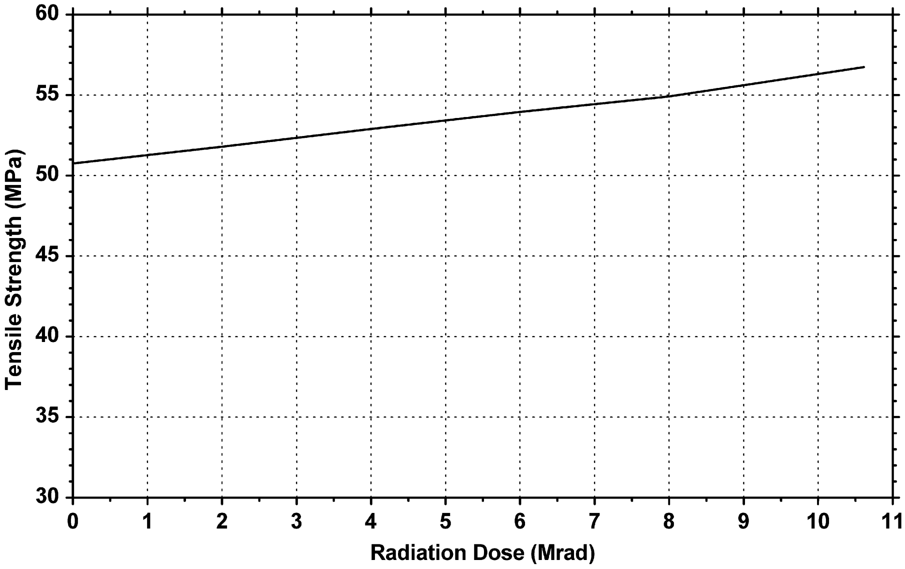


Figure 5.33 Beta radiation dose versus tensile strength of PETG.[20]

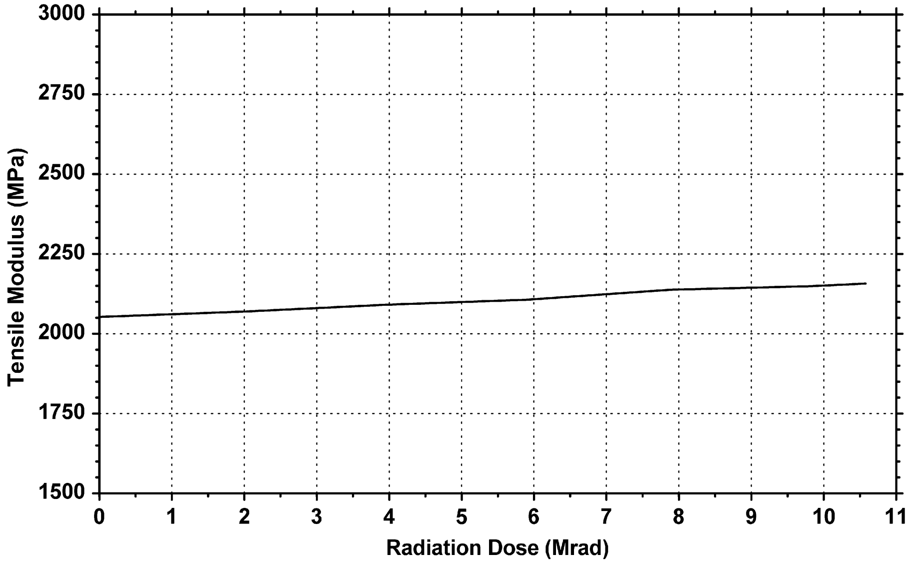


Figure 5.34 Beta radiation dose versus tensile modulus of PETG.[20]

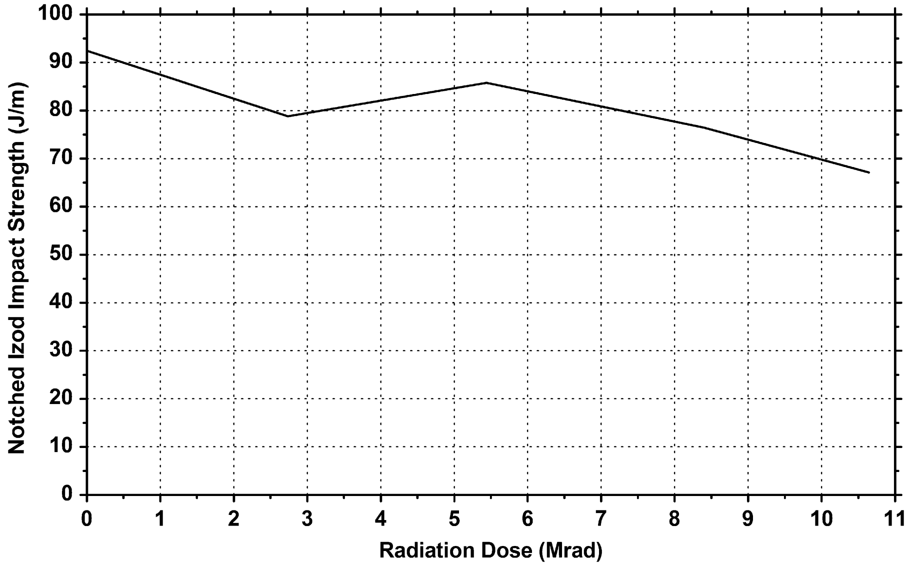


Figure 5.35 Beta radiation dose versus notched Izod impact strength of PETG.[20]

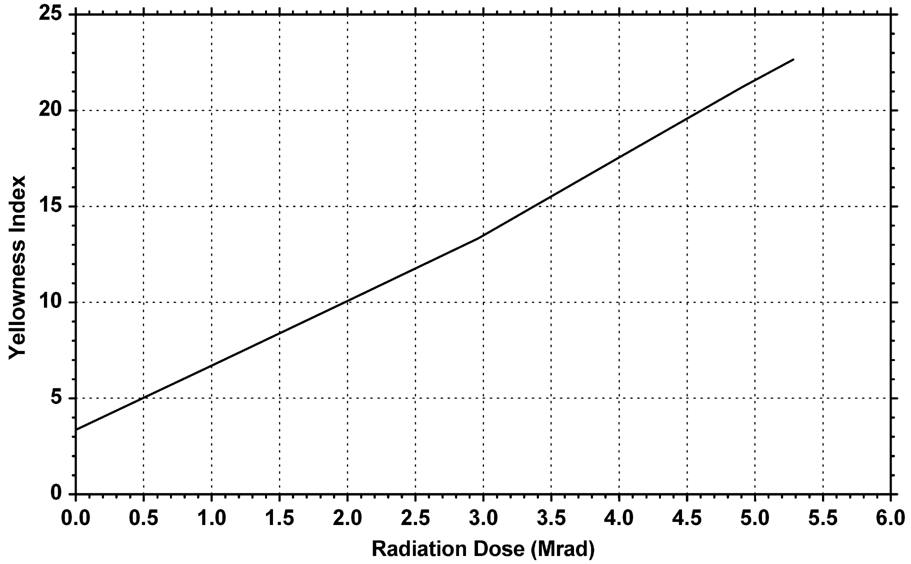
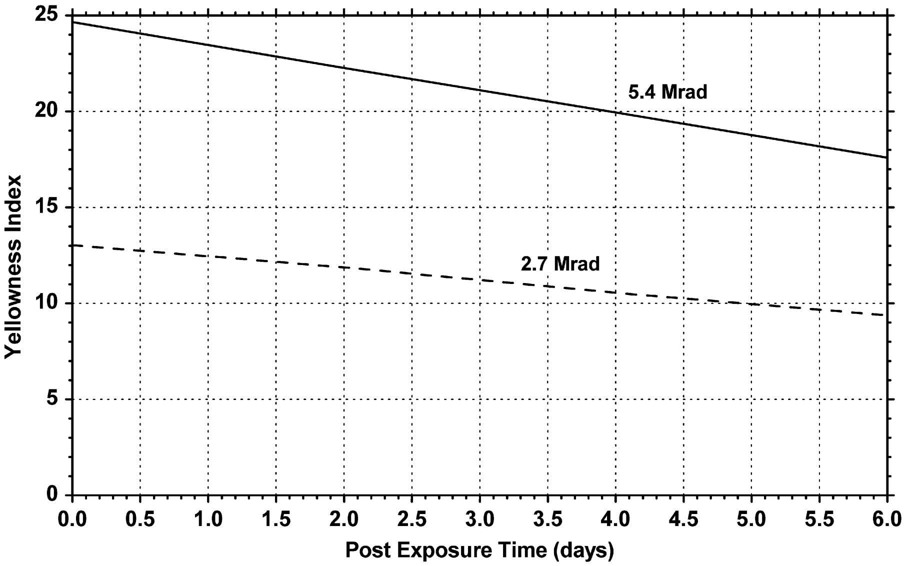


Figure 5.36 Beta radiation dose versus yellowness index of PETG.[20]

Figure 5.37 Post-beta radiation exposure time versus yellowness index of PETG.[20]



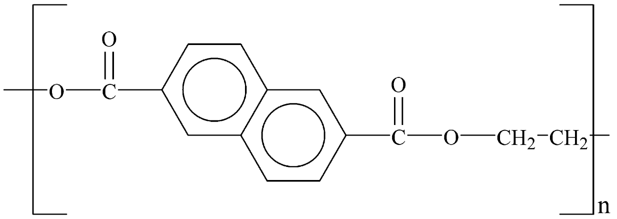


Figure 5.38 Structure of polyethylene napthalate.

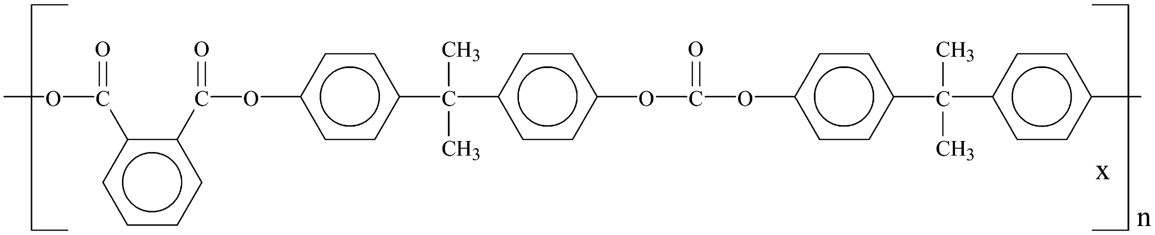


Figure 5.39 Chemical structure of polyphthalate carbonate polyester.

5.7 Polyethylene Naphthalate

Poly(ethylene 2,6-naphthalene dicarboxylate) (polyethylene naphthalate, PEN) is the condensation product of 2,6-naphthalene dicarboxylic acid and EG. PEN is similar to PET but has better temperature resistance. The CAS number for PEN is 25853-85-4. The structure of this polyester is shown in Fig. 5.38.

Manufacturers and trade names: DuPont™ Teijin Films TEONEX®, Eastman Eastar®, and Shell HiPertuf.

Applications and uses: Plastic beer bottles and baby food jars.

PEN withstands rigors of sterilization.[31]

Autoclave sterilization: Teonex® PEN retains more than 60% of its elongation at 200 h of autoclave exposure.

Ionizing radiation: PEN is known to have a very high resistance to ionizing radiation.

5.8 Polyphthalate Carbonate

Amorphous polyphthalate carbonate copolymer is another high-temperature polycarbonate. It provides excellent impact resistance, optical clarity, and abrasion resistance. The plastic offers ultraviolet protection as well. It is lightweight, impact-resistant, and can be reused after multiple exposures to sterilization. Its structure is shown in Fig. 5.39 (Tables 5.45–5.49).

Table 5.45 Polyphthalate Carbonate Retention of Physical Properties after 25 and 75 kGy Gamma Exposure[32]

Radiation Dose (kGy)	25	75
Flexural modulus	100	102
Flexural strength	99	98
Notched Izod	102	99
Tensile modulus	103	104
Tensile strength at yield	100	99
Tensile strength at break	102	98
Tensile elongation at yield	101	102
Tensile elongation at break	103	97

Table 5.46 Yellowness Index Shift after Gamma Irradiation for PPC[32] (0.125″ sample plaque)

	PPC	PPC + GS
Radiation Dose (kGy)	Δ Yellowness Index	
25	10	7
50	14	11
75	19	15

Note: PPC, polyphthalate carbonate; GS, gamma stabilizer additive.

Table 5.47 75 kGy Gamma Yellowness Index Shift after 8-Week Light/Dark Aging[32]

	PPC	PPC + GS
Posttreatment	Δ Yellowness Index	
Initial	19	16
8-week dark	17	15
8-week light	12	12

Note: PPC, polyphthalate carbonate; GS, gamma stabilizer additive.

Table 5.48 Yellowness Index Shift after E-Beam Irradiation for Polycarbonate and PPC Samples[32]

	PPC	PPC + GS
Radiation Dose (kGy)	Δ Yellowness Index	
20	12	7
40	19	11
60	120	13

Note: PPC, polyphthalate carbonate; GS, gamma stabilizer additive.

Table 5.49 75 kGy E-Beam Yellowness Index Shift after 8-Week Light/Dark Aging[32]

	PPC	PPC + GS
Posttreatment	Δ Yellowness Index	
Initial	21	13
8-week dark	15	12
8-week light	9	8

Note: PPC, polyphthalate carbonate; GS, gamma stabilizer additive.

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6 Polyimides

This chapter covers a series of plastics of which the imide group is an important part of the molecule. The imide group is formed by a condensation reaction of an aromatic anhydride group with an aromatic amine as shown in Fig. 6.1.

This group is very thermally stable. Aliphatic imides are possible, but the thermal stability is reduced, and thermal stability is one of the main reasons to use an imide-type polymer.

6.1 Polyamide-Imide

Polyamide-imides (PAIs) are thermoplastic amorphous polymers that have useful properties:

- Exceptional chemical resistance
- Outstanding mechanical strength
- Excellent thermal stability
- Performs from cryogenic up to 260 °C
- Excellent electrical properties.

The monomers used to make PAI resin are usually a diisocyanate and an acid anhydride such as those shown in Fig. 6.2.

When these two types of monomers are reacted, carbon dioxide is generated along with a PAI polymer. The closer the monomer ratio is to 1:1, the higher the molecular weight of the polymer shown in Fig. 6.3).

Manufacturers and trade names: Solvay Advanced Polymers Torlon®.

Sterile applications and uses: Surgical instruments and instrument components and parts that require tight tolerances and dimensional stability, micro-molded parts for cardiovascular repair procedures, and high-speed rotary microcomponents for pumps.

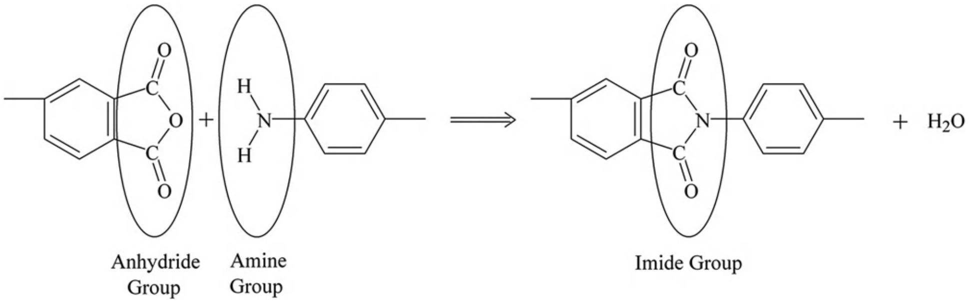


Figure 6.1 Reaction of amine with anhydride to form an imide.

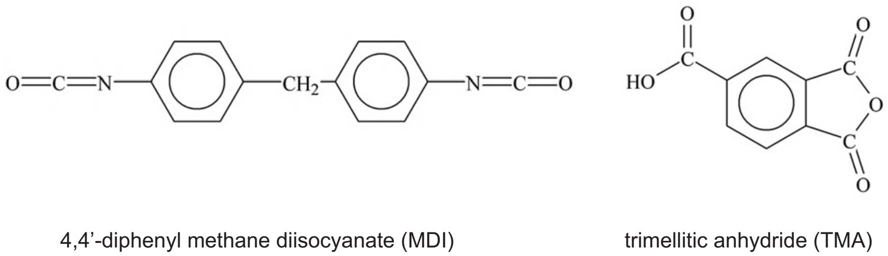


Figure 6.2 Chemical structures of monomer used to make polyamide-imides.

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00006-X

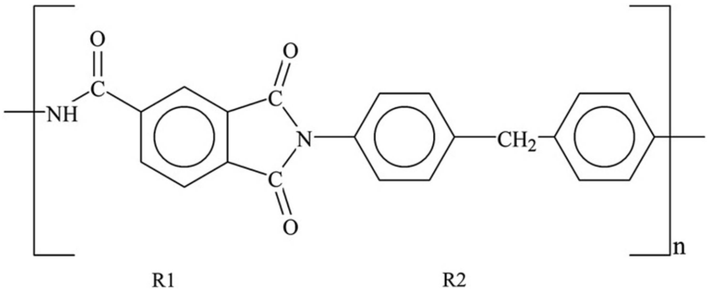


Figure 6.3 Chemical structure of a typical polyamide-imide.

PAIs are resistant to most dilute acids and bases and most organic solvents but strong bases will degrade the polymer. PAIs are capable of steam sterilization for up to 100 cycles. They can be sterilized by ethylene oxide, gamma, and electron beam (e-beam) radiation.

Data for PAI plastics are found in (Tables 6.1 and 6.2) and Fig. 6.4.

6.2 Polyetherimide

Polyetherimide (PEI) is an amorphous engineering thermoplastic. Thermoplastic PEIs provide the strength, heat resistance, and flame retardancy of traditional polyimides with the ease of simple melt processing seen in standard injection-molding resins like polycarbonate and acrylonitrile—butadiene—styrene.

The key performance features of PEI resins include:

- Excellent dimensional stability at high temperatures under load
- Smooth as-molded surfaces
- Transparency, though slightly yellow
- Good optical properties
- Very high strength and modulus
- High continuous use temperature
- Inherent ignition resistance without the use of additives
- Good electrical properties with low ion content.

There are several different polymers that are offered in various PEI plastics. The structures of these are shown in Figs 6.5—6.9 with references to one of the product lines that utilize that molecule. The CAS number is 61128-46-9.

The acid dianhydride used to make most of the PEIs is 4,4′-bisphenol A dianhydride (BPADA), the structure of which is shown in Fig. 6.10.

Some of the other monomers used in these PEIs are shown in Fig. 6.11.

Many products are called thermoplastic polyimides by their manufacturer. These can usually be classified as PEIs.

Manufacturers and trade names: Sabic Innovative Polymers Ultem®, DuPont™ Vespel® and Aurum®.

Sterile applications: Medical instrument trays, intravenous (IV) sets, pumps, pharmaceutical containers and accessories, medical, surgical, and dental instruments, surgical probes, pharmaceutical process equipment manifolds, stapler, tubing, and drug delivery equipment.

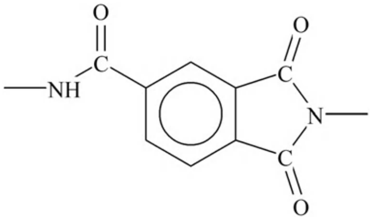
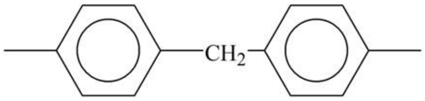
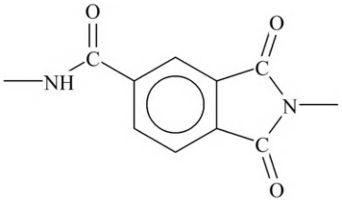
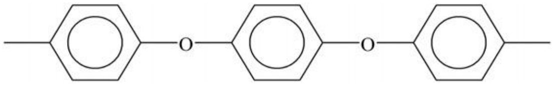
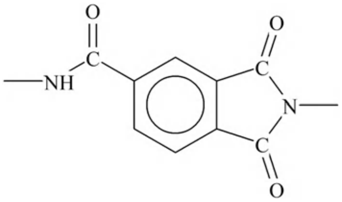
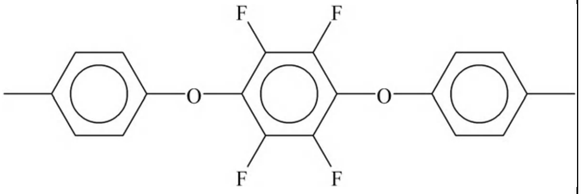
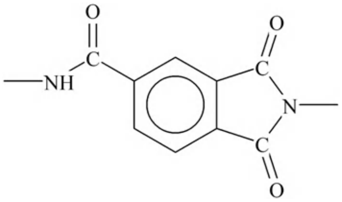
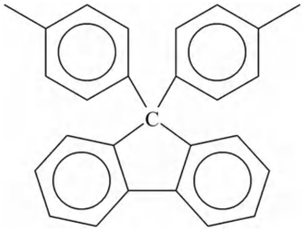
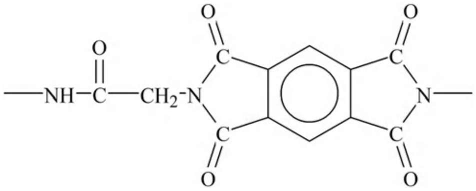
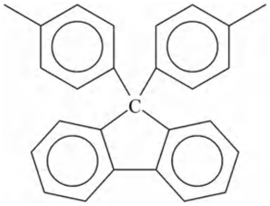
Gamma radiation resistance: Parts molded of Ultem® resin demonstrate resistance to gamma irradiation.

Ultem® 1000 and Ultem® HP retain their properties through 500 Mrad of gamma radiation.[4] A loss of less than 6% tensile strength was observed after cumulative exposure to 500 Mrad at the rate of 1 Mrad per hour using Cobalt-60.[3]

Ethylene oxide (EtO) resistance: Properties of Ultem® 1000 and Ultem® HP resins are unchanged after exposure to 100 EtO sterilization cycles.[4] After 100 EtO cycles, Ultem® 1000 resin retains 100% of its initial tensile strength and more that 75% of its initial tensile elongation. The appearance also remains unaffected.[11]

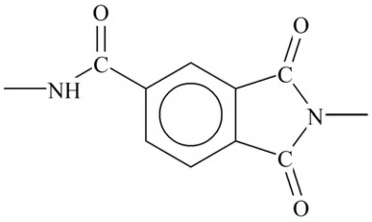
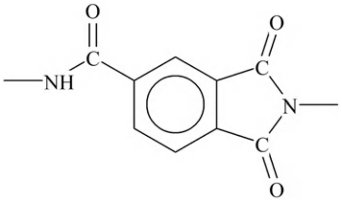
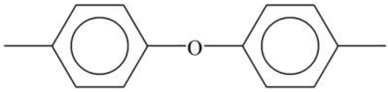
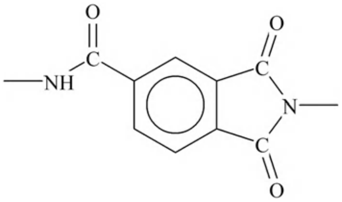
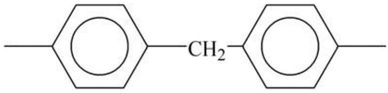
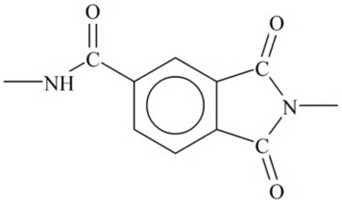
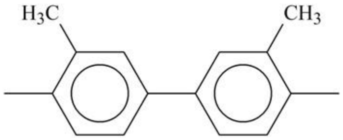
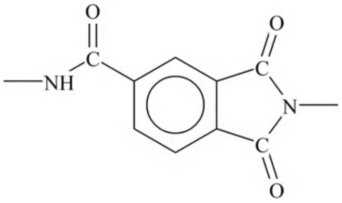
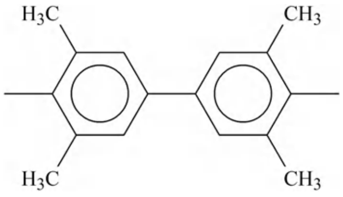
Steam resistance: Ultem® resin offers great property retention after repeated washing cycles and multiple sterilizations by autoclave.[5] Ultem® bars and disks retain tensile and yield strength properties through 2000 cycles. PEI trays show good resistance to crazing. After 500 cycles, no evidence of attack can be seen on the surface and small crazes are noted after 650 cycles. After 1500 cycles in 500 ppm

Table 6.1 The Polymer Units of Various Amide–Imide Polymers (refer to Fig. 6.3 for polymer structure)

PAI Code	R1 from Acid Anhydride	R2 from Diisocyanate
PAI (TMI/DPA)		
PAI (TMI/HEA)		
PAI (TMI/TFA)		
PAI (TMI/CDA)		
PAI (PMI/CDA)		

Note: PAI, polyamide-imide.

Table 6.2 The Polymer Units of Various Amide–Imide Polymers (refer to Fig. 6.3 for polymer structure)[1]

PAI Code	R1 from Acid Anhydride	R2 from Diisocyanate
PAP		
PAO		
PAM		
PAD		
PAT		

Note: PAI, polyamide-imide.

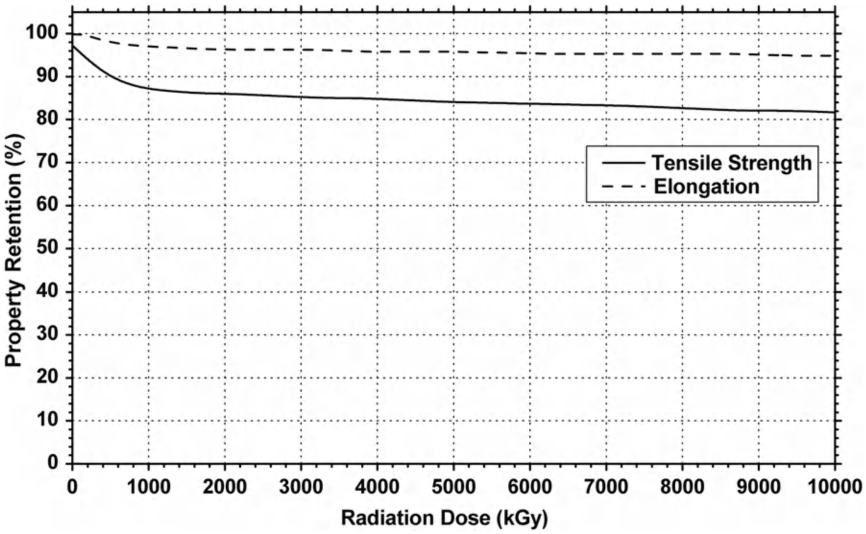


Figure 6.4 The effect of gamma radiation dose on the retention of properties of polyamide-imides.[2]

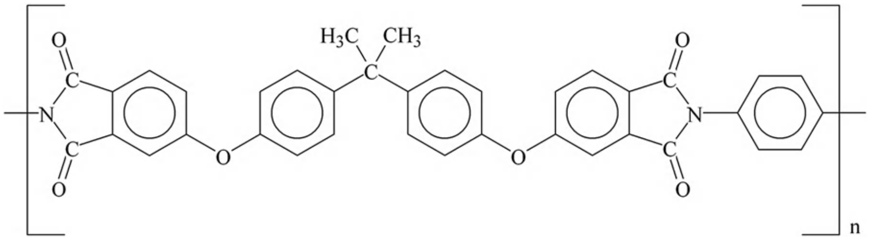


Figure 6.5 Chemical structure of BPADA-PPD polyetherimide (Ultem® 5000 series).

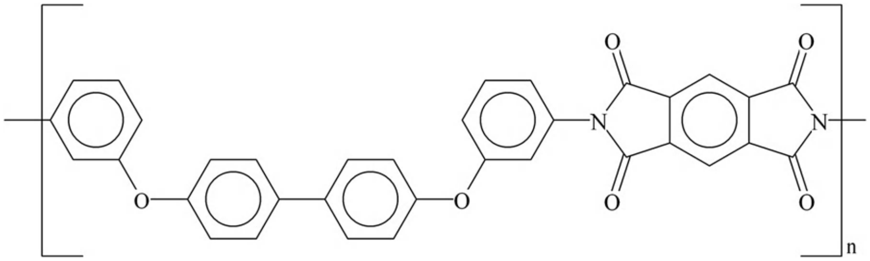


Figure 6.6 Chemical structure of bisphenol diamine PMDA polyetherimide (Aurum®, Vespel® TP-8000 series).

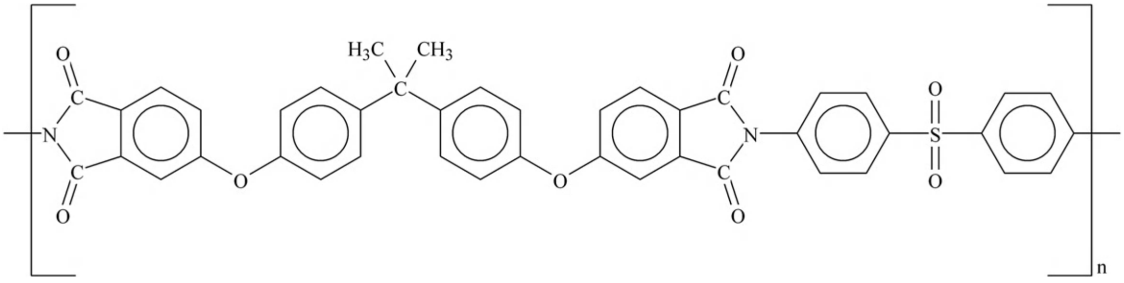


Figure 6.7 Chemical structure of BPADA-DDS polyetherimide sulfone (Ultem® XH6050).

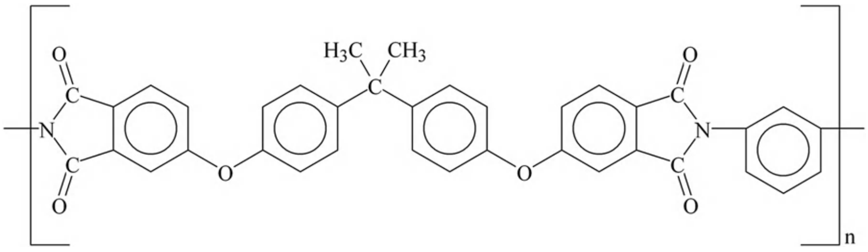


Figure 6.8 Chemical structure of BPADA-MPD polyetherimide (Ultem® 1000 series).

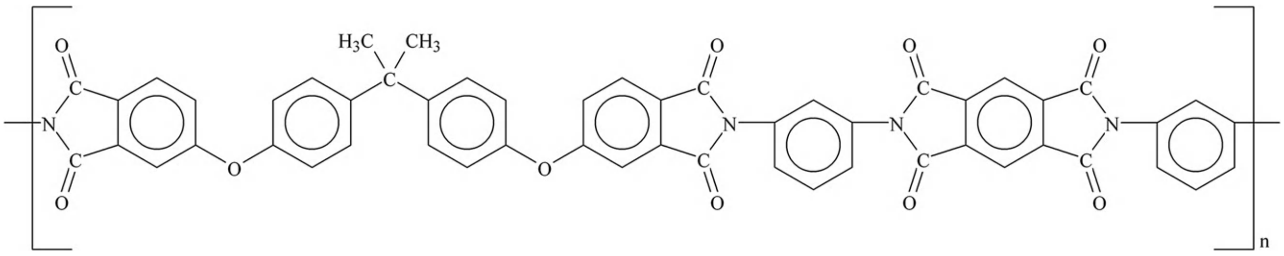


Figure 6.9 Chemical structure of BPADA-PMDA-MPD copolyetherimide (Ultem® 6000 Series).

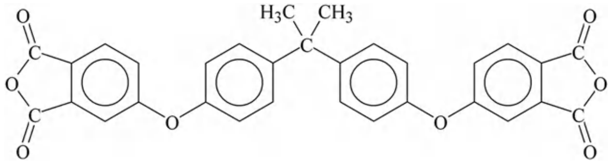


Figure 6.10 Chemical structure of 4,4′-bisphenol A dianhydride monomer.

morpholine steam autoclaving, the PEI trays remain serviceable with only a few crazes in very localized areas.[3]

Dry heat resistance: Ultem® HP resins can withstand 160 °C of dry heat sterilization.[6]

Regulatory status: Ultem® resins maintain full compliance with ISO 10993, FDA, and USP Class VI.[4]

Data for PAI plastics are found in Tables 6.3–6.9 and Figs 6.12–6.21.

6.3 Polyimide

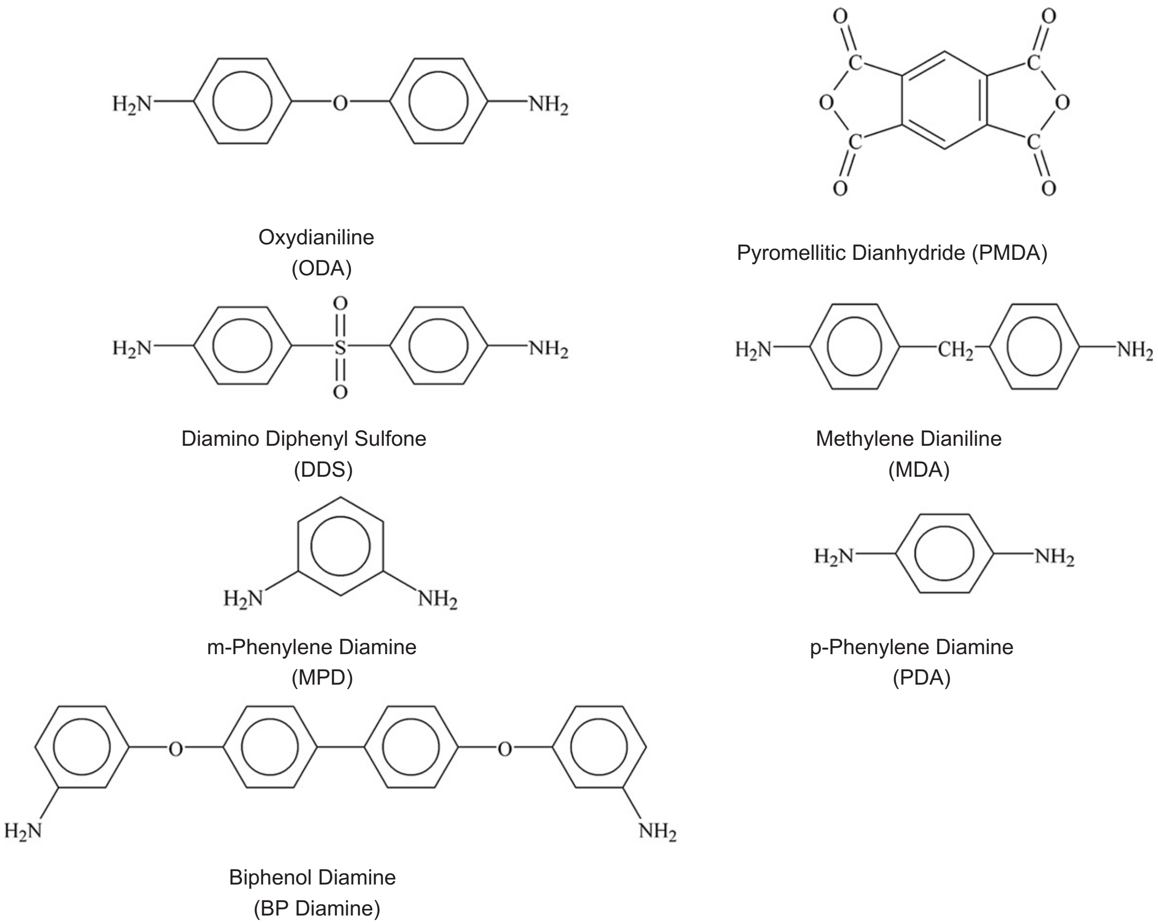
Polyimides (PIs) are high-temperature engineering polymers originally developed by the DuPont™ Company. Polyimides exhibit an exceptional combination of thermal stability (>500 °C), mechanical toughness, and chemical resistance. They have excellent dielectric properties and inherently low coefficient of thermal expansion. They are formed from diamines and dianhydrides such as those shown in Fig. 6.22.

Many other diamines and several other dianhydrides may be chosen to tailor the final properties of a polymer whose structure is like that shown in Fig. 6.23. The structures of two Ube Industries Upilex® polymers are shown in Fig. 6.24.

Polyimide thermoset plastic provides excellent mechanical, thermal, electrical, and chemical-resistant properties. Polyimide brings the following benefits to medical tubing: flexibility, high tensile strength, biocompatibility, low friction, transparency, tight tolerances, thin walls, smooth surface, pushability, and column strength. Polyimide is USP Class VI compliant and meets ISO 10993 biocompatibility requirements for a Class III device. Polyimide may be sterilized via gamma, EtO, and e-beam sterilization methods.

Manufacturers and trade names: DuPont™, Kapton®, and Ube Industries Upilex®.

Sterile applications: Thermoset polyimide tubing and coated wire is a highly versatile product, with a wide range of uses in high-performance medical devices. Typical medical applications include cardiovascular catheters, retrieval devices, push rings, marker bands, angioplasty, stent delivery devices, neurological devices, electrical insulator applications, and drug delivery systems.



Oxydianiline (ODA)

Pyromellitic Dianhydride (PMDA)

Diamino Diphenyl Sulfone (DDS)

Methylene Dianiline (MDA)

m-Phenylene Diamine (MPD)

p-Phenylene Diamine (PDA)

Biphenol Diamine (BP Diamine)

Figure 6.11 Chemical structures of other monomers used to make polyimides.

Table 6.3 Effect of Ethylene Oxide (EtO) Sterilization on Transparent Sabic Innovative Plastics Ultem® PEI[8]

Properties Retained (%)	
Tensile strength at yield	107
Elongation at yield	109
Tensile modulus	95

Note: (1) Preexposure conditioning: vacuum; 660−711 mmHg; 45−60% RH; 15 min. (2) Sterilization conditions: five cycles, 54.5 °C, 100% EtO.

Table 6.4 Effect of Ethylene Oxide (EtO) Sterilization Residuals on Sabic Innovative Plastics Ultem® PEI, after Aeration at Ambient Conditions[9]

Material Name	Sabic Innovative Plastics Ultem® 1100	Sabic Innovative Plastics Ultem® 1000	Sabic Innovative Plastics Ultem® 5011	Sabic Innovative Plastics Ultem® 5001
Material note	Transparent, pigmented	Transparent, natural resin, amber tint	Chemical resistance	Chemical resistance
Residuals (ppm)				
Ethylene chlorohydrin	<3	<3	<3	<3
Ethylene glycol	<21	<19	<19	<16

Note: (1) Preexposure conditioning: vacuum; 660−711 mmHg; 45−60% RH; 15 min. (2) Sterilization conditions: 8 h, 51.7 °C 100% EtO. (3) Postexposure conditioning: 336-h aeration; ambient conditions, 23 °C.

Table 6.5 Effect of Ethylene Oxide (EtO) Sterilization Residuals on Sabic Innovative Plastics Ultem® PEI, after Aeration with Fan[9]

Material Name	Sabic Innovative Plastics Ultem® 1100	Sabic Innovative Plastics Ultem® 1000	Sabic Innovative Plastics Ultem® 5011	Sabic Innovative Plastics Ultem® 5001
Material note	Transparent, pigmented	Transparent, natural resin, amber tint	Chemical resistance	Chemical resistance
Residuals (ppm)				
Ethylene chlorohydrin	<3	<3	<2	<3
Ethylene glycol	<18	<22	<15	<20

Note: (1) Preexposure conditioning: vacuum; 660−711 mmHg; 45−60% RH; 15 min. (2) Sterilization conditions: 8 h, 51.7 °C 100% EtO. (3) Postexposure conditioning: 336-h aeration with mechanical fan, 49 °C.

Table 6.6 Effect of Ethylene Oxide (EtO) Sterilization Residuals on Sabic Innovative Plastics Ultem® 1000 PEI, after Aeration with Fan[10]

Residuals Determined	Ethylene Oxide	Ethylene Chlorohydrin	Ethylene Glycol	Ethylene Oxide	Ethylene Chlorohydrin	Ethylene Glycol
24-h aeration	58	<1	34	111	<1	41
168-h aeration	34	−	−	59	−	−
336-h aeration	22	−	19	48	−	22

Note: (1) Preexposure conditioning: vacuum; 660−711 mmHg; 45−60% RH; 15 min. (2) Sterilization conditions: 5 h, 100% EtO. (3) Postexposure conditioning: aeration with mechanical fan, 49 °C.

Table 6.7 Effect of Steam Sterilization on Sabic Innovative Plastics Ultem® 1000 PEI[11]

Details	No Boiler Additive				50 ppm Morpholine in Feed Water			
Number of cycles	100	500	1000	1500	100	500	1000	1500
Properties Retained (%)								
Elongation at yield	53	50	41.7	28.3	21.7	28.3	16.7	25

Note: (1) Preexposure conditioning: dry time, 4 min. (2) Sterilization conditions: 5 min, 132 °C. (3) Postexposure vacuum, 9 min.

Table 6.8 Effect of Steam Sterilization on Sabic Innovative Plastics Ultem® 1100F PEI[11]

Details	No Boiler Additive				50 ppm Morpholine in Feed Water			
Number of cycles	100	500	1000	1500	100	500	1000	1500
Properties Retained (%)								
Elongation at yield	27.5	25	25	17.5	20	20	25	22.5

Note: (1) Preexposure conditioning: dry time, 4 min. (2) Sterilization conditions: 5 min, 132 °C. (3) Postexposure vacuum, 9 min.

Table 6.9 Effect of Low-Temperature Hydrogen Peroxide Gas Plasma (STERRAD® NX) Sterilization on Sabic Innovative Plastics Ultem® HU1004 PEI[14]

	Tensile Strength	Mass	Elongation	Dynatup Impact
Cycles	MPa	g	%	J
0	89	11.42	97	92
130	87	11.42	92	91
300	77	11.38	74	84

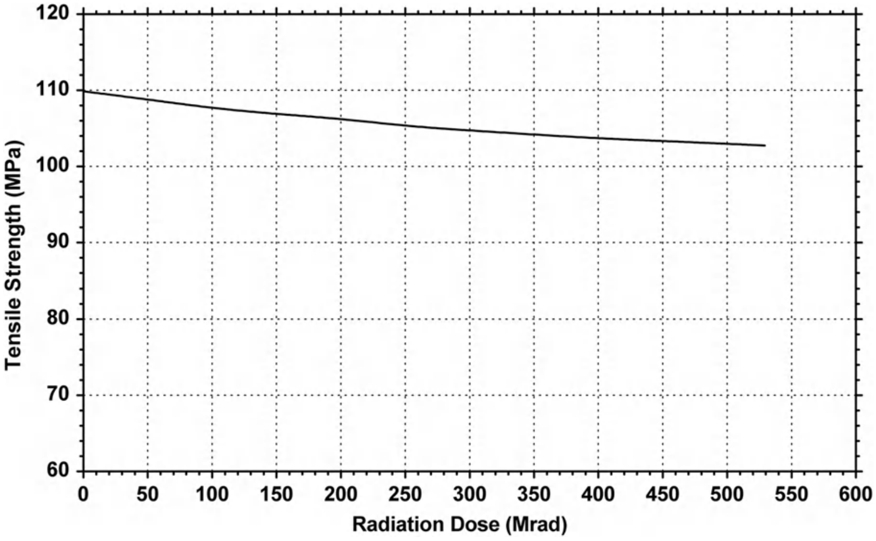


Figure 6.12 Gamma radiation dose versus tensile strength of Sabic Innovative Plastics Ultem® 1000 PEI.[7]

Figure 6.13 Gamma radiation dose versus elongation at break of Sabic Innovative Plastics Ultem® 1000 PEI.[7]

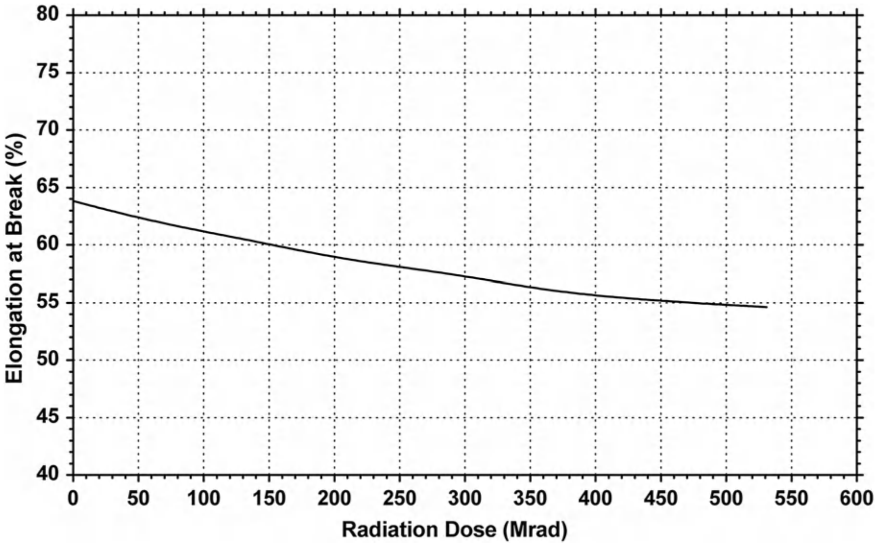


Figure 6.14 Gamma radiation dose versus elongation at yield of Sabic Innovative Plastics Ultem® 1000 PEI.[7]

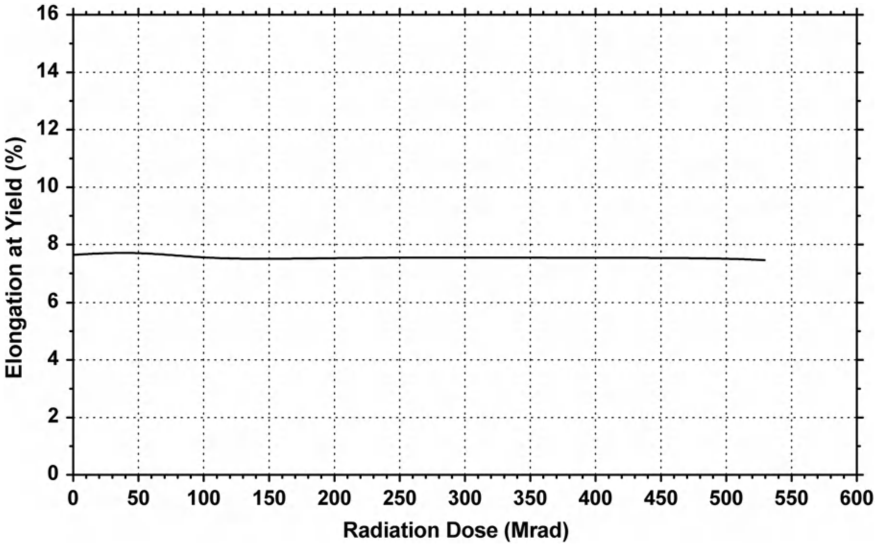
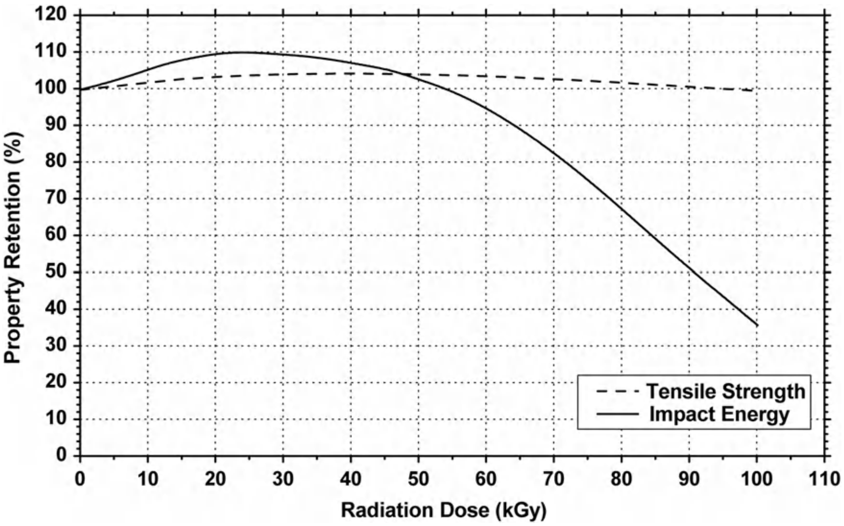


Figure 6.15 The effect of gamma sterilization on the property retention of polyetherimides.[2]



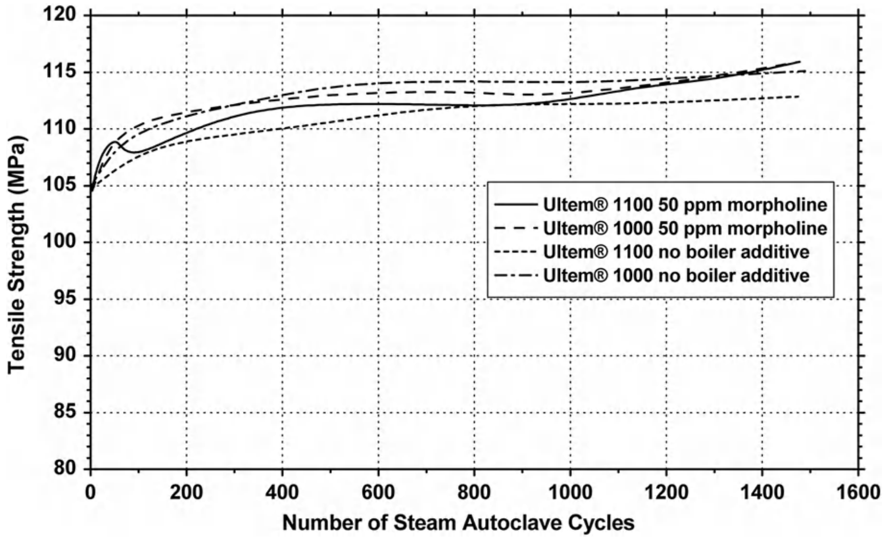


Figure 6.16 Number of steam sterilization cycles versus tensile strength of Sabic Innovative Plastics Ultem® 1000 PEI.[3]

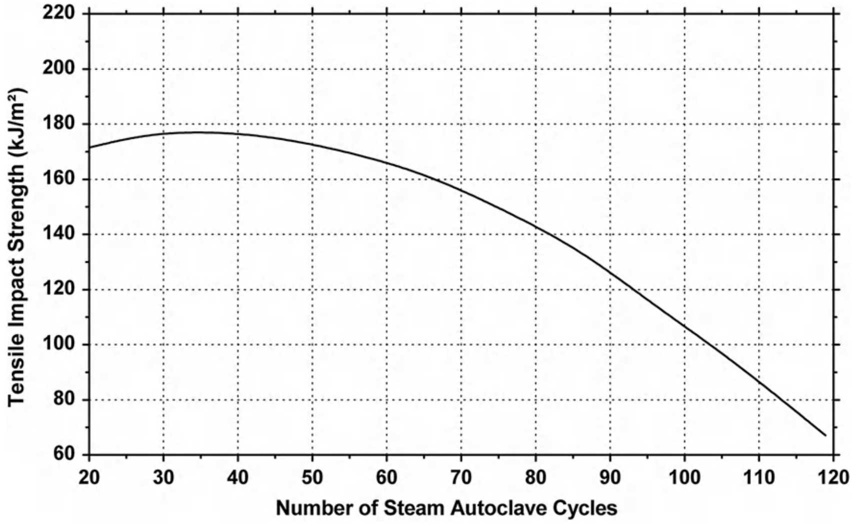


Figure 6.17 Number of steam sterilization cycles versus tensile impact strength of polyetherimides.[12]

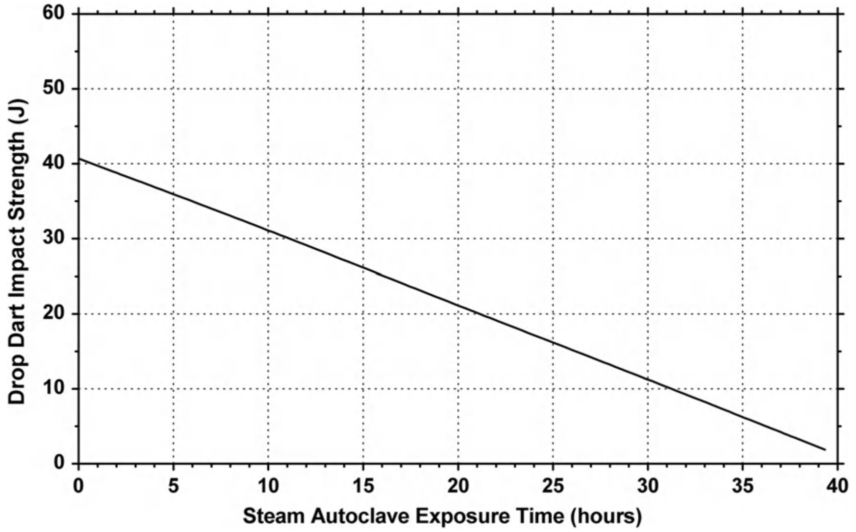


Figure 6.18 Number of steam sterilization cycles versus dart impact strength of polyetherimides.[13]

Figure 6.19 Steam sterilization property retention of polyetherimides.[2]

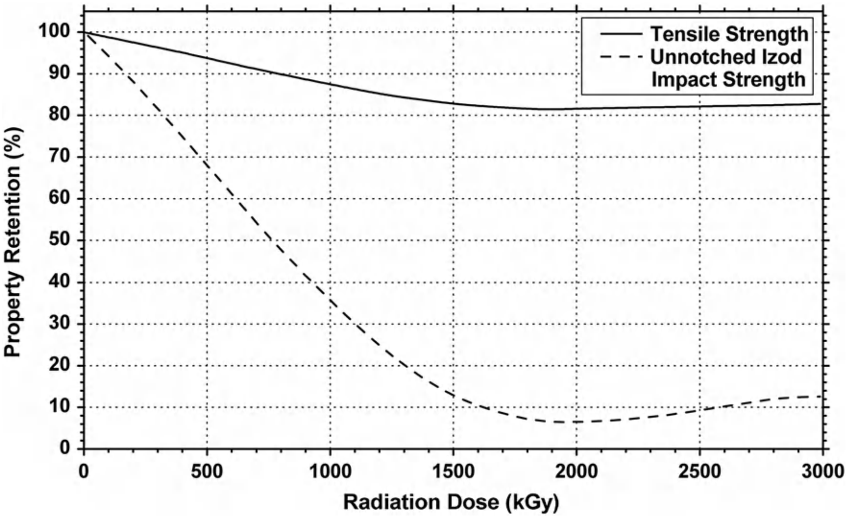


Figure 6.20 High-speed impact (Dynatup) after 134 °C autoclave cycles with 50 ppm Morpholine of Sabic Ultem® HU1004 PEI.[14]

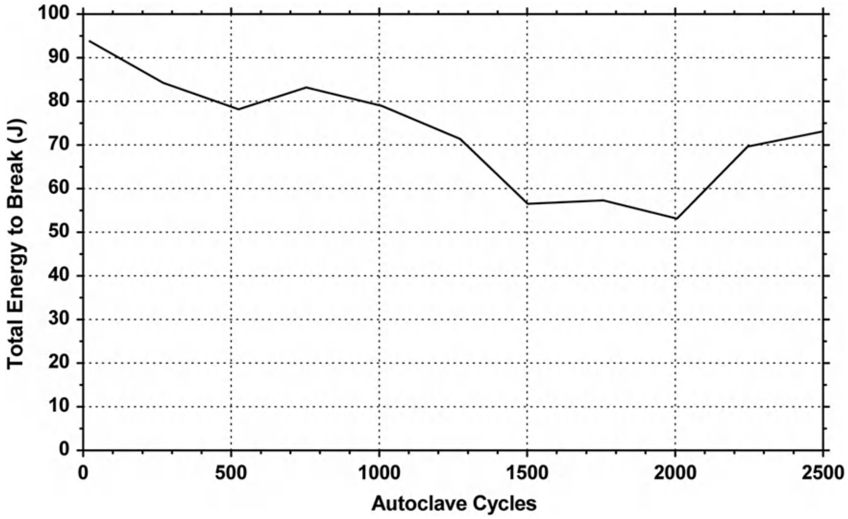
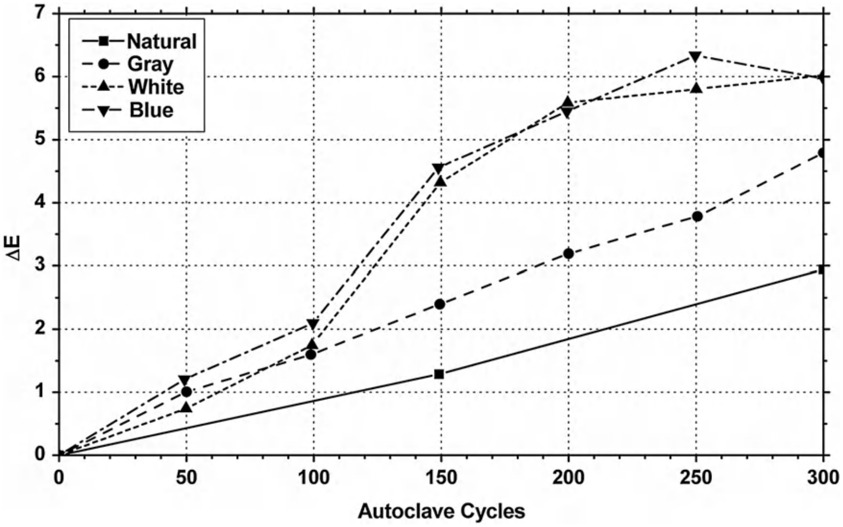
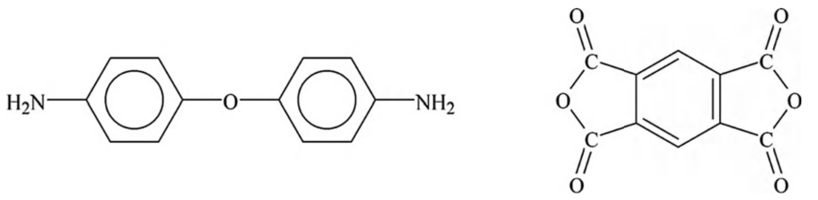


Figure 6.21 Color stability after low-temperature hydrogen peroxide gas plasma (STERRAD® NX) sterilization on different colors of Sabic Innovative Plastics Ultem® HU1004 PEI.[14]





4,4’-diaminodiphenyl ether oxydianiline (ODA)

Pyromellitic Dianhydride (PMDA)

Figure 6.22 Chemical structures of monomer used to make polyimides.

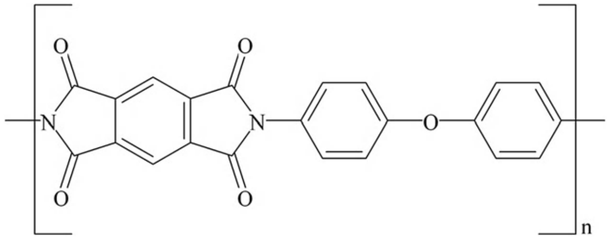


Figure 6.23 Chemical structure of a typical polyimide.

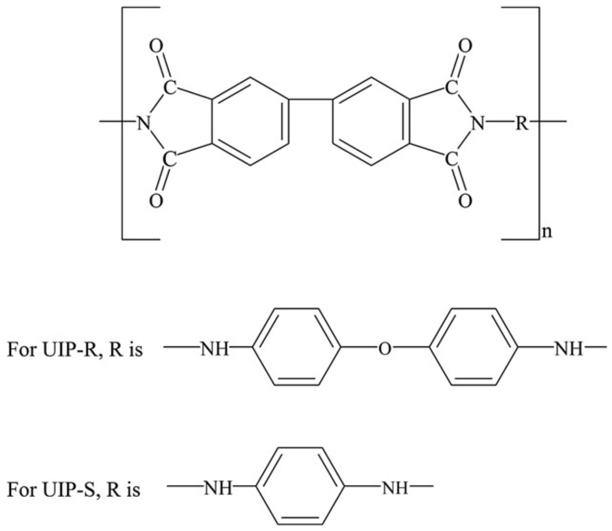


Figure 6.24 Chemical structures of Ube Industries Upilex® polyimides.

Table 6.10 Effect of Gamma Radiation Exposure on Kapton® Polyimide Film[15]

	Radiation Exposure				
Property	**Control, 1 mil Film**	**10^4 Gy, 1 h**	**10^5 Gy, 10 h**	**10^6 Gy, 4 Days**	**10^7 Gy, 42 Days**
Tensile strength (MPa)	207	207	214	214	152
Elongation (%)	80	78	78	79	42
Tensile modulus (MPa)	3172	3275	3378	3275	2903
Volume resistivity (Ω-cm × 10^{13} at 200 °C)	4.8	6.6	5.2	1.7	1.6
Dielectric constant 1 kHz at 23 °C	3.46	3.54	3.63	3.71	3.50
Dissipation factor 1 kHz at 23 °C	0.0020	0.0023	0.0024	0.0037	0.0029
Dielectric strength V/μm (kV/mm)	256	223	218	221	254

Note: Cobalt-60 Source.

Table 6.11 Effect of Electron Exposure on Kapton® Polyimide Film Mixed Neutron and Gamma[15]

Dose	5×10^7 Gy	10^8 Gy
Effect	Film darkened	Film darkened and tough

Conditions: 5×10^{12} neutrons/cm/s Flux at 175 °C

Data for polyimide plastics are found in Tables 6.10 and 6.11.

References

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7 Polyamides (Nylons)

High molecular weight polyamides are commonly known as nylon. Polyamides are crystalline polymers typically produced by the condensation of a diacid and a diamine. There are several types and each type is often described by a number, such as Nylon 66 or Polyamide 66 (PA66). The numeric suffixes refer to the number of carbon atoms present in the molecular structures of the amine and acid respectively (or a single suffix if the amine and acid groups are part of the same molecule).

The polyamide plastic materials discussed in this book and the monomers used to make them are given in Table 7.1.

The general reaction is shown in Fig. 7.1.

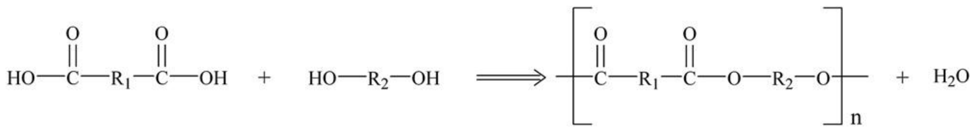
The $-COOH$ acid group reacts with the $-NH_2$ amine group to form the amide. A molecule of water is given off as the nylon polymer is formed. The properties of the polymer are determined by the R1 and R2 groups in the monomers. In Nylon 66 R2 = 6C and R1 = 4C alkanes, but one also has to include the two carboxyl carbons in the diacid to get the number it designates to the chain.

The structures of these diamine monomers are shown in Fig. 7.2, and the diacid monomers are shown in Fig. 7.3. Figure 7.4 shows the amino acid monomers. These structures only show the functional groups, the CH_2 connecting groups are implied at the bond intersections.

All polyamides tend to absorb moisture, which can affect their properties. Properties are often reported as DAM (dry as molded) or conditioned [usually at equilibrium in 50% relative humidity (RH) at 23 °C]. The absorbed water tends to act like a plasticizer and can have a significant effect on the plastics' properties.

Table 7.1 Monomers Used to Make Specific Polyamides/Nylons

Polyamide/ Nylon Type	Monomers Used
Nylon 6	Caprolactam
Nylon 11	Aminoundecanoic acid
Nylon 12	Aminolauric acid
Nylon 66	1,6-Hexamethylene diamine and adipic acid
Nylon 610	1,6-Hexamethylene diamine and sebacic acid
Nylon 612	1,6-Hexamethylene diamine and 1,12-dodecanedioic acid
Nylon 666	Copolymer based on Nylon 6 and Nylon 66
Nylon 46	1,4-Diaminobutane and adipic acid
Nylon amorphous	Trimethyl hexamethylene diamine and terephthalic acid
Polyphthalamide	Any diamine and isophthalic acid and/or terephthalic acid



$$HO-\overset{O}{\overset{\|}{C}}-R_1-\overset{O}{\overset{\|}{C}}-OH + HO-R_2-OH \Longrightarrow \left[-\overset{O}{\overset{\|}{C}}-R_1-\overset{O}{\overset{\|}{C}}-O-R_2-O-\right]_n + H_2O$$

Figure 7.1 Generalized polyamide reaction.

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00007-1

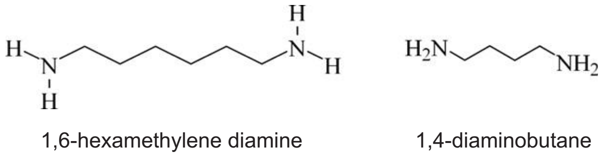


Figure 7.2 Chemical structures of diamines used to make polyamides.

All polyamides can be sterilized by ethylene oxide. Steam and autoclave sterilization should be limited to a few cycles because polyamides absorb moisture and hence warp or degrade. Aliphatic polyamides like Nylon 6, Nylon 66, Nylon 612, and Nylon 12 are reasonably resistant to small doses of gamma radiation, typically up to 40−50 kGy.

Absorption of water acts like a plasticizer to Nylons; elongation often increases significantly.

7.1 Polyamide 6 (Nylon 6)

Nylon 6 begins as pure caprolactam, which is a ring-structured molecule. This is unique in that the ring is opened and the molecule polymerizes with itself. Since caprolactam has six carbon atoms, the nylon that it produces is called Nylon 6, which is nearly the same as Nylon 66 described in Section 7.4. The structure of Nylon 6 is shown in Fig. 7.5 below,

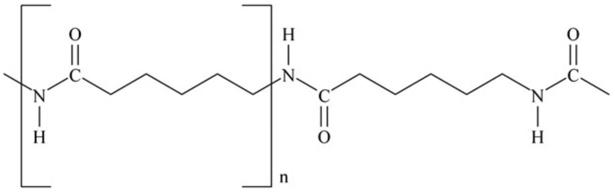


Figure 7.5 Chemical structure of Nylon 6.

Figure 7.3 Chemical structures of diacids used to make polyamides.

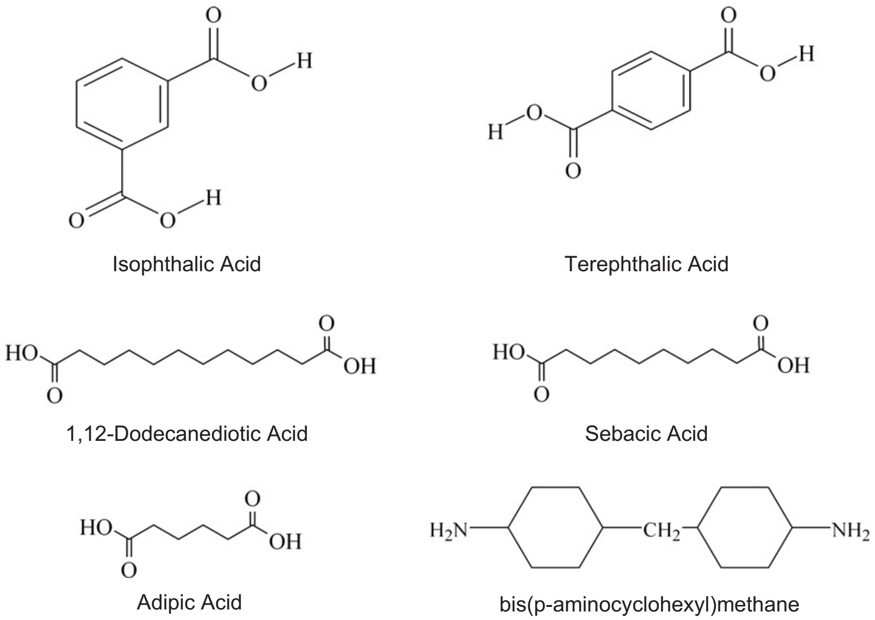
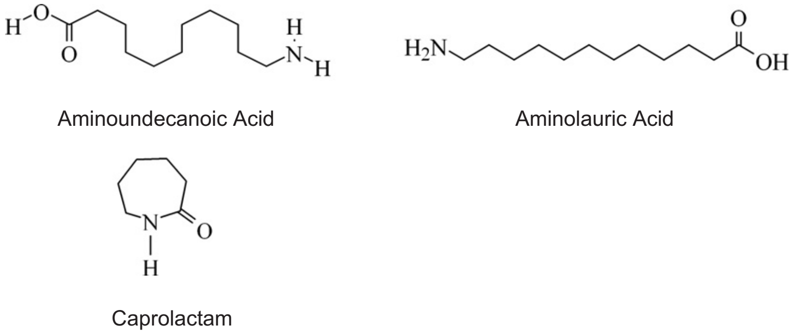


Figure 7.4 Chemical structures of amino acids used to make polyamides.



with the repeating unit in the brackets. The CAS number is 628-02-4.

Some of the Nylon 6 characteristics:

- Outstanding balance of mechanical properties
- Outstanding toughness in equilibrium moisture content
- Outstanding chemical resistance and oil resistance
- Outstanding wear and abrasion resistance
- Almost all grades are self-extinguishing. The flame-resistant grades are rated UL 94VO
- Outstanding long-term heat resistance (at a long-term continuous maximum temperature ranging between 80 and 150 °C)
- Grades reinforced with glass fiber and other materials offer superior elastic modulus and strength
- Offers low gasoline permeability and outstanding gas barrier properties
- Highest rate of water absorption and highest equilibrium water content (8% or more)
- Excellent surface finish even when reinforced
- Poor chemical resistance to strong acids and bases.

Manufacturers and trade names: BASF Ultramid® B, Honeywell Capran®, Aegis®, EMS Grilon® B, and Ube Industries.

Sterile applications and uses: Multilayer packaging (food and medical), surgical instruments, sutures, and tubing.

Data for polyamide 6 plastics are found in Table 7.2 and Figs 7.6–7.8.

7.2 Polyamide 11 (Nylon 11)

Nylon 11 has only one monomer, aminoundecanoic acid. It has the necessary amine group on one end and the acid group on the other. It polymerizes with itself

Table 7.2 Retention of Properties after Ethylene Oxide Sterilization of Nylon 6[1]

	One Sterilization Cycle		Three Sterilization Cycles	
Property Retained (%)	**1 Week**	**8 Weeks**	**1 Week**	**8 Weeks**
Elongation	69	132	71	102
Tensile strength	105	95	106	96

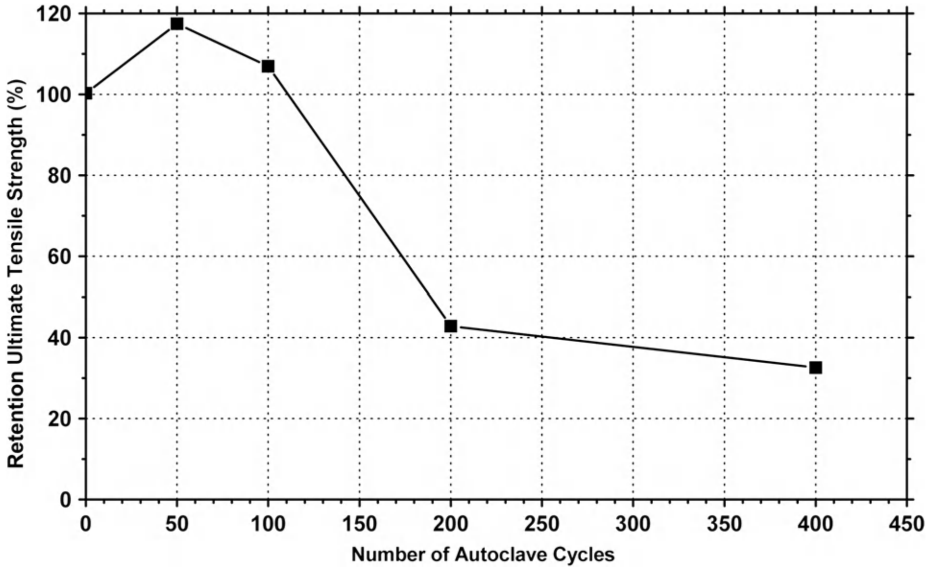


Figure 7.6 Retention of ultimate tensile strength after autoclave sterilization of Nylon 6.[1]

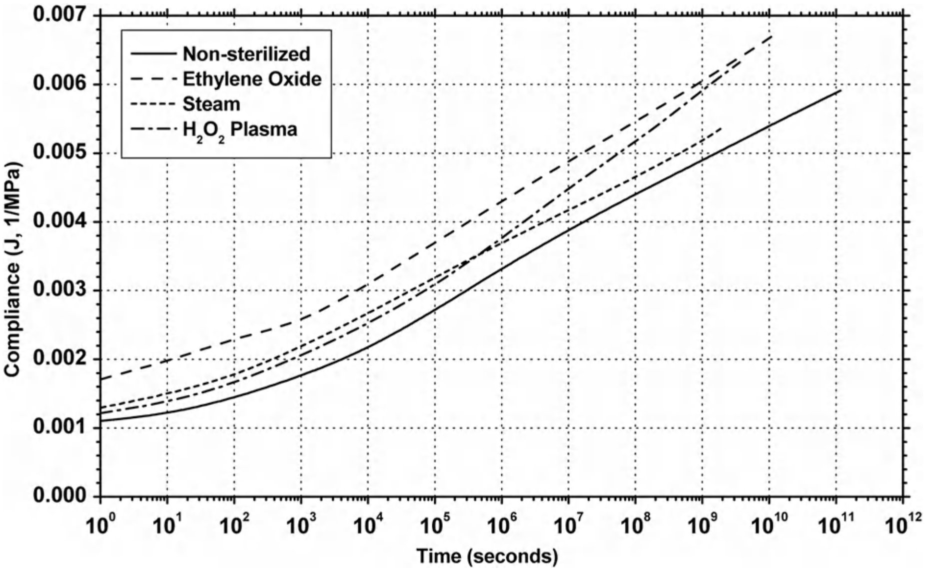


Figure 7.7 Comparison of creep compliances of various sterilization methods to non-sterilized monomodal PA6 at 37 °C.[2]

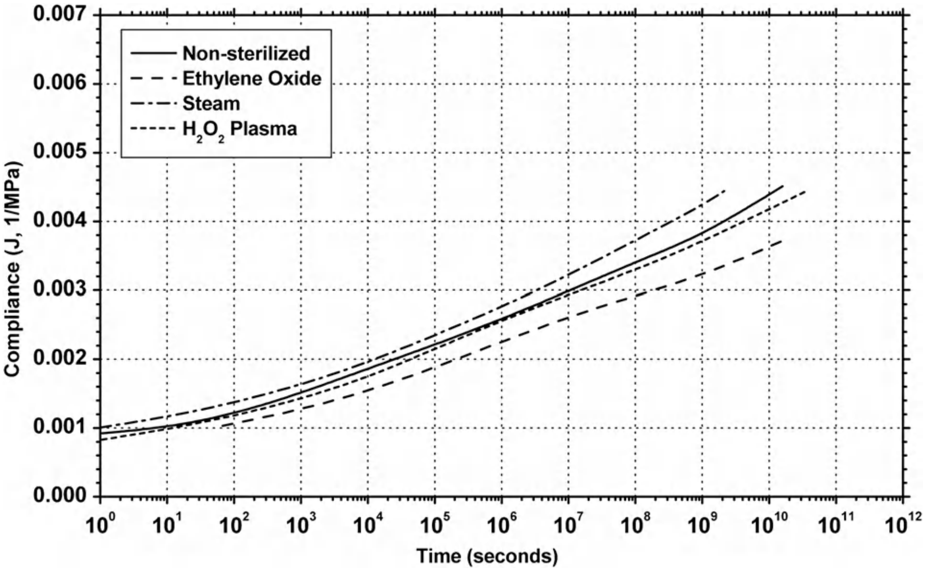


Figure 7.8 Comparison of creep compliances of various sterilization methods to non-sterilized bimodal PA6 at 37 °C.[2]

to produce the polyamide containing 11 carbons between the nitrogen of the amide groups. Its structure is shown in Fig. 7.9 and it has a CAS number of 25035-04-5.

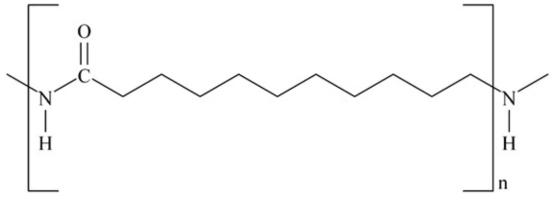


Figure 7.9 Chemical structure of Nylon 11.

Rilsan® PA11 is produced from a "green" raw material – castor beans.

Some of the Nylon 11 characteristics:

- Low water absorption for Nylon (2.5% at saturation)
- Reasonable UV resistance
- Higher strength
- Ability to accept high loading of fillers
- Better heat resistance than Nylon 12
- More expensive than Nylon 6 or Nylon 6/6
- Relatively low impact strength.

Manufacturers and trade names: Arkema Rilsan® B and Suzhou Hipro Polymers Hiprolon®.

Applications and uses: Medical catheters and tubing.

Data for polyamide 11 plastics are found in Figs 7.10 and 7.11.

7.3 Polyamide 12 (Nylon 12)

Nylon 12 has only one monomer, aminolauric acid. It has the necessary amine group on one end and the acid group on the other. It polymerizes with itself to produce the polyamide containing 12 carbons between the two nitrogen atoms of the two amide groups. Its structure is shown in Fig. 7.12.

The properties of semicrystalline polyamides are determined by the concentration of amide groups in the macromolecules. Polyamide 12 has the lowest amide group concentration of all commercially available polyamides thereby substantially promoting its characteristics:

- Lowest moisture absorption (~2%): parts show largest dimensional stability under conditions of changing humidity

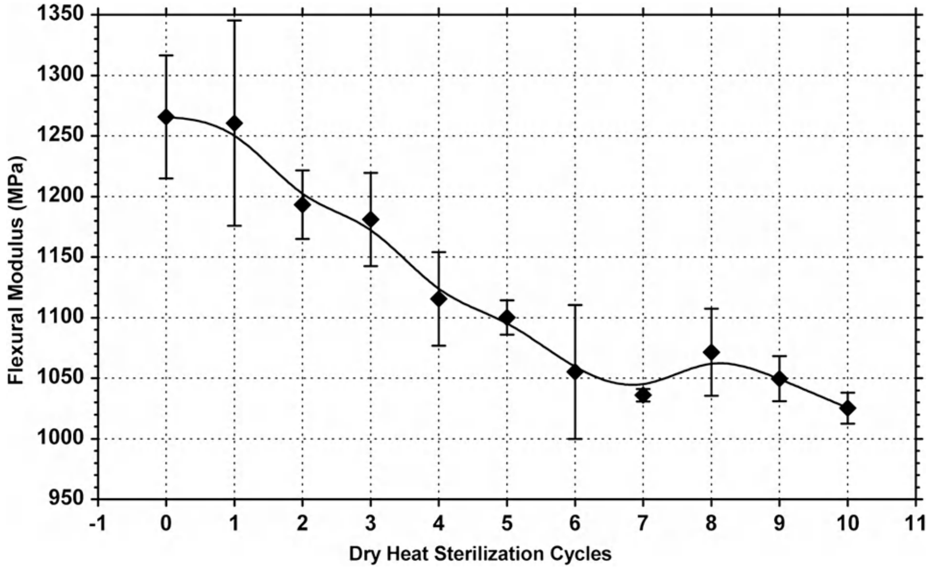


Figure 7.10 Flexural modulus versus dry heat sterilization cycles of polyamide 11.[3]

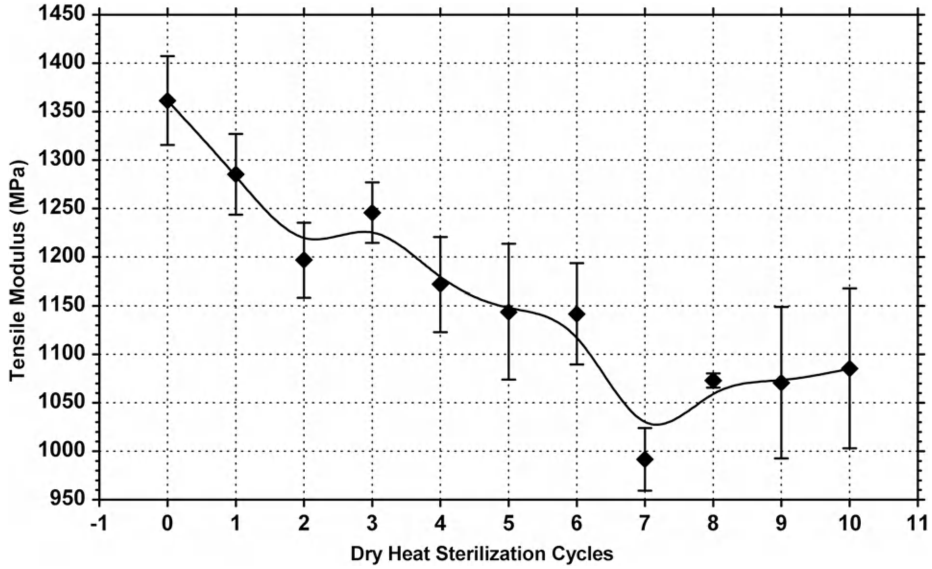


Figure 7.11 Tensile modulus versus dry heat sterilization cycles of polyamide 11.[3]

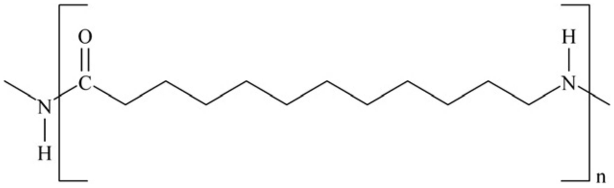


Figure 7.12 Chemical structure of Nylon 12.

- Exceptional impact and notched impact strength, even at temperatures well below the freezing point
- Good to excellent resistance against greases, oils, fuels, hydraulic fluids, various solvents, salt solutions, and other chemicals
- Exceptional resistance to stress cracking, including metal parts encapsulated by injection molding or embedded
- Excellent abrasion resistance
- Low coefficient of sliding friction
- Noise and vibration damping properties
- Good fatigue resistance under high-frequency cyclical loading conditions
- High processability
- Expensive
- Lowest strength and heat resistance of any polyamide unmodified generic.

Manufacturers and trade names: Arkema Rilsan® A, EMS-Grivory® Grilamid®; Exopack® Dartek®; and Degussa Vestamid®.

Sterile applications and uses: Drip-feeding stopcocks, tubing, and catheters.

PA12 has a high resistance to ionizing radiation. For example, films manufactured from Vestamid® L1901 (0.03- to 0.1-mm thick) were exposed to irradiation dosages of 25 kGy (=2.5 Mrad), 50 kGy, and 100 kGy. It was not until the dosage reached 100 kGy that a decided reduction in strain at break occurred and a slight graying was observed. Thicker test specimens made of Vestamid® L1940 were irradiated with electron beam doses of 400 kGy without any noticeable changes in the mechanical properties.[4]

7.4 Polyamide 66 (Nylon 66)

The structure of Nylon 66 is shown in Fig. 7.13. The CAS number is 32131-17-2.

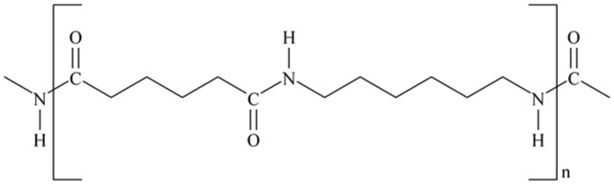


Figure 7.13 Chemical structure of Nylon 66.

Some of the Nylon 66 characteristics:

- Outstanding balance of mechanical properties
- Outstanding toughness in equilibrium moisture content
- Outstanding chemical resistance and oil resistance
- Outstanding wear and abrasion resistance
- Almost all grades are self-extinguishing. The flame-resistant grades are rated UL 94V0
- Outstanding long-term heat resistance (at a long-term continuous maximum temperature ranging between 80 and 150 °C)
- Grades reinforced with glass fiber and other materials offer superior elastic modulus and strength
- Offers low gasoline permeability and outstanding gas barrier properties
- High water absorption
- Poor chemical resistance to strong acids and bases.

Manufacturers and trade names: Exopack Performance Films Inc. Dartek®; DuPont™ Zytel®.

Sterile applications and uses: Packaging for meat and cheese, industrial end uses, pouch and primal bag, stiff packages, snacks, condiments, shredded cheese, coffee, and potable water.

Data for polyamide 66 plastics are found in Tables 7.3–7.6 and Figs 7.14–7.17.

7.5 Polyarylamide

Another partially aromatic high-performance polyamide is polyarylamide (PAA). The primary commercial polymer, PAMXD6, is formed by the reaction of m-xylylenediamine and adipic acid giving the structure shown in Fig. 7.18. It is a semicrystalline polymer.

Table 7.3 Effect of Gamma Radiation on SABIC Innovative Plastics LNP Lubriloy Nylon 6/6 Alloy

Radiation Conditions	**Unexposed**	**3.5 Mrad**		
Time poststerilization	–	0 Months	6 Months	
Properties Retained (%)				**Test Method**
Izod impact (J/M)	77.4	66.8	67.8	D256
Tensile strength (MPa)	49.7	49.2	46.0	D638
Exposure Conditions				
Type	Unexposed	3.5 Mrad	Δ*E*	D1925
Yellowness index	15.7	23.1	7.41	–

Table 7.4 Effect of Ethylene Oxide Sterilization on DuPont Zytel® 101 Nylon 66[6]

Details	**12% EtO and 88% Freon**				**8.6% EtO and 91.4% HCFC-124**			
Number of cycles	1		2		1		2	
Postexposure Conditioning II, Ambient								
Time (h)	168	1344	168	1344	168	1344	168	1344
Properties Retained (%)								
Tensile strength at yield	100.3	101.6	96.6	97.4	94	102.3	100.5	100.7
Elongation	72	62	50	64.5	59	85.5	78.5	65.5
Modulus	87.1	102.9	79.4	85.3	74.3	97.9	89.8	93.8
Dart impact (total energy)	98.5	123.1	101.5	104.6	100	73.8	101.5	120
Dart impact (peak energy)	73.8	92.9	78.6	81	73.8	64.3	76.2	92.9
Surface and Appearance								
Δ*E* color	0.61	0.5	0.7	0.84	0.54	0.65	0.59	0.51

Note: (1) Preconditioning note time: 18 h; temperature: 37.8 °C; RH: 60%. (2) Postexposure conditioning I: aeration; pressure: 127 mmHg, 32.2 °C. (3) Sterilization cycle: RH: 60%; 48.9 °C, 6 h.

Table 7.5 Effect of Ethylene Oxide Sterilization on DuPont Zytel® 101 Nylon 66[7]

Exposure Conditions				
Details	12% EtO and 88% Freon		8.6% EtO and 91.4% HCFC-124	
Postexposure Conditioning				
Aeration	10 air changes per hour	30 air changes per hour	10 air changes per hour	30 air changes per hour
Temperature (°C)	32.2	54.4	32.2	54.4
Ethylene Oxide Residuals (ppm)				
Little or no aeration	65	65	77	77
17-h aeration	13	3	54	16
24-h aeration	5	1	44	9
48-h aeration	2		34	7
72-h aeration	<2		17	

Note: (1) Preconditioning note time: 18 h; temperature: 37.8 °C; RH: 60%. (2) Sterilization cycle: RH: 60%; 48.9 °C, 6 h.

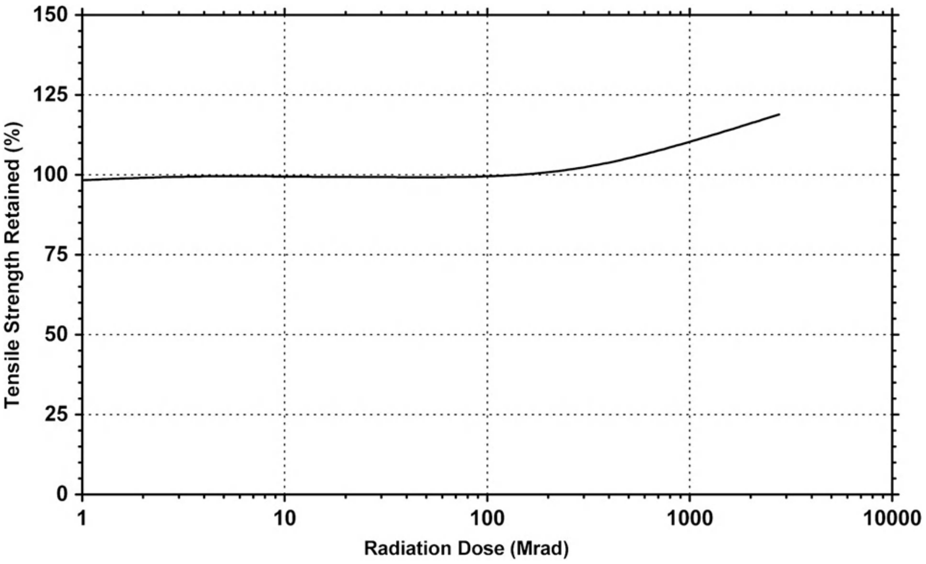
- Very high rigidity
- High strength
- Very low creep
- Excellent surface finish even for a reinforced product even with high glass-fiber content.
- Ease of processing
- Good dimensional stability
- Slow rate of water absorption.

Table 7.6 Effect of Steam Sterilization on DuPont Zytel® 122L Nylon 66

Sterilization Time		
Time (h)	200	400
Properties Retained (%)		
Tensile strength	101.9	97.1
Elongation	36.7	29.3

Note: (1) Sterilization cycle: 120 °C.

Figure 7.14 Electron beam radiation dose versus tensile strength retained of BASF Ultramid® A3 unreinforced Nylon 66.[8]



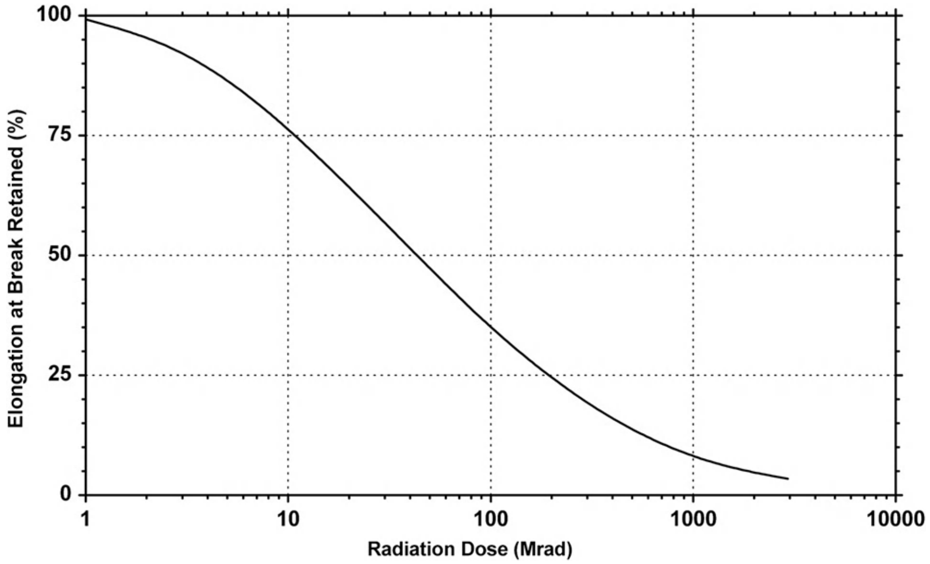


Figure 7.15 Electron beam radiation dose versus retained elongation at break of BASF Ultramid® A3 Nylon 66.[8]

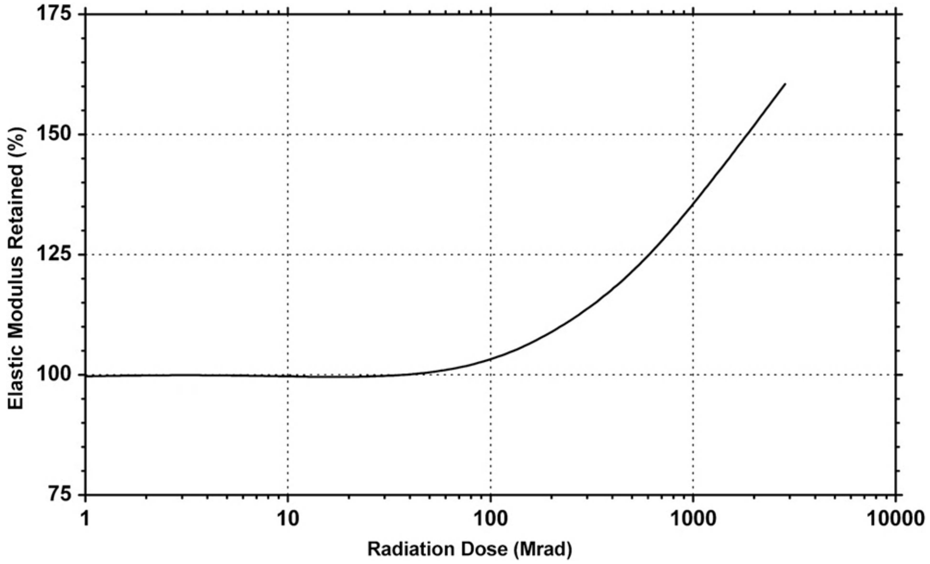


Figure 7.16 Electron beam radiation dose versus elastic modulus retained of BASF Ultramid® A3 Nylon 66.[8]

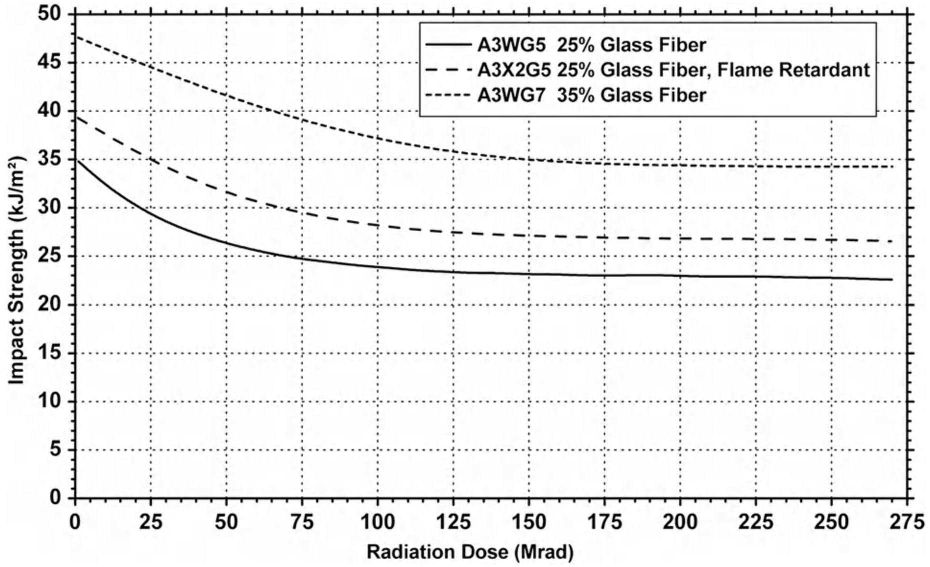


Figure 7.17 Electron beam radiation dose versus impact strength of glass-filled BASF Ultramid® A3 Nylon 66.[8]

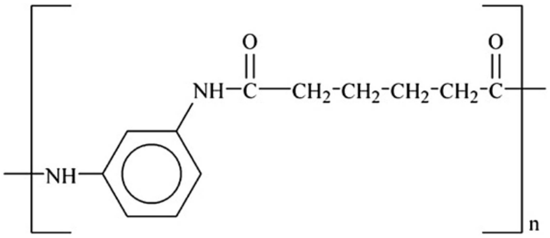


Figure 7.18 Chemical structure of PAMXD6 polyarylamide.

Because the polyamides do absorb water, and that affects the properties, some of the data are dry, or better dry as molded. Some of the data are for conditioned specimen; they have reached equilibrium water absorption from 50% RH at 23 °C.

Manufacturers and trade names: Solvay Advanced Polymers Ixef®, Mitsuibishi Gas Chemical Co. Nylon-MXD6, Nanocor®, and Imperm®.

Applications and uses: Packaging.

Data for polyarylamide plastics are found in Tables 7.7–7.9 and Figs 7.19–7.24.

7.6 Copolymers/Terpolymers

Polyamide copolymers are usually designed to make amorphous materials that give no crystallinity to the polymer structure. One such amorphous polyamide is Grilamid TR55 and is a polymer made from the three monomers shown in Fig. 7.25.

Table 7.7 Tensile Strength after Gamma Sterilization of Solvay Advanced Polymers Ixef® NT and WH PAA[9]

Radiation Dose (kGy)	Tensile Strength (MPa)
Control	2944
20	2929
40	2948

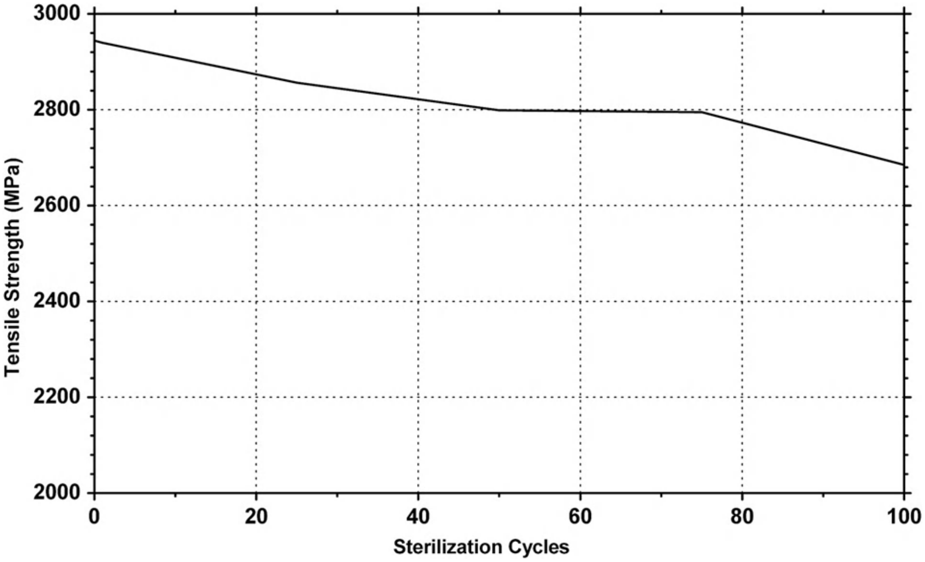
Table 7.8 Tensile Modulus after Gamma Sterilization of Solvay Advanced Polymers Ixef® PAA[9]

Radiation Dose (kGy)	Tensile Modulus (MPa)
Control	18,350
20	18,900
40	18,580

Table 7.9 Color Change after Gamma Sterilization of Solvay Advanced Polymers Ixef® PAA[9]

Radiation Dose (kGy)	Δ*E*	
	Ixef® NT	Ixef® WH
20	31	6.5
40	36	8

Figure 7.19 Tensile strength versus ethylene oxide sterilization cycles of Solvay IXEF® PAA.[9]



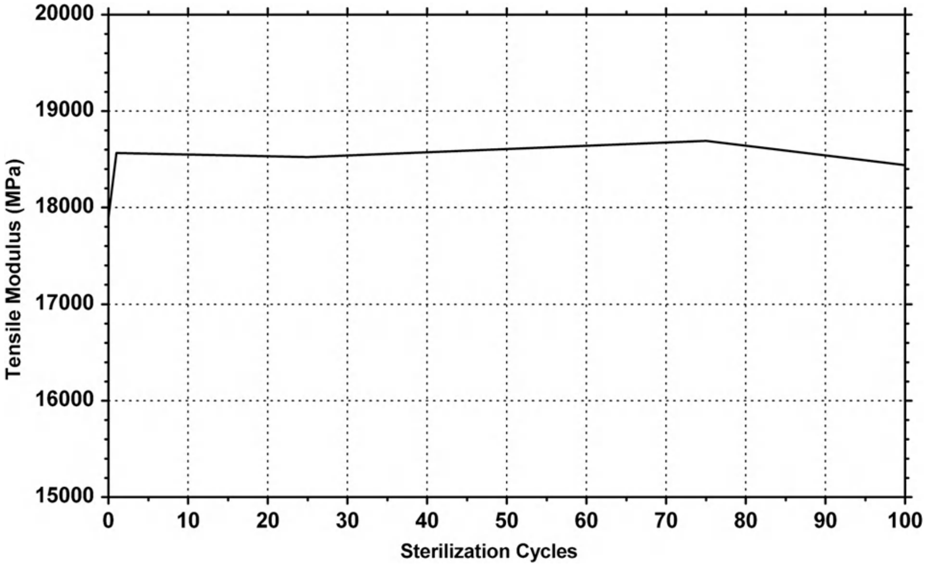


Figure 7.20 Tensile modulus versus ethylene oxide sterilization cycles of Solvay IXEF® PAA.[9]

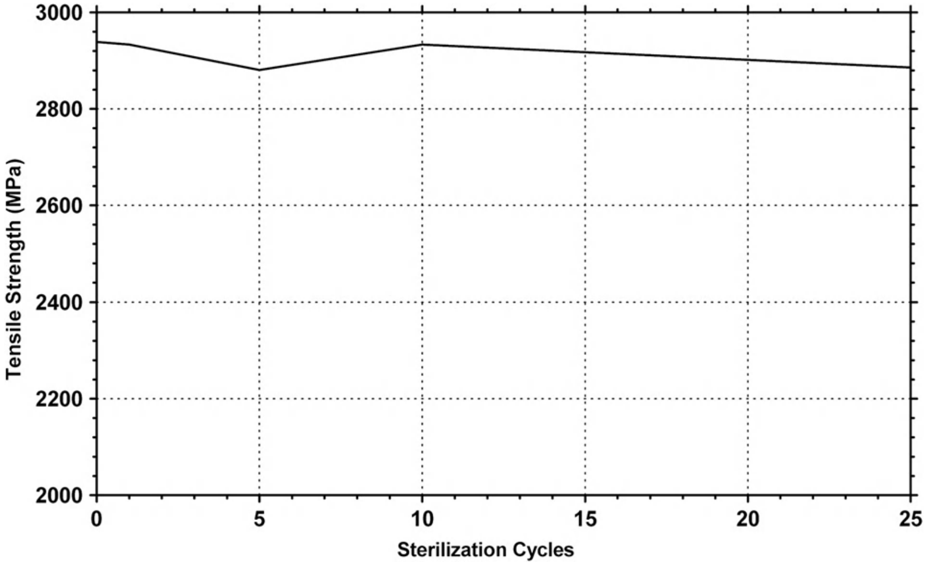


Figure 7.21 Tensile strength versus vapor hydrogen peroxide sterilization cycles of Solvay IXEF® PAA.[9]

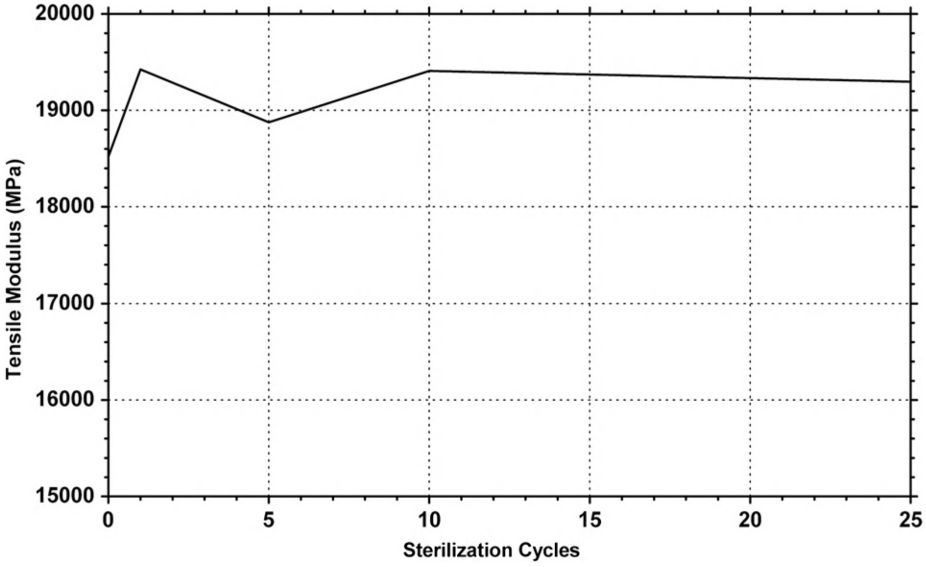


Figure 7.22 Tensile modulus versus vapor hydrogen peroxide sterilization cycles of Solvay IXEF® PAA.[9]

Figure 7.23 Tensile strength versus steam sterilization cycles of Solvay IXEF® PAA.[9]

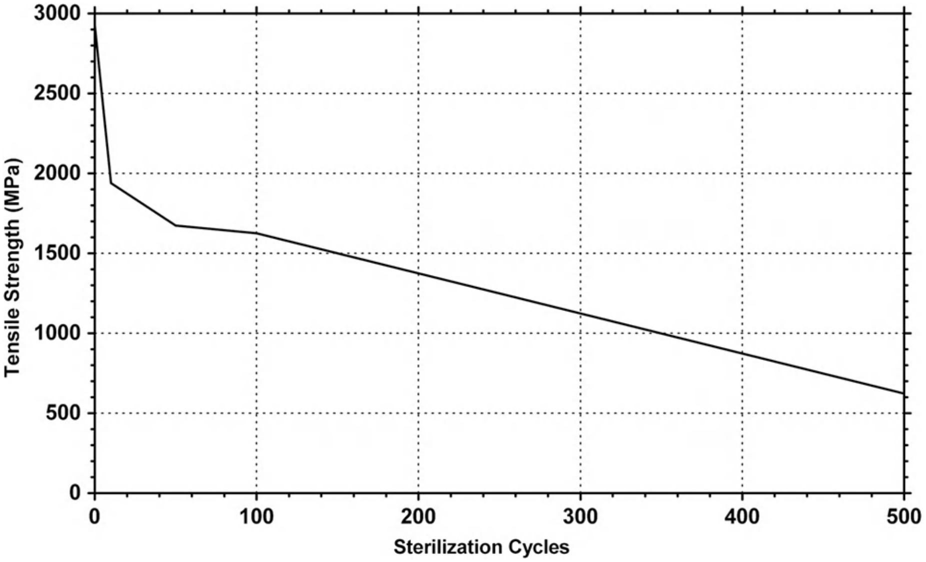
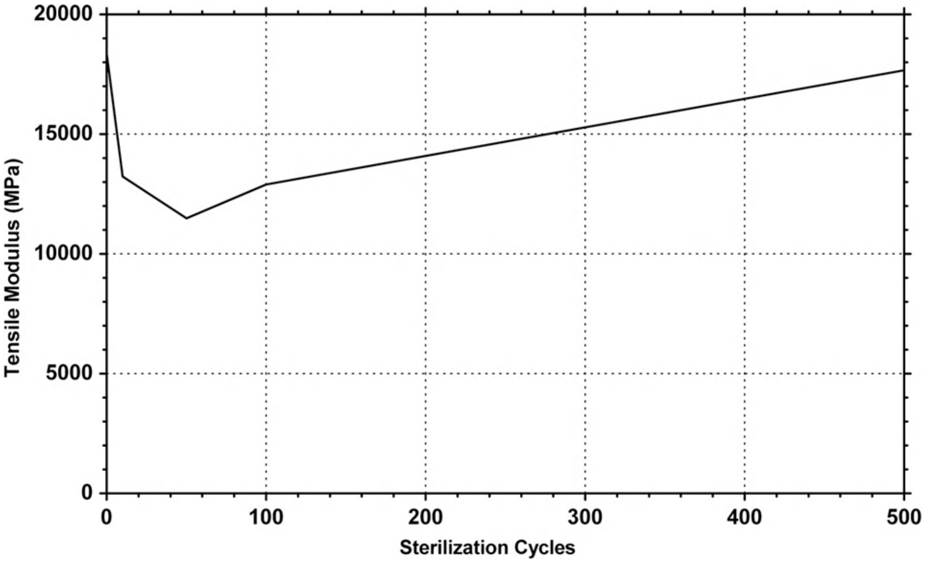
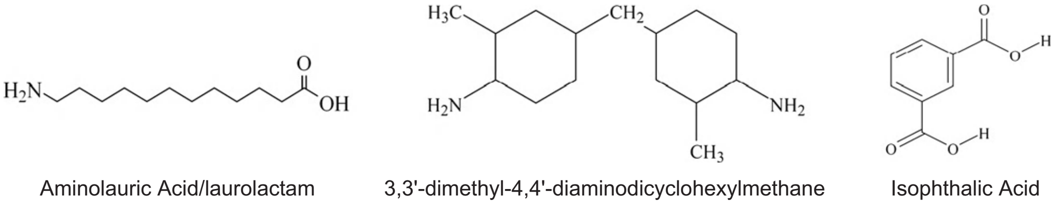


Figure 7.24 Tensile modulus versus steam sterilization cycles of Solvay IXEF® PAA.[9]





Aminolauric Acid/laurolactam 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane Isophthalic Acid

Figure 7.25 Monomers used to make Grilamid TR55 amorphous polyamide.

Some of the amorphous nylon characteristics:

- Crystal-clear, high optical transparency
- High mechanical stability
- High heat deflection temperature
- High impact strength
- Good chemical resistance compared to other plastics
- Good electrical properties
- Low mold shrinkage.

Blending even low percentages (20%) of Selar® PA with Nylon 6, Nylon 66, and nylon copolymers will result in a product that behaves like an amorphous polymer. These blends retain all the advantages of the Selar® PA resin with some of the mechanical property advantages of semicrystalline nylon.

Manufacturers and trade names: DuPont™ Selar® PA, and EMS Grivory Grilamid TR.

Sterile applications: Grilamid TR55 is used in applications where high transparency is required.

Data for polyamide copolymer and terpolymer plastics are found in Table 7.10 and Figs 7.26–7.33.

Table 7.10 Effect of Gamma Radiation Sterilization on EMS Grivory Grilamid TR55[10]

Radiation Dose (Mrad)	2.83	5.71	7.51	10	12	14.87	
Properties Retained (%)							**Test Method**
Tensile strength at break	99.1	94.3	102.6	91	89	91	ASTM D638
Tensile strength at yield	98.9	98.8	99.7	100	99.6	99.5	ASTM D638
Elongation at break	107.9	107.3	98.8	102.4	93.9	96.3	ASTM D638
Elongation at yield	100	100	100	100	100	100	ASTM D638
Flexural strength	99.6	100.4	100.4	101.3	100	102.6	ASTM D790
Flexural modulus	101.8	95.8	105.4	101.8	102.7	103	ASTM D790
Notched Izod impact	100	101.2	92.2	100	109.6	96.4	ASTM D256
Gardner impact	116.2	102.4	96.9	114	96.2	88.4	ASTM D1822
Surface and Appearance							
ΔL color	−0.06	−0.15	−0.03	0.26	0.17	2.62	MacBeth Color Eye
Δa color	−0.2	−0.44	−0.61	−0.98	−1.38	−0.77	MacBeth Color Eye
Δb color	0.72	1.33	1.72	2.83	3.86	6.61	MacBeth Color Eye

Figure 7.26 Gamma radiation dose versus tensile strength of EMS Grivory Grilamid TR55.[10]

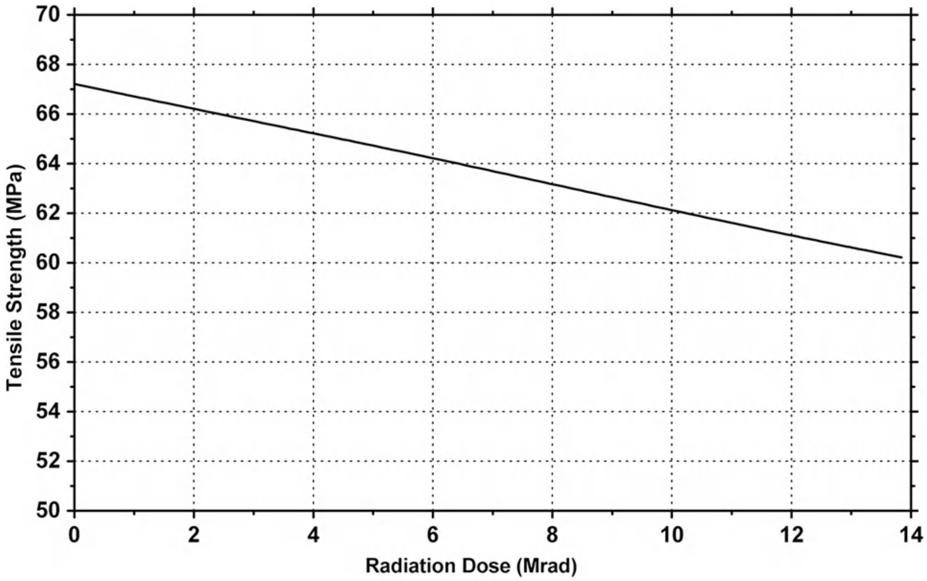


Figure 7.27 Gamma radiation dose versus elongation at break of EMS Grivory Grilamid TR55.[10]

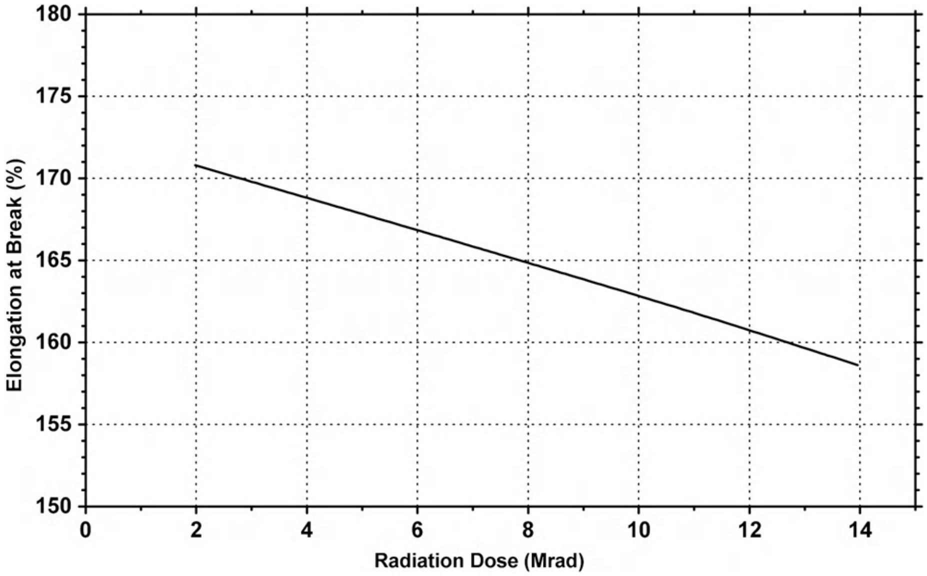
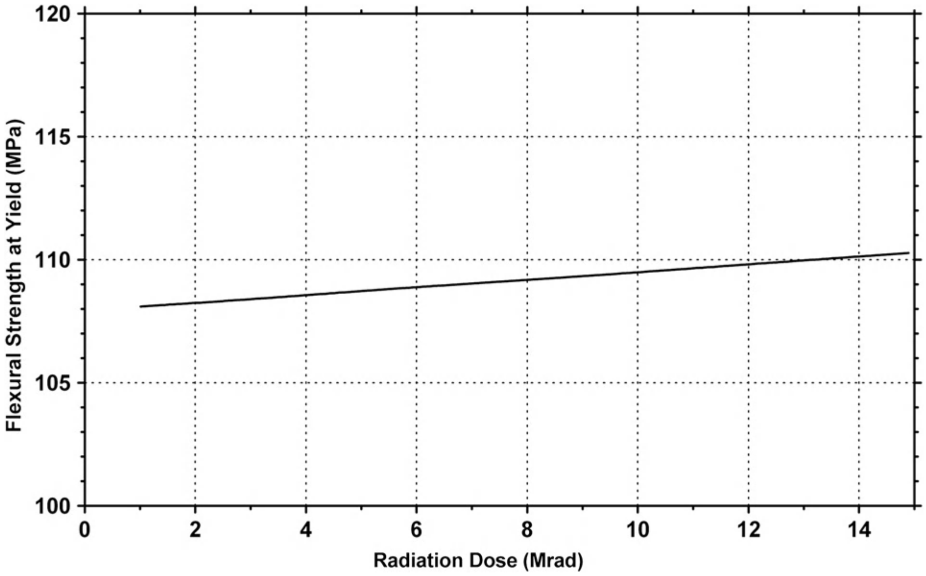


Figure 7.28 Gamma radiation dose versus flexural yield strength of EMS Grivory Grilamid TR55.[10]



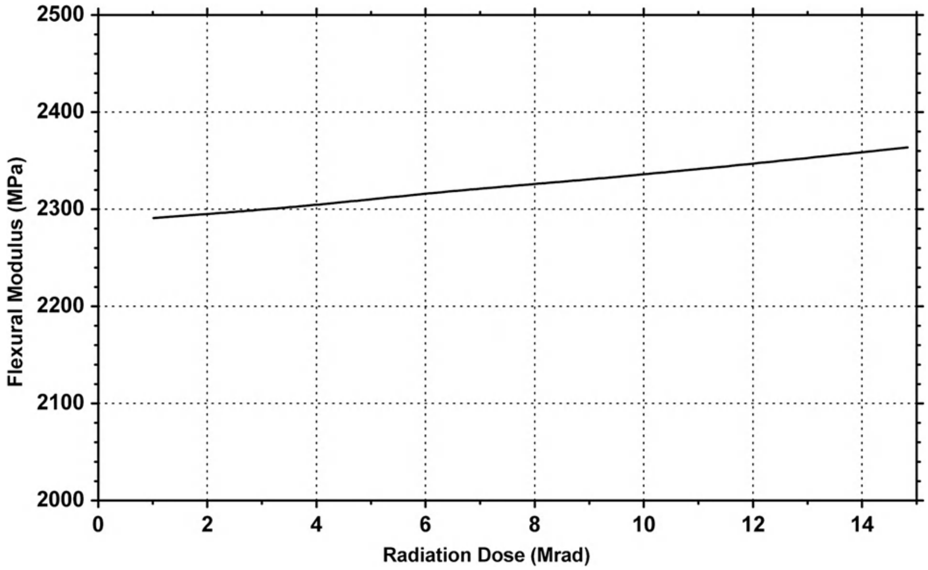


Figure 7.29 Gamma radiation dose versus flexural modulus of EMS Grivory Grilamid TR55.[10]

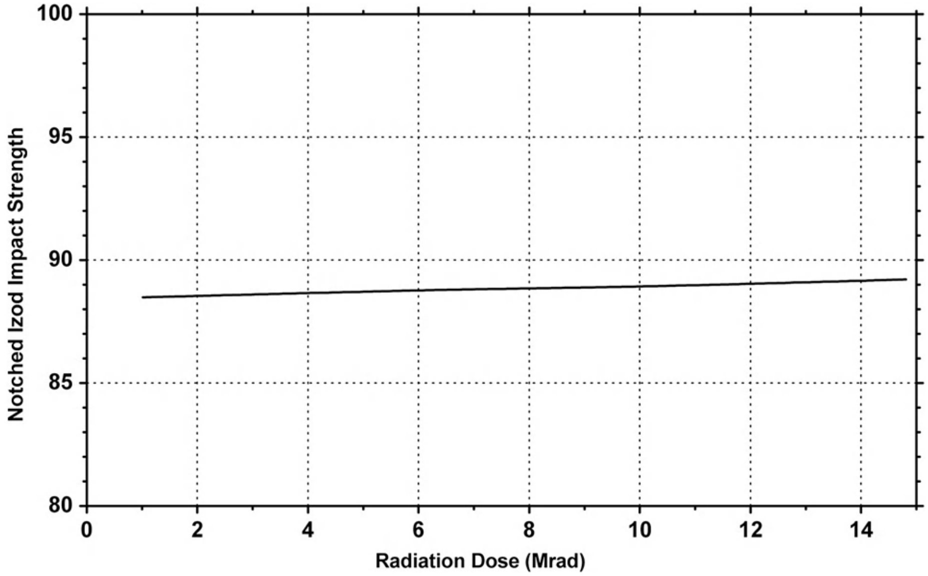


Figure 7.30 Gamma radiation dose versus notched Izod impact strength of EMS Grivory Grilamid TR55.[10]

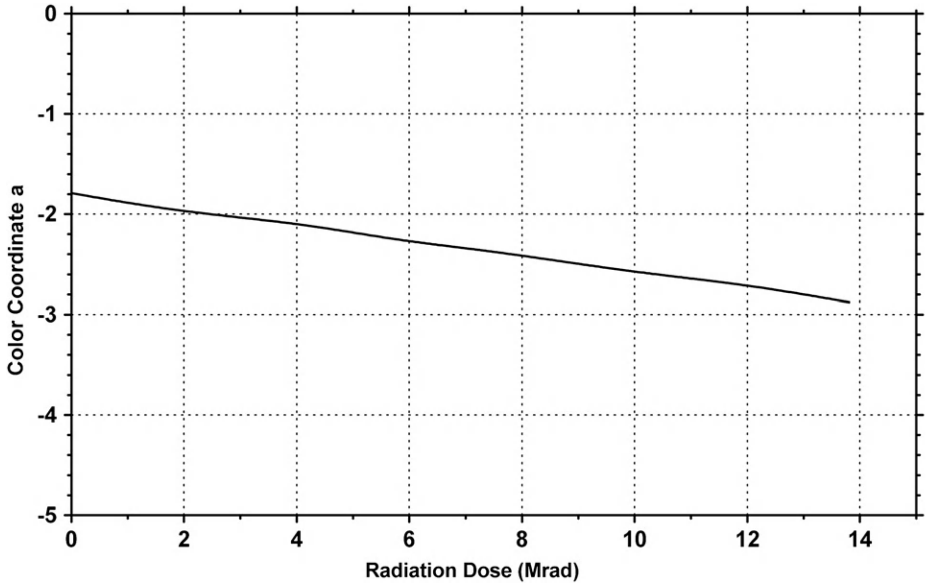


Figure 7.31 Gamma radiation dose versus color coordinate *a* of EMS Grivory Grilamid TR55.[10]

Figure 7.32 Gamma radiation dose versus color coordinate *b* of EMS Grivory Grilamid TR55.[10]

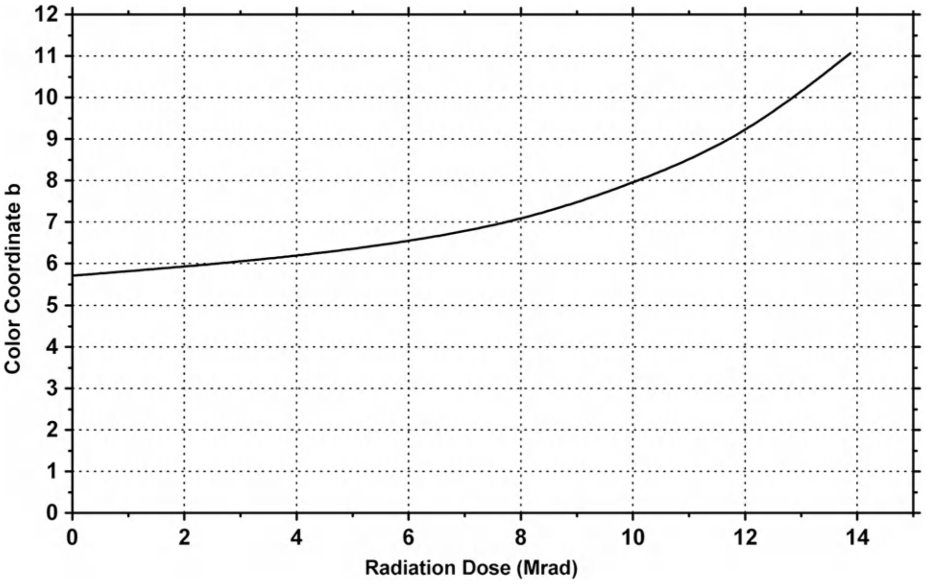
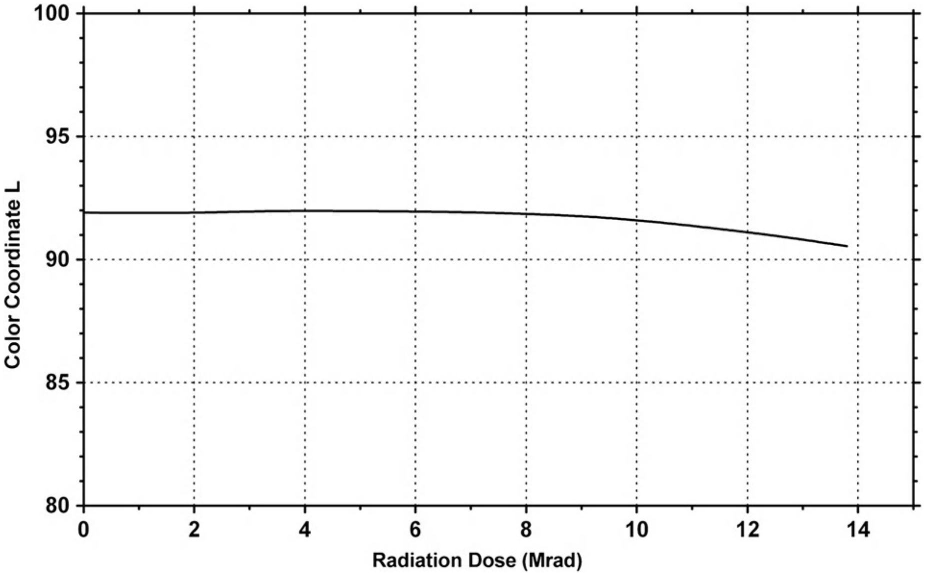


Figure 7.33 Gamma radiation dose versus color coordinate *L* of EMS Grivory Grilamid TR55.[10]



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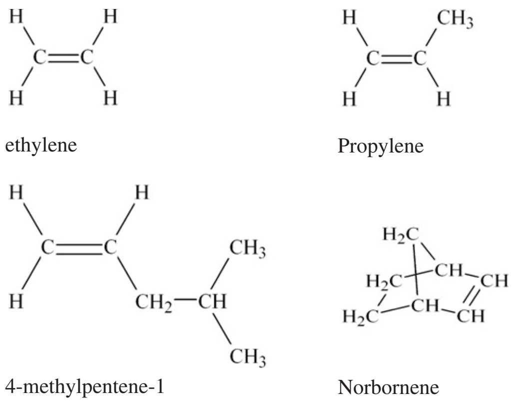
8 Polyolefins

This chapter focuses on polymers made from hydrocarbon monomers that contain a carbon−carbon double bond through which the polymer is made by addition polymerization as discussed in Section 2.1.1. An alkene, also called an olefin, is a chemical compound made of only carbon and hydrogen atoms containing at least one carbon-to-carbon double bond. The simplest alkenes, with only one double bond and no other functional groups, form a homologous series of hydrocarbons with the general formula C_nH_{2n}. The two simplest alkenes of this series are ethylene and propylene. When these are polymerized, they form polyethylene (PE) and polypropylene (PP), which are two of the plastics discussed in this chapter. A slightly more complex alkene is 4-methylpentene-1, the basis of poly (methyl pentene), known under the trade name of TPX™.

The structures of some of these monomers are shown in Fig. 8.1. Structures of the polymers may be found in the appropriate sections containing the data for those materials.

8.1 Polyethylene

PE can be made in a number of ways. The way it is produced can affect its physical properties. It can also have very small amounts of comonomers, which will alter its structure and properties.


ethylene

Propylene

4-methylpentene-1

Norbornene

Figure 8.1 Chemical structures of some monomers used to make polyolefins.

The basic types or classifications of PE, according the ASTM D1248, are:

- Ultra low-density polyethylene (ULDPE), polymers with densities ranging from 0.890 to 0.905 g/cm^3, contains comonomer
- Very low-density polyethylene (VLDPE), polymers with densities ranging from 0.905 to 0.915 g/cm^3, contains comonomer
- Linear low-density polyethylene (LLDPE), polymers with densities ranging from 0.915 to 0.935 g/cm^3, contains comonomer
- Low-density polyethylene (LDPE), polymers with densities ranging from about 0.915 to 0.935 g/cm^3
- Medium-density polyethylene (MDPE), polymers with densities ranging from 0.926 to 0.940 g/cm^3, may or may not contain comonomer
- High-density polyethylene (HDPE), polymers with densities ranging from 0.940 to 0.970 g/cm^3, may or may not contain comonomer.

Figure 8.2 shows the differences graphically. The differences in the branches in terms of number and length affect the density and melting points of some of the types.

Branching affects the crystallinity. A diagram of a representation of the crystal structure of PE is shown in Fig. 8.3. One can imagine how branching in the polymer chain can disrupt the crystalline regions. The crystalline regions are the highly ordered areas in the shaded rectangles of Fig. 8.3. A high degree of branching would reduce the size of the crystalline regions, which leads to lower crystallinity.

The data tables and graphs that follow will be in the order of the basic types or classifications of PE described in the first part of this section, except that data on unspecified PE and data that cover the range of PE molecular weights will be first.

The low heat deflection temperatures of PE plastics (30−50 °C) make them unsuitable for steam and

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00008-3

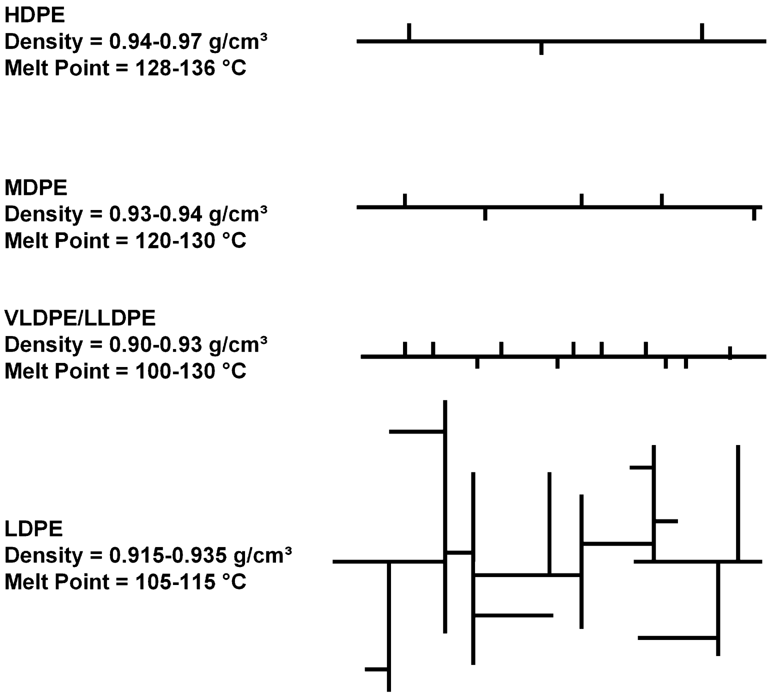


Figure 8.2 Graphical depictions of polyethylene types.

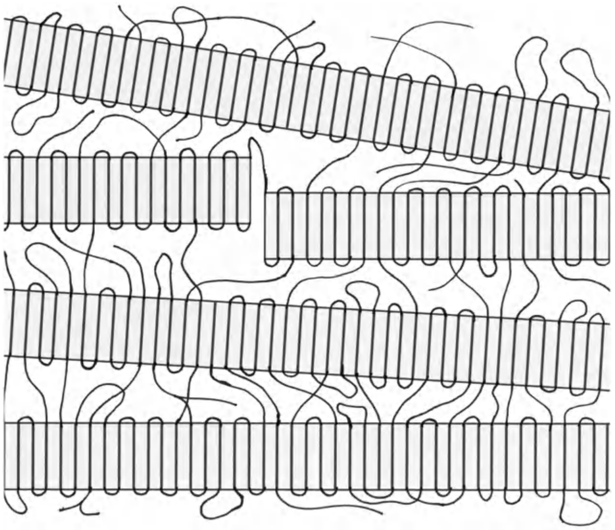


Figure 8.3 Graphical diagram of polyethylene crystal structure.

autoclave sterilization. The plastics would bend, warp, and deform under the temperatures (100−130 °C) used in these sterilization methods. Ethylene oxide, gamma radiation, and electron-beam (e-beam) sterilization methods are suitable.

Ethylene oxide has no effect on the properties of high-density PE as is shown in the data for the different types of PE in the following sections of this chapter. PE will oxidize or cross-link under high-energy radiation and needs to be stabilized to reduce it. In some cases, ultrahigh molecular-weight polyethylene (UHMWPE) is deliberately cross-linked with high-energy radiation to improve the wear behavior in knee and hip implants. Radiation doses of 50−100 kGy are used for cross-linking and standard doses of 25−40 kGy (in an inert atmosphere) are used to sterilize the UHMWPE parts.

8.1.1 Ultra Low-Density Polyethylene

Manufacturers and trade names: Dow Chemical ATTANE™.

Sterile applications: Blown and cast film for packaging cheese, meat, and coffee.

ATTANE™ ULDPE resins can accept relatively high levels of radiation with little or no adverse effect on property performance.

8.1.2 Linear Low-Density Polyethylene

LLDPE differs structurally from conventional LDPE because of the absence of long-chain branching. It is made by a polymerization process that is initiated by transition metal catalysts, particularly Ziegler or Philips type.

Manufacturers and trade names: Dow Chemical Dowlex®, Exopack® Sclairfilm®, and ExxonMobil Chemical.

Sterile applications: Blown and cast film, injection molding, and rotomolding.

Gamma radiation resistance: Exposure to gamma radiation doses up to 10 Mrad does not alter the tensile and impact properties. The flexural property of the resin decreases upon irradiation.

Ethylene oxide (EtO) resistance: LLDPE is compatible with multiple cycles of ethylene oxide sterilization due primarily to its excellent chemical resistance characteristics.

Data for LLDPE plastics are found in Tables 8.1 and 8.2.

8.1.3 Low-Density Polyethylene (LDPE)

- Blueridge Films BFI 345 is homopolymer film with premium clarity
- Purell PE 3420F resin from LyondellBasell is an LDPE grade for use in pharmaceutical packaging
- Unipac Embalagens Ltda Unipac-PE-60.

If sterilization is needed, certain regulations require infusion solutions to be sterilized at 121 °C for 15 min, even when filled under aseptic blow-fill-seal technology processing conditions. However, LDPE typically cannot be sterilized at this temperature due to its melting point which is lower than 121 °C. Regulatory authorities accept lower sterilization temperatures if the treatment time is increased in parallel (equivalence method). Sterilization time for a standard LDPE used in this process may range from 130 to 195 min, and by using Purell PE 3420F resins this time can be reduced to approximately 30−50 min. Unipac-PE-60 film irradiated with gamma and e-beam in doses higher than 15 kGy presented a yellowish coloration and also emitted an unpleasant odor. The intensity of such alterations increased with the irradiation dose.

Data for LDPE plastics are found in Figs 8.4−8.8.

8.1.4 High-Density Polyethylene

HDPE polymers are highly crystalline, tough materials. High molecular-weight, high-density polyethylenes (HMW-HDPE) are a special class of linear resins with molecular weights in the 200,000−500,000 range. To obtain processability along with end-use properties, control of the molecular-weight distribution is critical. Some

Table 8.1 Effect of Gamma Radiation Sterilization on Linear Low-Density Polyethylene[1]

	Radiation Dose (Mrad)						
	2.5			10			
Postexposure Conditioning							
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	72.9	97.5	96	96.2	101.4	102	ASTM D638
Tensile strength at yield	101.7	104.1	102.1	102.8	107.7	105.4	ASTM D638
Elongation at break	>80.1	84.6	68.8	90.4	89.9	87.8	ASTM D638
Dart impact (total energy)	104.1	95.9	95.9	112.3	94	113.1	ASTM D3763
Notched Izod impact strength	100	100	100	100	100	100	ASTM D256

Note: (1) Postexposure conditioning: 21 °C, dark.

Table 8.2 Effect of Ethylene Oxide (EtO) Sterilization on Linear Low-Density Polyethylene[1]

Sterilization Conditions							
Number of cycles	1			5			
Postexposure Conditioning III							
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	–	88.1	82.3	94.3	104.3	84.6	ASTM D638
Tensile strength at yield	–	102.6	105.1	108.4	104.2	104.1	ASTM D638
Elongation at break	–	84.9	84.6	92.9	107.7	88.3	ASTM D638
Dart impact (total energy)	100.4	98.1	89.6	97	89.2	89.6	ASTM D3763
Notched Izod impact strength	100	100	100	100	100	100	ASTM D256

Note: (1) Preexposure conditioning: 8 h; 37.8 °C; 60% RH. (2) Sterilization conditions: 12% EtO and 88% Freon, 60% RH, 49 °C, 6 h. (3) Postexposure conditioning I: vacuum 127 mmHg; postexposure conditioning II: aeration, 32.2 °C, ≥16 h; postexposure conditioning III: storage in dark, 21 °C.

materials are produced with "bimodal" molecular weight distribution to obtain the necessary balance.

Manufacturers and trade names: DuPont Tyvek®; LyondellBasell Alathon®, Petrolene; ExxonMobil™ Paxon™, Pax-Plus™; Chevron Philips Marlex®; and NOVA Chemicals Sclair®.

Sterile applications: Pouches, lidstock, breather patches, and headers for bags.

Tyvek® is a brand of flash-spun HDPE fibers; the name is a registered trademark of DuPont. The material is very strong; it is difficult to tear but can easily be cut with scissors or a knife.

Sterilization resistance: Tyvek® is extremely stable when exposed to sterilant gases and high-energy sterilization processes, retaining protective properties, and color and flexibility poststerilization.

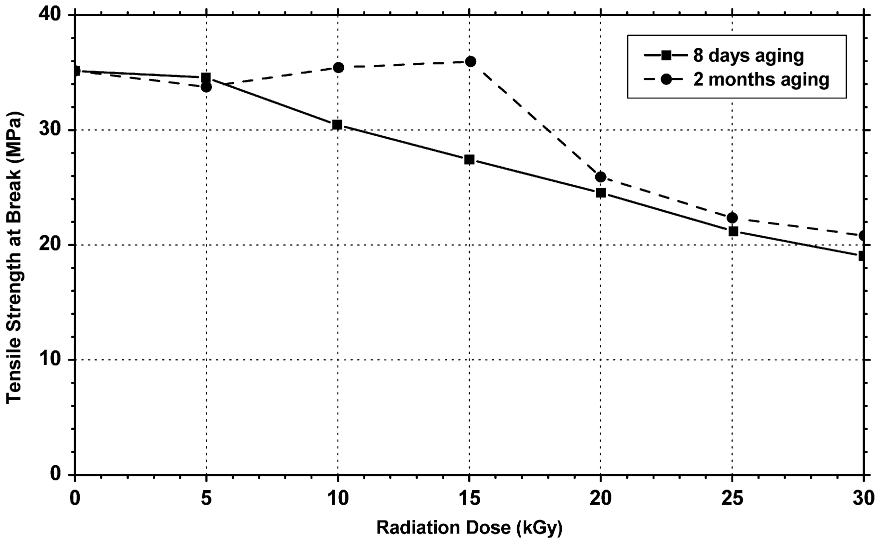


Figure 8.4 Effect of gamma radiation sterilization and post-aging on tensile strength at break of Unipac-PE-60 LDPE.[2]

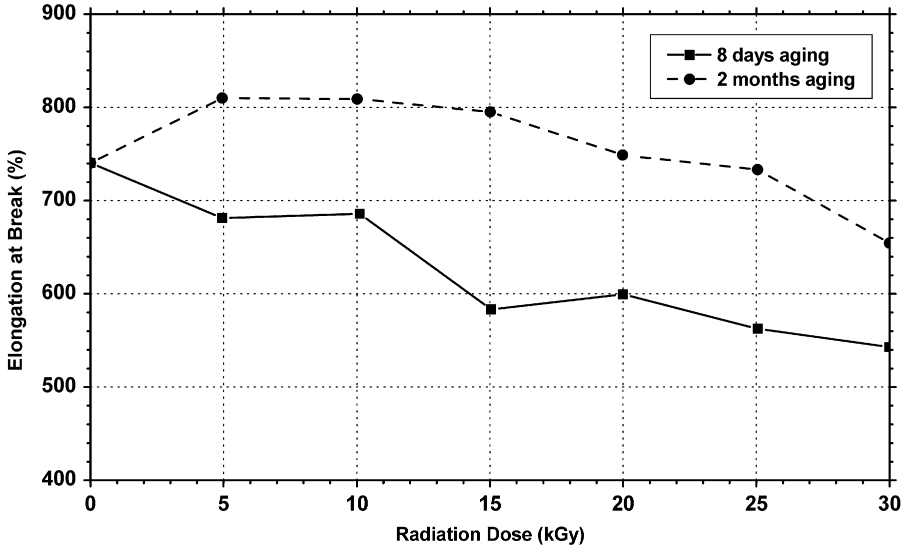


Figure 8.5 Effect of gamma radiation sterilization and post-aging on elongation at break of Unipac-PE-60 LDPE.[2]

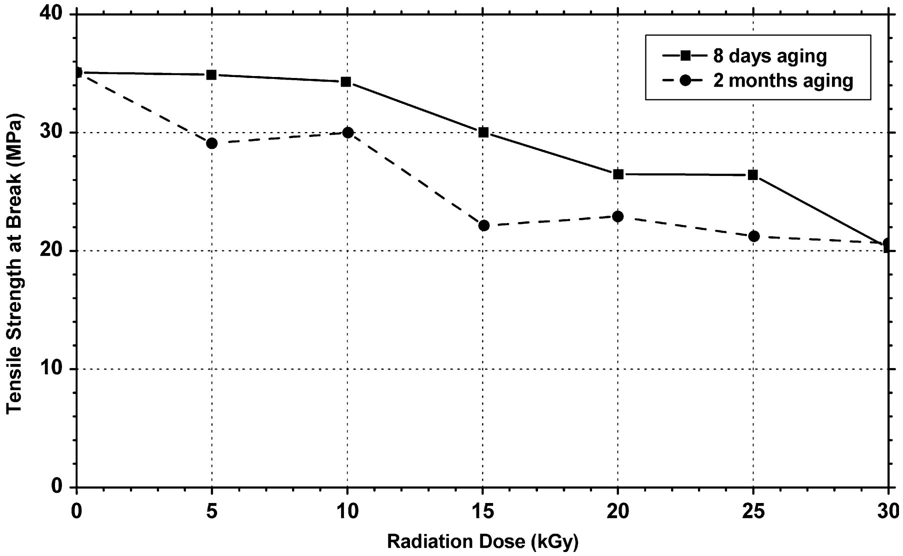


Figure 8.6 Effect of electron beam sterilization and post-aging on tensile strength at break of Unipac-PE-60 LDPE.[2]

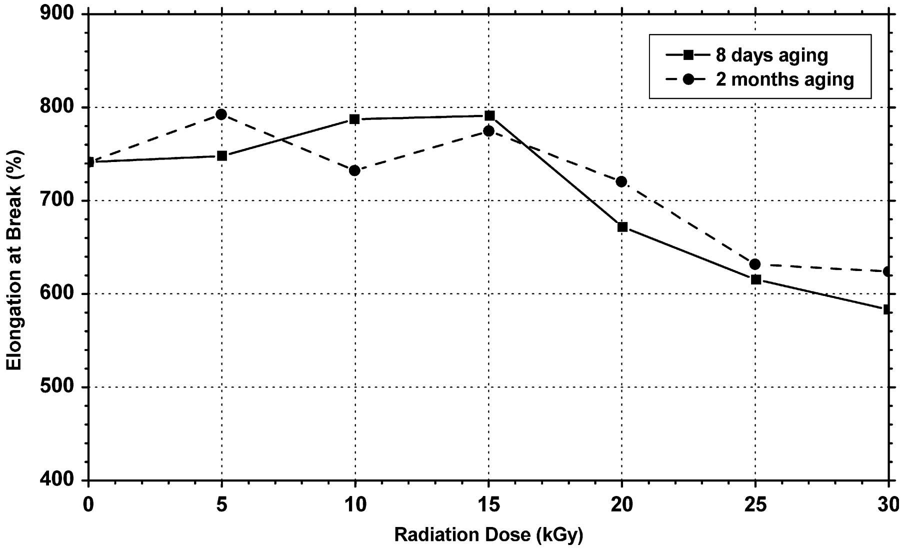


Figure 8.7 Effect of electron beam sterilization and post-aging on elongation at break of Unipac-PE-60 LDPE.[2]

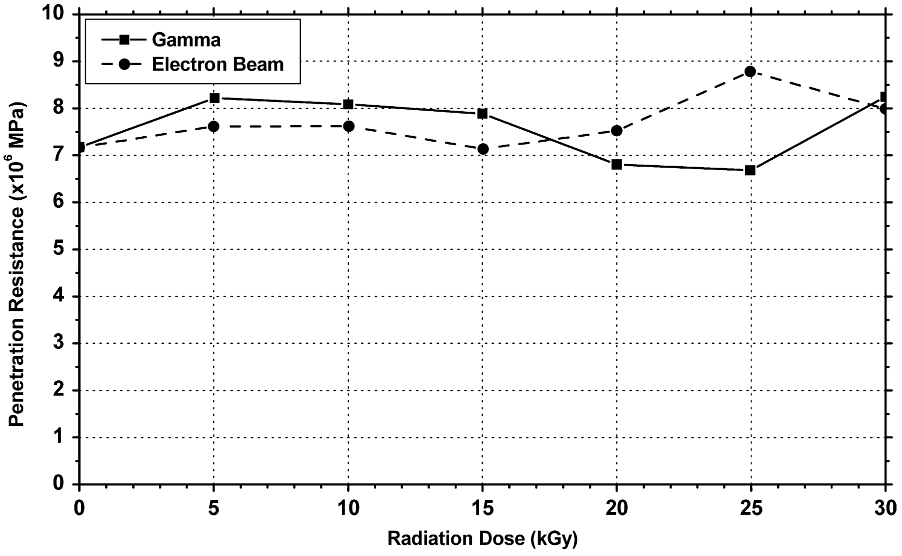


Figure 8.8 Effect of gamma and electron beam radiation sterilization after 8 days of aging on penetration resistance (ASTM F1306) of Unipac-PE-60 LDPE.[2]

Compatible sterilization methods include ethylene oxide (EtO), gamma, e-beam, steam (under controlled conditions), and plasma/hydrogen peroxide.

Tyvek® is engineered to enable sterilant gases and steam to penetrate and escape quickly.

Radiation resistance: Under radiation sterilization doses typically used in the industry, Tyvek® maintains excellent microbial barrier properties and experiences only slight changes in tensile strength, elongation, and color and resists poststerilization

Table 8.3 Real-Time Aging Test Results for Tyvek® 1059B and Tyvek® 1073B HDPE after Gamma Radiation Sterilization[4]

	Tensile Strength, Machine Direction MD, N/2.54 cm	Tensile Strength, Cross Direction, N/2.54 cm	Microbial Barrier, LRV2
Gamma Radiation 50 kGy			
Tyvek® 1059B			
Original	163	178	4.7
Initial	122	138	–
After 7 years	118	127	4.1
Tyvek® 1073B			
Original	187	213	5.2
Initial	147	175	–
After 7 years	142	148	5.2
Gamma Radiation 100 kGy			
Tyvek® 1059B			
Original	163	178	4.7
After 7 years	85	99	4.2
Tyvek® 1073B			
Original	187	213	5.2
After 7 years	103	130	5.1

Table 8.4 Accelerated and Real-Time Aging Test Results for Tyvek® 1073B HDPE Exposed to Gamma Radiation[4]

	Aging Time	Seal Strength, N/2.54 cm
Original		4.07
Sterilized with 30 kGy	4.22	
Accelerated aging	2 weeks	4.14
	4 weeks	3.81
	6 weeks	4.24
	8 weeks	3.95
	10 weeks	3.77
Real-time aging	3 years	3.46
	5 years	3.79

brittleness. Because Tyvek® is porous, undesirable odors produced by radiation sterilization pass through. Tyvek® can easily withstand resterilization with either gamma or e-beam, remaining flexible after resterilization and continuing to provide an excellent microbial barrier.

Ethylene oxide (EtO) resistance: Ethylene oxide (EtO) does not absorb well into Tyvek®; thus, it desorbs completely within six minutes, leaving no residues.

Steam resistance: Under controlled conditions of 121 to 127 °C at 30 psi for 30 min, Tyvek® retains its dimensional stability and integrity with no discoloration.

Plasma/hydrogen peroxide resistance: Tyvek® is suitable for use with the Sterrad Sterilization System from Advanced Sterilization Products, a Johnson & Johnson company. This environmentally safe sterilization alternative uses low-temperature

Table 8.5 Results from Tests Comparing Strength and Microbial Barrier of Medical-Grade Styles of Tyvek® HDPE Both before and after Gamma Radiation at Various Doses[*,4]

Product Code	Sterilized?	Radiation Dose (kGy)	Tensile Strength, Machine Direction** (N/2.54 cm)	Microbial Barrier LRV***
Tyvek® 1073B	Unsterilized	–	187	5.2
	Sterilized	25	174	5.2
		30	–	5.3
		50	159	5.2
		60	–	5.4
		100	103	5.1
Tyvek® Asuron™	Unsterilized	–	172	4.7
	Sterilized	25	140	4.7
		50	127	4.6
Tyvek® 1059B	Unsterilized	–	163	4.7
	Sterilized	25	128	4.7
		30	–	5.1
		50	118	4.1
		60	–	4.5
		100	85	4.2
Tyvek® 2FS™	Unsterilized	–	137	3.6
	Sterilized	30	112	3.6
		60	94	3.4

25 kGy and 30 kGy were single doses; all others were cumulative amounts from double doses (i.e. 50 kGy represents a double dose of 25 kGy, etc.).ASTM D5035 and DIN EN ISO 1924-2; modified for speed and gauge length.***Log reduction value as tested per ASTM F1608.*

Table 8.6 Real-Time Aging Test Results for Tyvek® 1059B and Tyvek® 1073B HDPE after E-Beam Radiation Sterilization[4]

	Tensile Strength, Machine Direction, N/2.54 cm	Tensile Strength, Cross Direction CD, N/2.54 cm	Microbial Barrier LRV2
E-beam Radiation 50 kGy			
Tyvek® 1059B			
Original	163	178	4.7
Initial	143	145	–
After 7 years	135	124	4.9
Tyvek® 1073B			
Original	187	213	5.2
Initial	164	157	–
After 7 years	159	145	5.2
E-beam Radiation 100 kGy			
Tyvek® 1059B			
Original	163	178	4.7
Initial	106	121	–
After 7 years	94	93	4.3
Tyvek® 1073B			
Original	187	213	5.2
Initial	120	120	–
After 7 years	96	113	5.2

Table 8.7 Results from Tests Comparing Strength and Microbial Barrier of Medical-Grade Styles of Tyvek® HDPE both before and after Electron Beam Sterilization at Various Doses[*,4]

Product Code	Sterilized?	Radiation Dose (kGy)	Tensile Strength, Machine Direction** (N/2.54 cm)	Microbial Barrier LRV***
Tyvek® 1073B	Unsterilized	–	187	5.2
	Sterilized	50	158	5.2
		100	96	5.2
Tyvek® Asuron™	Unsterilized	–	172	4.7
	Sterilized	25	150	4.5
		50	130	4.7
Tyvek® 1059B	Unsterilized	–	163	4.7
	Sterilized	60	135	4.9
		100	94	4.3

25 kGy and 30 kGy were single doses; all others were cumulative amounts from double doses (i.e. 50 kGy represents a double dose of 25 kGy, etc.).ASTM D5035 and DIN EN ISO 1924-2; modified for speed and gauge length.***Log reduction value as tested per ASTM F1608.*

Table 8.8 Effects of Beta Irradiation on the Properties of Chevron Phillips Marlex HDPE[3]

Typical Properties	Temperature (°C)	Beta Irradiation Dosage (Mrad)				
		0	5	10	15	50
Tensile strength (MPa)	28	28.3	29.1	30	30.3	31.4
	93	8.98	10.8	11.3	7.7	10.8
	132	–	1.2	1.46	3.13	5.13
Elongation (%)	28	20	18	22	20	20
	93	167	375	520	505	133
	132	–	510	445	385	110
Hardness (Shore D)		64	67	67	68	70
Density (g/cm^3)		0.96	0.96	0.96	0.96	0.96
Color		White	White	Ivory	Ivory	Tan

Table 8.9 Effects of Beta Irradiation on the Properties of Chevron Phillips Marlex HDPE[3]

Typical Properties	Temperature (°C)	Gamma Irradiation Dosage (Mrad)			
		0	1	10	100
Tensile strength (MPa)	28	40.2	51.7	49.1	57.6
Elongation (%)	28	13	15	15	1
Hardness (Shore D)		64	68	70	70
Density (g/cm^3)		0.952	0.955	0.955	0.967

Table 8.10 Strength and Barrier Properties before and after EtO Sterilization of DuPont Tyvek® HDPE[4]

Product Code	Treatment	Tensile Strength, Machine Direction MD*, N/2.54 cm	Microbial Barrier LRV**
Tyvek® 1073B	Unsterilized	196	5.2
	Sterilized	205	5.3
Tyvek® Asuron™	Unsterilized	172	4.7
	Sterilized	164	4.9
Tyvek® 1059B	Unsterilized	165	4.7
	Sterilized	156	4.7
Tyvek® 2FS™	Unsterilized	138	3.6
	Sterilized	147	3.3

**Per ASTM D5035 and DIN EN ISO 1924-2; modified for speed and gauge length. **Log reduction value as tested per ASTM F1608.*

gas plasma to avoid the degrading effects of steam or the residues of EtO. Tyvek® products include:

- Tyvek® 1073B: Tyvek in its highest weight. Ideal for heavy, sharp, or bulky devices such as implants.
- Tyvek® 1059B: The superior protection of Tyvek® in a slightly lighter version for less demanding applications. Ideal for smaller devices like syringes and for devices with rounded edges.

Table 8.11 Physical Properties of Tyvek® HDPE Sterilized by Ethylene Oxide (EtO) before and after Five-Year Shelf-Life Test[4]

Property	Test Method	Units	Tyvek® 1059B		Tyvek® 1073B	
			Initial	After 5 Years	Initial	After 5 Years
Delamination	ASTM D2724	N/2.54 cm	2	2	2	2
Gurley Hill porosity	TAPPI T460******	s/100 cc	30	28	37	37
	ISO 5636-5					
Microbial barrier	Internal DuPont	Log reduction value	4.7*	Unchanged	5.2*	Unchanged
Hydrostatic head	AATCC TM 127	cm H_2O	150+	150+	150+	150+
	DIN EN 20811**					
Tensile strength, Machine Direction	DIN EN ISO 1924-23***	N/2.54 cm	163	160	196	201
Seal strength	*****	N/2.54 cm	6	6	7	7

**** Modified for 9/16 in. (14.28 mm) diameter probe.

***** Sealing conditions: temperature — 290 °F (143 °C); dwell time — 1 s; pressure (seal through the film) — 90 psi (621 kPa).

**Typical values. ASTM F1608 Standard did not exist so barrier was tested by internal DuPont method similar to the current standard. Property remained unchanged after 5 years.*

***Rate of use: 60 cm H_2O/min.*

****Modified for speed and gauge length.*

Table 8.12 Accelerated Aging Test Results for Ethylene Oxide Sterilized DuPont™ Tyvek® 1059B and 1073B HDPE[4]

Property	Test Method	Units	Tyvek® 1059B			Tyvek® 1073B		
				After			After	
			Initial	Six Cycles	Five Years	Initial	Six Cycles	Five Years
Tensile strength, MD	DIN EN ISO 1924-21	N/2.54 cm	165	174	174	187	187	178
Microbial barrier	ASTM F1608	Log reduction value	4.7	Unchanged		5.2	Unchanged	

Note: (1) Modified for speed and gauge length. (2) Typical value.

Table 8.13 Accelerated Aging Test Ethylene Oxide Sterilized for Tyvek® 2FS™[4]

Property	Test Method	Units	Initial	After 36.5 Weeks
Tensile strength, MD	DIN EN ISO 1924-21	N/2.54 cm	137	137
Elongation, MD	DIN EN ISO 1924-21	%	17	17
Microbial barrier	ASTM F1608	Log reduction value	3.1	Unchanged

Note: MD-Machine Direction.

Table 8.14 The Effect of EtO Sterilization on the Properties of High-Density Polyethylene[5]

Carrier Gas	Sterilization	Postexposure Time	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Instrumented Dart Impact Peak Energy (J)	Izod (J/m)
Control	Unexposed		24	294	950	22	661	17	37
Average standard deviation (%)			2	43	5	5	13	23	0
HCFC-124	One cycle	1 week	22	258	830	21	703	17	37
		8 weeks	23	332	890	23	646	15	148
	Three cycles	1 week	22	261	850	23	716	15	43
		8 weeks	23	383	850	23	686	15	43
Average standard deviation (%)			2	24	6	5	9	17	14
HCFC-124/22	One cycle	1 week	23	348	880	23	737	15	48
		8 weeks	23	102	920	23	761	15	37
	Three cycles	1 week	23	125	910	23	769	14	53
		8 weeks	23	55	910	23	745	14	37
Average standard deviation (%)			2	30	5	5	8	36	13
EtO	One cycle	1 week	22	316	840	22	686	14	43
		8 weeks	23	277	850	22	660	14	48
	Three cycles	1 week	22	175	830	23	740	12	43
		8 weeks	23	173	860	22	697	14	43

Table 8.15 Physical Properties of Medical-Grade Types of Tyvek® HDPE both before and after Steam Sterilization[4]

Product Code	Sterilized?	Temperature (°C)	Tensile Strength, Machine Direction* (N/2.54 cm)	Microbial Barrier LRV**	Shrinkage Autoclave (%)	Gurley Hill*** (s/ 100 cc)
Tyvek® 1073B	Unsterilized	–	186	5.2	–	24
	Sterilized 30 min	121	192	4.8	0.5	24
		124	215	4.8	0.3	26
		127	214	5.2	1.4	25
Tyvek® Asuron™	Unsterilized	–	172	4.7	–	40
	Sterilized 30 min	25	162	4.7	–	34
Tyvek® 1059B	Unsterilized	–	157	4.7	–	19
	Sterilized 30 min	121	160	4.7	1.0	21
		124	172	5.1	0.5	34
		127	179	4.1	1.5	23
Tyvek® 2FS™	Unsterilized	–	124	3.6	–	18
	Sterilized 30 min	121	119	3.1	0.8	20
		124	127	3.1	0.3	20
		127	129	3.3	0.9	17

*ASTM D5035 and DIN EN ISO 1924-2; modified for speed and gauge length.**Log reduction value as tested per ASTM F1608.***Comparable methods: TAPPI T460 and ISO 5636-5.

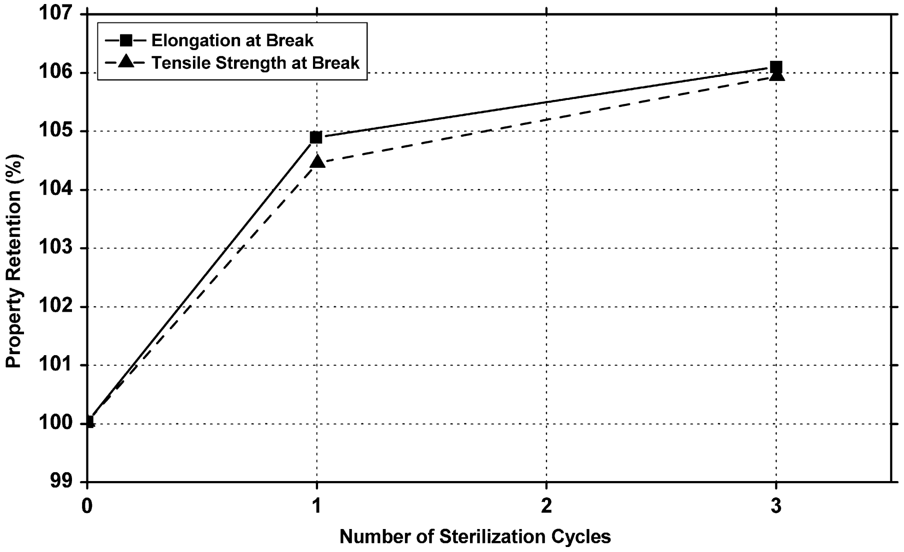


Figure 8.9 Effect of ethylene oxide sterilization on the property retention of high-density polyethylene.[6]

Table 8.16 Volumetric Wear of Sterilized Ultrahigh Molecular Weight Polyethylene[5]

Sterilization Method	Wear Cycles in Millions	Volumetric Wear (mm^3)	
		Unaged	**Aged**
Ethylene oxide	1	58	9
	2	120	51
	3	–	86
Gamma	1	58	51
	2	87	170
	3	–	220

- Tyvek® Asuron™: The most printable Tyvek® product for medical packaging. Additionally, has improved seal appearance at higher temperatures. Due to the addition of titanium dioxide, the material is less likely to show transparitization.
- Tyvek® 2FS™: The lightest form of Tyvek®, yet superior to paper in toughness, and particularly well suited for form—fill—seal applications.

Data for HDPE plastics are found in Tables 8.3—8.15 and Fig. 8.9.

8.1.5 Ultrahigh Molecular Weight Polyethylene

Sterile applications: UHMWPE is used as the wear-bearing surface of hip and knee arthroplasty and total joint replacement.

Gamma radiation resistance: Gamma radiation has been a common sterilization method for UHMWPE used in total joint replacement. The products are sterilized by gamma radiation from a Cobalt-60 source. Gamma radiation can lead to extensive oxidation in PE. Gamma radiation improves cross-linking of UHMWPE resulting in an interpenetrating network of HMW polyethylene chains with the potential benefit of increased strength, thus increasing resistance to wear. However, sterilization in air may be particularly harmful because it may initiate a long-term oxidative process that has a negative impact on the implant's mechanical properties.

Ethylene oxide (EtO) resistance: EtO sterilization does not cause oxidative degradation.

Data for UHMWPE plastics are found in Table 8.16 and Figs 8.10—8.12.

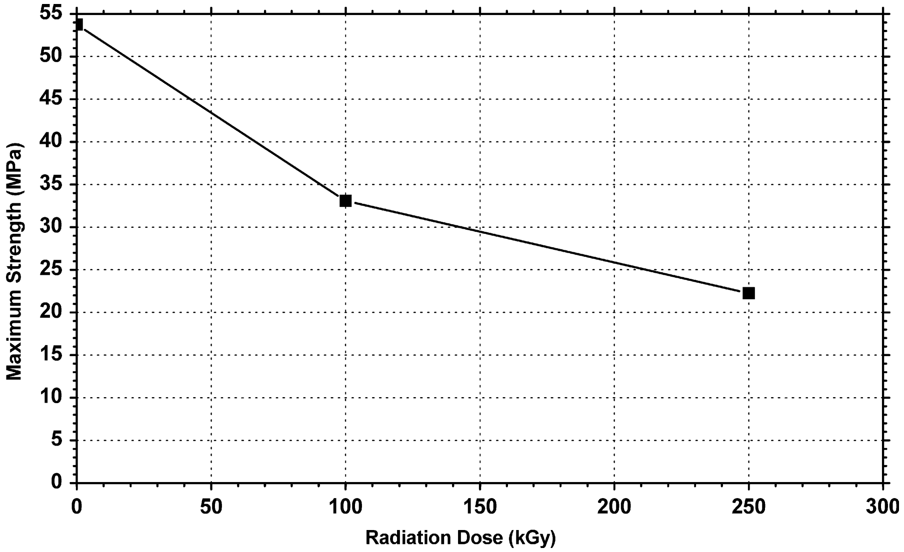


Figure 8.10 Effect of gamma radiation dose on the maximum strength of ultrahigh molecular weight polyethylene.[6]

Figure 8.11 Effect of gamma radiation dose on the elongation ultrahigh molecular weight polyethylene.[6]

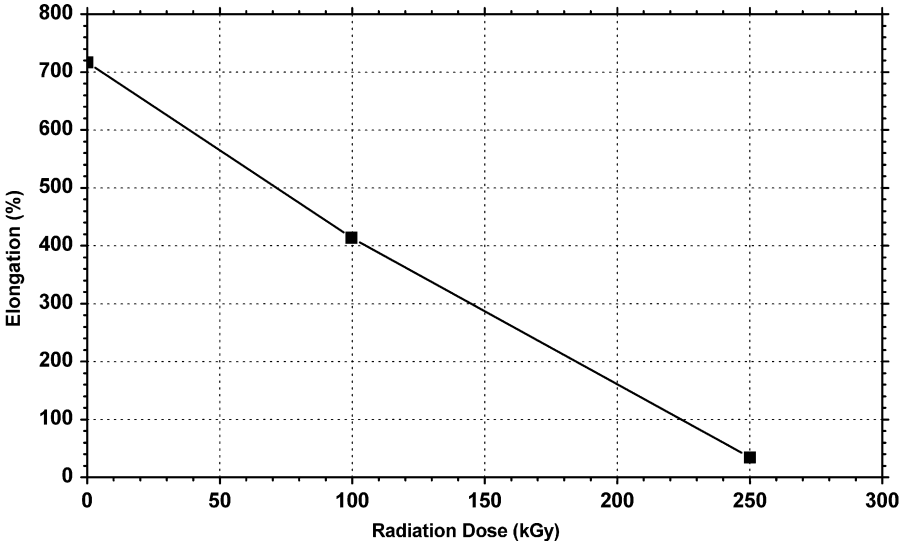


Figure 8.12 Wear rate versus radiation dose for ultrahigh molecular weight polyethylene UHMWPE used in total knee replacements.[7]

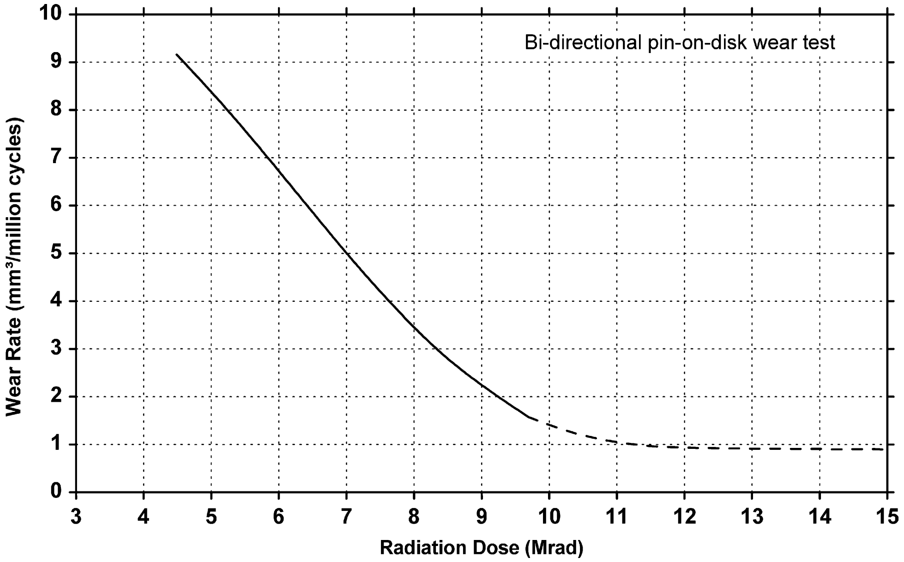


Figure 8.13 Degradation and oxidation of polypropylene when exposed to high-energy radiation.[6]

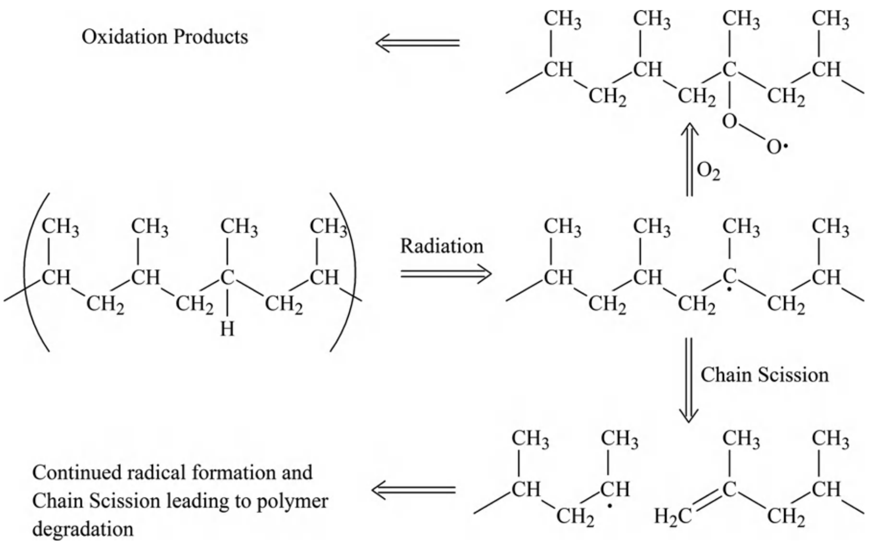


Table 8.17 Effect of Gamma Radiation Sterilization on Flint Hill Resources 13R9A Polypropylene[9]

	Radiation Dose (Mrad)						
	6.1*	6.1*	6.1*	5	5	5	5
Postexposure Conditioning II							
Type		Forced draft air oven	Type: forced draft air oven		Type: forced draft air oven	Type: forced draft air oven	Type: ambient conditions
Temperature (°C)		120	120		80	80	23
Time (h)	0	24	168	0	504	1008	8760
Properties Retained (%)							
Tensile strength at yield	106.7	113.1	0	94.1	106.3	106.3	104.8
Elongation	100	6.5	3.2	100	50	60	53.3
Surface and Appearance							
Δ Yellowness index	5.9	9.7	18.7	1	2.9	3.2	2.3

Note: (1) Sterilization conditions: Cobalt-60. (2) Postexposure conditions I: ASTM conditioning.
**Doses of 3.1 Mrad and 3.0 Mrad on consecutive days.*

8.2 Polypropylene

The three main types of PP generally available:

- **Homopolymers** are made in a single reactor with propylene and catalyst. It is the stiffest of the three propylene types and has the highest tensile strength at yield. In the natural state (no colorant added), it is translucent and has excellent see-through or contact clarity with liquids. In comparison to the other two types, it has less impact resistance, especially below 0 °C.
- **Random copolymers** (homophasic copolymers) are made in a single reactor with a small amount of ethylene (<5%) added, which disrupts the crystallinity of the polymer allowing this type to be the clearest. It is also the most flexible with the lowest tensile strength of the three. It has better room-temperature impact than homopolymer but shares the same relatively poor impact resistance at low temperatures.
- **Impact copolymers** (heterophasic copolymers), also known as block copolymers, are made in

Table 8.18 Effect of Gamma Radiation Sterilization Conditions on the Properties of Flint Hill Resources 13R9A Polypropylene[9]

Sterilization Conditions						
Radiation dose (Mrad)	5	5	3	3	3	3
Radiation intensity (megacuries)			1.6	2.0	3.5	1.5
Times reprocessed	0	7				
Properties Retained (%)						
Tensile strength at yield	103.4	97.8	98.9	99.3	96.7	95.9
Elongation	91.7	63.3	93.3	86.7	73.3	83.3
Surface and Appearance						
Δ Yellowness index	2.1	1.4	0.9	3	1.4	10

Table 8.19 Effect of Gamma Radiation Sterilization and Fluorescent Light Postconditioning for 336 and 2190 h on the Properties of Flint Hill Resources 13R9A Polypropylene[9]

Sterilization Conditions						
Radiation dose (Mrad)	1.5	3	5	1.5	3	5
Postexposure Conditioning						
Time (h)	336	336	336	2190	2190	2190
Properties Retained (%)						
Tensile strength at yield	100.8	101.8	102.3	100.7	100.5	101
Elongation	100	100	82.9	100	100	82.9
Melt flow rate	430.6	736.1	625	578.6	857.1	652.9
Surface and Appearance						
Δ Yellowness index	3.4	4.9	6.7	2.4	2.9	3

Note: (1) Postexposure conditions: storage under fluorescent light.

Table 8.20 Effect of Gamma Radiation Sterilization after Fluorescent Light Postconditioning for 4380 and 8766 h on the Properties of Flint Hill Resources 13R9A Polypropylene[9]

Sterilization Conditions						
Radiation dose (Mrad)	1.5	3	5	1.5	3	5
Postexposure Conditioning						
Time (h)	4380	4380	4380	8766	8766	8766
Properties Retained (%)						
Tensile strength at yield	100.7	100.2	101	99.5	98.3	97.8
Elongation	100	100	75.7	100	100	100
Melt flow rate	567.6	689.2	689.2	691.7	805.6	534.7
Surface and Appearance						
Δ Yellowness index	2.4	2.4	2.8	2.2	2.2	2.3

Note: (1) Postexposure conditions: storage under fluorescent light.

Table 8.21 Effect of Gamma Radiation Sterilization and Fluorescent Light Postconditioning for 13,140 and 17,531 h on the Properties of Flint Hill Resources 13R9A Polypropylene[9]

Sterilization Conditions						
Radiation dose (Mrad)	1.5	3	5	1.5	3	5
Postexposure Conditioning						
Time (h)	13140	13140	13140	17531	17531	17531
Properties Retained (%)						
Tensile strength @ yield	99.3	99.5	99	100	100.2	101
Elongation	100	100	100	100	100	100
Melt flow rate	691.7	805.6	534.7	554.1	770.3	752.7
Surface and Appearance						
Δ Yellowness index	1.8	2	2	0.9	0.7	0.7

Note: (1) Postexposure conditions: storage under fluorescent light.

Table 8.22 Effect of Gamma Radiation Sterilization and Storage in the Dark Postconditioning for 336 and 2190 h on the Yellowness Index of Flint Hill Resources 13R9A Polypropylene Polypropylene[9]

Sterilization Conditions						
Radiation dose (Mrad)	1.5	3	5	1.5	3	5
Postexposure Conditioning						
Time (h)	336	336	336	2190	2190	2190
Surface and Appearance						
Δ Yellowness index	3.5	4.9	6.7	4.5	5.7	6.9

Note: (1) Postexposure conditions: storage in dark.

Table 8.23 Effect of Gamma Radiation Sterilization and storage in the dark postconditioning for 4380 and 8765 h on the Yellowness Index of Flint Hill Resources 13R9A Polypropylene[9]

Sterilization Conditions						
Radiation dose (Mrad)	1.5	3	5	1.5	3	5
Postexposure Conditioning						
Time (h)	4380	4380	4380	8765	8765	8765
Surface and Appearance						
Δ Yellowness index	3.4	5.2	7.1	5.1	7.2	7.1

Note: (1) Postexposure conditions: storage in dark.

Table 8.24 Effect of Gamma Radiation Sterilization and Storage in the Dark Postconditioning for 13,140 and 17,531 h on the Yellowness Index of Flint Hill Resources 13R9A Polypropylene[9]

Sterilization Conditions						
Radiation dose (Mrad)	1.5	3	5	1.5	3	5
Postexposure Conditioning						
Time (h)	13,140	13,140	13,140	17,531	17,531	17,531
Surface and Appearance						
Δ Yellowness index	5.5	6.6	7.4	5.6	6.6	7.3

Note: (1) Postexposure conditions: storage in dark.

a two reactor system where the homopolymer matrix is made in the first reactor and then transferred to the second reactor where ethylene and propylene are polymerized to create ethylene propylene rubber in the form of microscopic nodules dispersed in the homopolymer matrix phase. These nodules impart impact resistance both at ambient and cold temperatures to the compound. This type has intermediate stiffness and tensile strength and is quite cloudy. In general, the more ethylene monomer is added, the greater the impact resistance with correspondingly lower stiffness and tensile strength.

Oriented and multilayered films of PP are also common.

Manufacturers and trade names: Ineos polypropylene; LlyondellBasell Adflex™, Mophen; ExxonMobil™ Bicor™, OPPalyte; Dow Chemical; and Flint Hill Resources.

Sterile applications and uses:

- Homopolymer: Thermoforming, slit film, and oriented fibers, high-clarity syringes and closures, sutures, drapes, and gowns.
- Random copolymer: Food, household chemicals, beauty aid products, clear containers, and hot-fill applications.
- Impact copolymers: Film, sheet, profiles, high-pressure resistance, medical trays, and thin-wall parts.

Table 8.25 Effect of Ethylene Oxide (EtO) Sterilization on LyondellBasell Pro-fax PF511 Polypropylene[11]

Gas Composition	**12% EtO and 88% Freon**				**8.6% EtO and 91.4% HCFC-124**				
Number of cycles	1		2		1		2		
Postexposure Conditioning II									
Time (h)	168	1344	168	1344	168	1344	168	1344	
Properties Retained (%)									**Test Method**
Tensile strength at yield	99.4	100	98.6	96.1	94	80	97.9	98.8	ASTM D638
Elongation at break	156.7	143.6	131	83.6	94	159.4	84.2	121.8	ASTM D638
Tensile modulus	69.6	109.8	54.3	20.7	23.4	96.2	83.2	22.3	ASTM D638
Dart impact (total energy)	128.6	100	164.3	42.9	114.3	142.9	178.6	142.9	ASTM D3763
Dart impact (peak energy)	71.4	71.4	100	35.7	78.6	107.1	92.9	100	ASTM D3763
Surface and Appearance									
Δ*E* Color	0.24	0.05	0.05	0.13	0	0.1	0.11	0.18	

Note: (1) Preexposure conditioning: 18 h, 37.8 °C, 60% RH. (2) Sterilization process: gas mixture as noted in table, 48.9 °C, 6 h, 60% RH. (3) Postexposure conditioning I: aeration, 127 mmHg, 37.8 °C, 18 h; postexposure conditioning II: ambient conditions, time as noted in table.

Sterilization resistance: The use of PP films in radiation-sterilized applications is somewhat limited. The high ratio of film surface area to mass, combined with the sensitivity of irradiated PP to oxygen-promoted degradation, causes them to be severely embrittled after normal sterilizing doses of radiation. Even resin formulations that yield highly radiation-resistant injection molded devices are badly degraded after irradiation in thin film form. Special formulations of medical PP are coming to market specifically to overcome this disadvantage. Blends of PP and metallocene-catalyzed, ethylene-based plastomers are particularly suited to the construction of highly radiation-resistant, thin-gauge medical device packages.

Gamma radiation resistance: Basell offers several grades that are specially formulated to minimize the effects after typical radiation sterilization dosages of up to 5 Mrad, as tested by Basell protocol. Catastrophic

Table 8.26 Effect of Ethylene Oxide (EtO) Sterilization on LyondellBasell Pro-fax 6323 Polypropylene[10]

Details	**12% EtO and 88% Freon**		**8.6% EtO and 91.4% HCFC-124**	
Postexposure Conditioning				
Aeration; air changes per hour	10	30	10	30
Temperature (°C)	32.2	54.4	32.2	54.4
Ethylene Oxide Residuals Determined (ppm)				
Little or no aeration	451	451	415	415
17-h aeration	–	34	–	40
24-h aeration	138	25	163	36
48-h aeration	49	14	140	26
72-h aeration	25	–	64	–

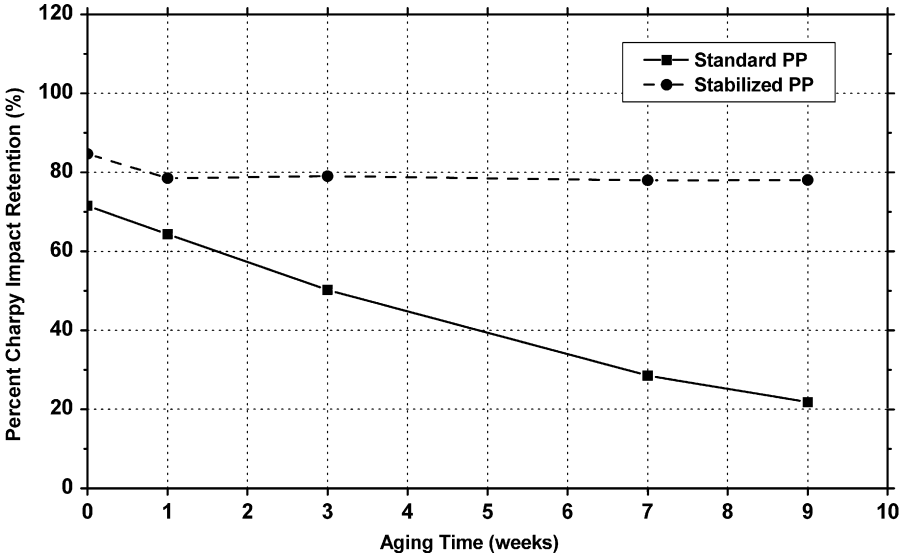
Note: (1) Preexposure conditioning: 18 h, 37.8 °C; 60% RH. (2) Sterilization process: gas mixture as noted in table, 48.9 °C, 6 h, 60% RH. (3) Postexposure conditioning: aeration as indicated, 37.8 °C, 18 h; 60% RH.

Table 8.27 The Effect of EtO Sterilization on the Properties of Polypropylene[5]

Carrier Gas	Sterilization	Postexposure Time	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Instrumented Dart Impact Peak Energy (J)	Izod (J/m)
Control	Unexposed		32	204	1370	42	1380	n/a	32
Average standard deviation (%)			2	14	10	4	5		0
HCFC-124	One cycle	1 week	33	61	1330	44	1520	n/a	27
		8 weeks	33	72	1280	49	1620	n/a	32
	Three cycles	1 week	33	61	1360	45	1470	n/a	32
		8 weeks	33	53	1300	49	1580	n/a	32
Average standard deviation (%)			2	86	5	3	7		0
HCFC-124/22	One cycle	1 week	33	73	1340	45	1450	n/a	43
		8 weeks	33	103	1330	46	1590	n/a	43
	Three cycles	1 week	33	59	1250	47	1500	n/a	43
		8 weeks	34	75	1340	46	1530	n/a	37
Average standard deviation (%)			2	65	16	3	7		0
EtO	One cycle	1 week	32	118	1260	45	1580	n/a	32
		8 weeks	33	72	1210	47	1600	n/a	37
	Three cycles	1 week	32	117	1230	48	1530	n/a	27
		8 weeks	33	55	1300	48	1560	n/a	37

Note: n/a, not applicable.

Figure 8.14 Impact retention properties of stabilized and unstabilized polypropylene after exposure to 38 kGy gamma radiation and aging at 80 °C.[6]



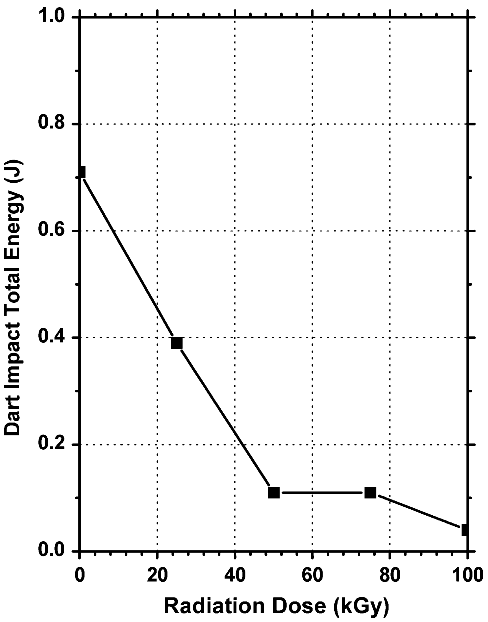


Figure 8.15 Dart drop impact resistance of gamma-irradiated polypropylene after aging 21 days at 60 °C.[10]

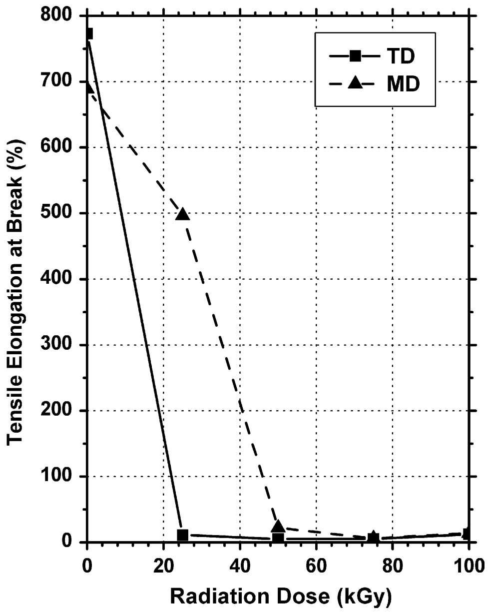


Figure 8.16 Tensile elongation at break of gamma-irradiated polypropylene (TD-Transverse direction and MD-machine direction) after aging 21 days at 60 °C.[10]

failures have been reported in gamma sterilized PP materials that experienced shelf-life storage. This was a result of long-term degradation. "Long-lived free radicals trapped in the crystalline domains migrated toward the crystalline/amorphous interface combining with available oxygen to form peroxy and hydroperoxy radicals that initiated degradation near the interface. As enough tie molecules between crystallites were cut through the chain scission process, significant reduction of PP's elongation could occur which would lead to catastrophic failures."[8]

PP materials that are adequately stabilized can survive the radiation stabilization process with enough antioxidant remaining to protect the sterilized product from further degradation. The stability of sterilized PP depends on the supplier stabilizer

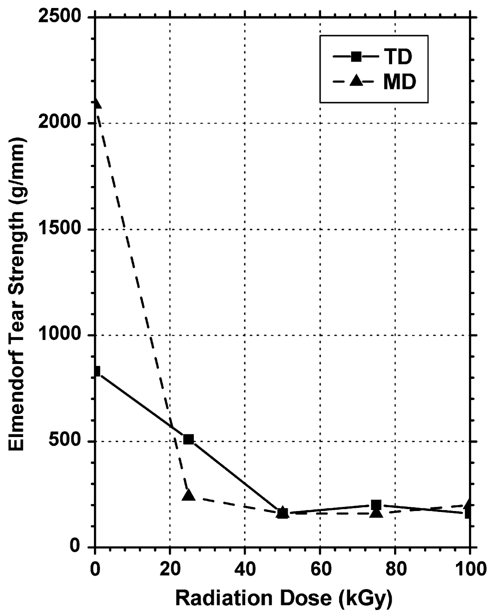


Figure 8.17 Elmendorf tear strength of gamma-irradiated polypropylene (TD-transverse direction and MD-machine direction) after aging 21 days at 60 °C.[10]

system, and the stability of a radiation-sterilized PP can be simply and rapidly determined by oxygen induction testing.[8]

The degradation reactions as a result of high-energy radiation are shown in Fig. 8.13.

Autoclave sterilization: PP has a melting temperature high enough for autoclave application.

Data for PP plastics are found in Tables 8.17–8.27 and Figs 8.14–8.18.

Flint Hill Resources 13R9A is random propylene–ethylene copolymer, gamma radiation stabilized.

8.3 Poly-4-Methyl-1-Pentene

4-Methyl-1-pentene based polyolefin is a lightweight, functional polymer that displays a unique combination of physical properties and characteristics due to its distinctive molecular structure, which includes a bulky side chain as shown in Fig. 8.19. Polymethyl pentene (PMP) possesses many characteristics inherent in traditional polyolefins such as excellent electrical insulating properties and strong hydrolysis resistance. Moreover, it features low dielectric, superb clarity, transparency, gas permeability, heat and chemical resistance, and release qualities. Its CAS number is 89-25-8.

Manufacturers and trade names: Mitsui Chemicals TPX™ Opulent™, Honeywell PMP; and Chevron Philips Crystalor – discontinued.

Sterile applications and uses: It can be used for extruded and film products, injection molded and blow molded application items, including:

- Paper coatings and baking cartons
- Release film and release paper
- High-frequency films
- Food packaging such as gas permeable packages for fruit and vegetables.

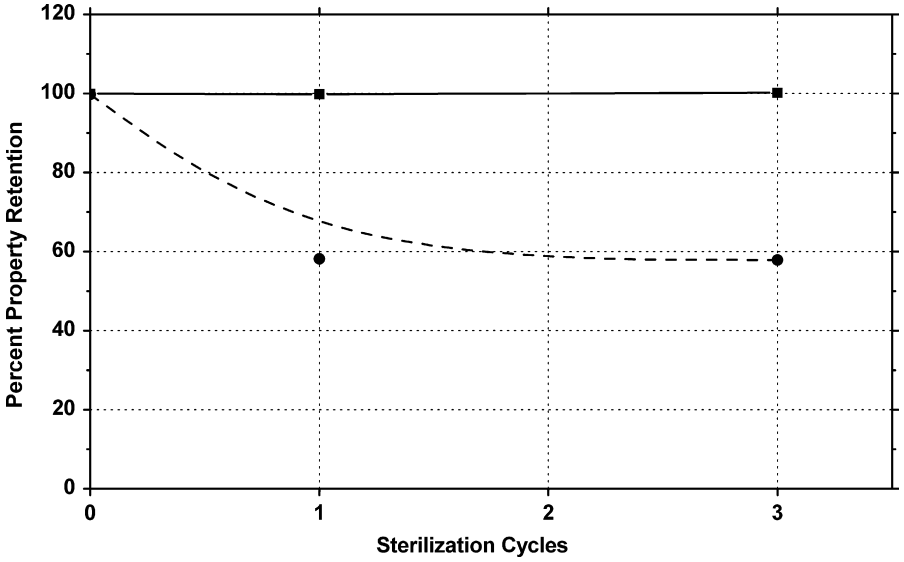


Figure 8.18 Effect of ethylene oxide sterilization on the property retention of propylene.[6]

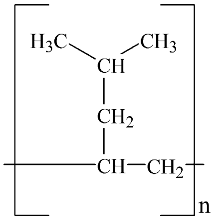


Figure 8.19 Structure of Poly-4-Methyl-1-Pentene.

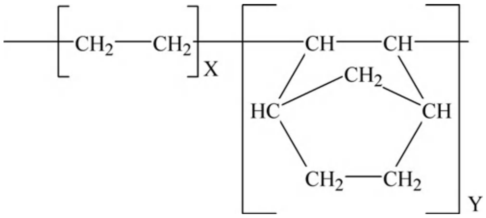


Figure 8.20 Chemical structure of cyclic olefin copolymers.

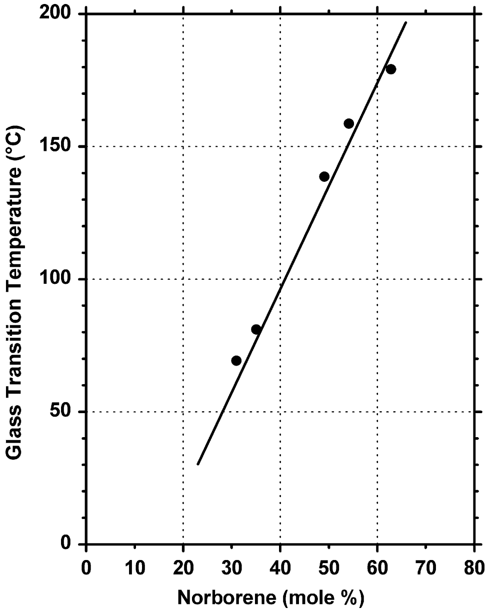


Figure 8.21 TOPAS® glass transition temperature versus norbornene content.

Table 8.28 Compatibility of Sterilization Methods with Ticona TOPAS® COC[12]

TOPAS Product Code	Hot Steam			EtO	High-Energy Radiation	
	121 °C	134 °C	143 °C		Gamma	Electrons
8007	−	−	−	+	+	+
5013	−	−	−	+	+	+
6013	+	−	−	+	+	+
6015	+	+	+	+	+	+

Table 8.29 The Effect of EtO Sterilization on the Properties of Polyolefin Plastomer[5]

Carrier Gas	Sterilization	Postexposure Time	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Instrumented Dart Impact Peak Energy (J)	Izod (J/m)
Control	Unexposed		3.9	>600	27	n/a	n/a	12	n/a
Average standard deviation (%)			4		4			43	
HCFC-124	One cycle	1 week	3.8	>600	17	n/a	n/a	15	n/a
		8 weeks	4.1	>600	16	n/a	n/a	9	n/a
	Three cycles	1 week	3.9	>600	16	n/a	n/a	9	n/a
		8 weeks	4.1	>600	15	n/a	n/a	8	n/a
Average standard deviation (%)			7		10			33	
HCFC-124/22	One cycle	1 week	4.0	>600	17	n/a	n/a	6	n/a
		8 weeks	4.0	>600	20	n/a	n/a	8	n/a
	Three cycles	1 week	4.0	>600	18	n/a	n/a	12	n/a
		8 weeks	3.9	>600	210	n/a	n/a	10	n/a
Average standard deviation (%)			4		33			20	
EtO	One cycle	1 week	4.0	>600	16	n/a	n/a	14	n/a
		8 weeks	4.1	>600	21	n/a	n/a	6	n/a
	Three cycles	1 week	4.1	>600	17	n/a	n/a	6	n/a
		8 weeks	3.9	>600	17	n/a	n/a	9	n/a

Note: n/a, not applicable.

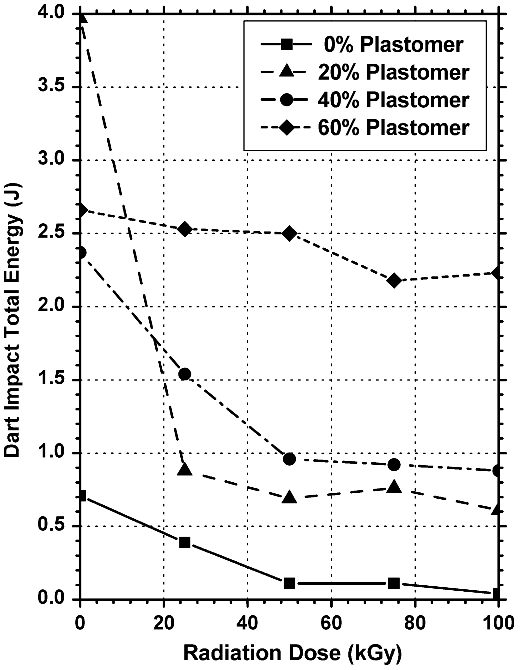


Figure 8.22 Dart drop impact resistance of gamma-irradiated polypropylene/plastomer blends after aging 21 days at 60 °C.[10]

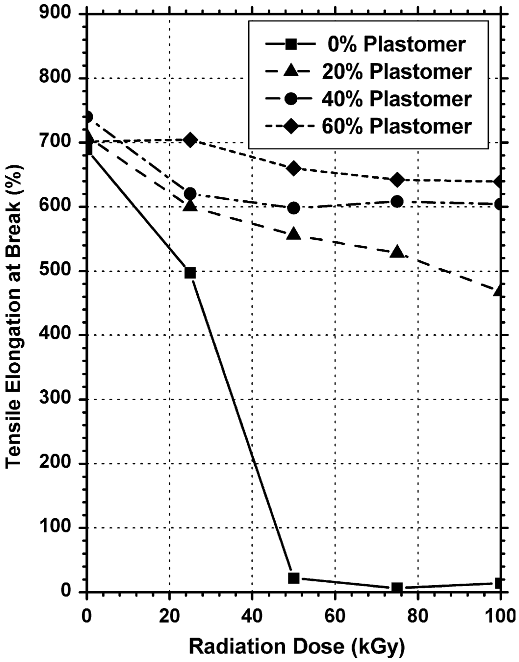


Figure 8.24 Tensile elongation (MD-machine direction) at break of gamma-irradiated polypropylene/plastomer blends after aging 21 days at 60 °C.[10]

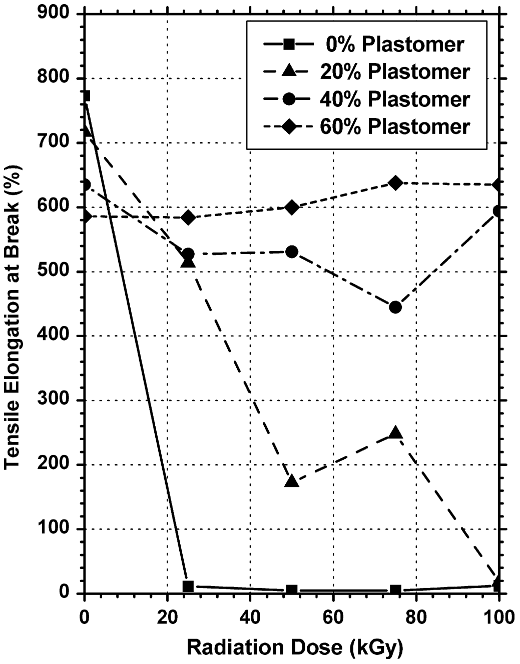


Figure 8.23 Tensile elongation (TD-transverse direction) at break of gamma-irradiated polypropylene/plastomer blends after aging 21 days at 60 °C.[10]

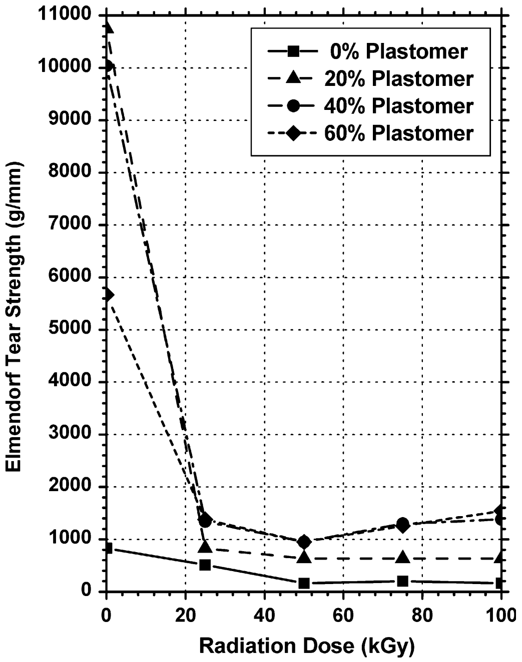


Figure 8.25 Elmendorf tear strength (TD transverse direction) of gamma-irradiated polypropylene/plastomer blends after aging 21 days at 60 °C.[10]

The water absorption of Mitsui Chemicals TPX® and other PMPs is very low and therefore dimensional change caused by hydrolysis cannot be observed. Even in boiling water, PMP does not hydrolyze. Therefore, PMP is an excellent material for such applications that require steam sterilization.

8.4 Cyclic Olefin Copolymer

Cyclic olefin copolymer (COC) is an amorphous polyolefin made by reaction of ethylene and norbornene in varying ratios. Its structure is given in Fig. 8.20. The norbornene structure in Fig. 8.20 is designated "Y." The properties can be customized by changing the ratio of the monomers found in the polymer. Figure 8.21 shows the effect of norbornene content on the glass transition temperature of the polymer. Being amorphous it is transparent. Other performance benefits include:

- Low density
- Extremely low water absorption
- Excellent water vapor barrier properties
- High rigidity, strength, and hardness
- Variable heat deflection temperature up to 170 °C
- Very good resistance to acids and alkalis.

Manufacturers and trade names: Mitsui Chemical APEL; Ticona; and TOPAS®.

Sterile applications and uses: TOPAS® COC is used as a core layer in push-through packaging, either in five-layer coextruded or three-layer laminated film structures; flexible and rigid packaging for food and consumer items; syringes, vials, and other prefillable containers. COC can be used in laboratory and diagnostic devices including syringes, vials and ampoules, cuvettes, microtiter plates, test tubes, petri dishes, pipettes, and specialized labware; needleless injectors, injector pens, inhalers, and blister packs.

Standard TOPAS film grades:

- TOPAS 9506F-04: High-clarity extrusion grade for use in food and medical packaging as either a discrete layer in multilayer film or in blends with PE. It has a low glass transition temperature (T_g) and provides excellent clarity, stiffness, water vapor barrier, and good thermoformability.
- TOPAS 9506: This is especially recommended for use as discrete layers in blown films due to its higher molecular weight and increased melt strength for better bubble stability.
- TOPAS 8007F-04: High-clarity extrusion grade for pharmaceutical, medical, and food packaging. It is most often used in coextruded cast film applications, e.g. blister film, and offers excellent clarity, stiffness, water vapor barrier, and thermoformability. This grade has the broadest range of regulatory approvals within the packaging portfolio.
- TOPAS 8007F-400: Standard extrusion grade with a broader extrusion processing window (equipment and conditions) and is recommended for the extrusion of discrete 100% TOPAS layers or high (>65%) COC content blends. It is especially recommended for use in grooved feed extruders.
- TOPAS 6013F-04: High-clarity extrusion grade having high temperature resistance for pharmaceutical, medical, and food packaging. It has a high glass transition temperature (T_g) and provides excellent clarity, stiffness, water vapor barrier, and thermoformability. It can be used in coextruded films as a discrete layer or in blends with PE.

COCs can undergo sterilization by gamma radiation and ethylene oxide. Those copolymers that have a high glass transition temperature and a high heat deflection temperature can undergo steam and dry heat sterilization. COC grades for steam and dry heat sterilization should be selected appropriately. See Table 8.28 for guidance on sterilization methods for TOPAS® COC products. TOPAS is also compatible with peroxide plasma sterilization.

8.5 Plastomer

Polyolefin Plastomers (POPs) are characterized by their narrow composition distribution and narrow molecular weight distribution. This makes them extremely tough and exceptionally clear and gives them improved taste, color, and odor properties and very good sealability. They are typically polyolefin copolymers that are prepared with special catalysts and processes that allow control of molecular weight and crystallinity distribution. The unique molecular

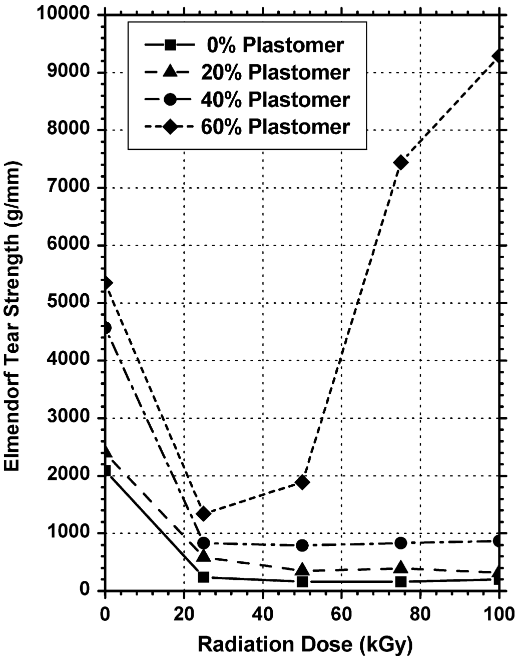


Figure 8.26 Elmendorf tear strength (MD-machine direction) of gamma-irradiated polypropylene/plastomer blends after aging 21 days at 60 °C.[10]

architecture of POPs provides films, fibers, sheet, and molded parts with an outstanding combination of excellent optics, sealing and hot tack performance, plus elasticity, flexibility, softness, and compatibility in blends.

Manufacturers and trade names: Dow VERSIFY™, AFFINITY™, ExxonMobil Exact™, and Japan Polychem Kernel®.

Dow Chemical VERSIFY™ and AFFINITY™ POPs are a versatile family of specialty propylene–ethylene copolymers produced with a revolutionary catalyst in combination with Dow's proprietary INSITE™ Technology and Solution Process.

ExxonMobil Exact™ POPs are ethylene alpha olefin copolymers that bridge the gap between elastomers and plastics, with rubber-like properties and the processability of plastic.

Data for plastomer plastics are found in Table 8.29 and Figs 8.22–8.26.

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9 Polyvinyls and Acrylics

This chapter focuses on polymers made from monomers that contain a carbon−carbon double bond through which the polymer is made by addition polymerization as discussed in Section 2.1.1. An alkene, also called an olefin, is a chemical compound made of only carbon and hydrogen atoms containing at least one carbon-to-carbon double bond. The simplest alkenes, with only one double bond and no other functional groups, form a homologous series of hydrocarbons with the general formula C_nH_{2n}. The two simplest alkene of this series is ethylene. If one of the hydrogens on the ethylene molecule is changed to chlorine, the molecule is called vinyl chloride, the basis of polyvinyl chloride, commonly called PVC. There are many other vinyl monomers that substitute different functional groups onto the carbon−carbon double bond. Vinyl alcohol is a particularly important one. Acrylic polymers are also polymerized through the carbon−carbon double bond. Methyl methacrylate is the monomer used to make poly(methyl methacrylate).

This chapter covers those additional polymers that are not strictly hydrocarbons, containing only carbon and hydrogen.

9.1 Ethylene−Vinyl Acetate Copolymer

Ethylene−vinyl acetate (EVA) is a copolymer of ethylene and vinyl acetate as shown in Fig. 9.1. Its CAS number is 24937-78-8. Commercial resins range in vinyl acetate content from 7.5 to 33 wt%. Some grades are available with antiblock and slip additives. DuPont™ Elvax® grades vary by vinyl acetate content.

EVA properties vary depending on vinyl acetate content:

Higher vinyl acetate content results in:

- Increased gas permeability
- Increased impact strength − toughness
- Improved optical qualities − clarity
- Increased flex-crack resistance
- Increased cling
- Increased solubility
- Increased coefficient of friction
- Decreased sealing temperature-softening point
- Increased crystallinity
- Reduced stiffness
- Reduced surface hardness.

Manufacturers and trade names: DuPont™ Appeel® and Elvax®, Celanese EVA Performance Polymers Ateva®, Lanxess Levapren®, Baymond® L and Levamelt®, and Arkema Evatane®.

Sterile applications: EVA is used as a monolayer film in applications where PVC cannot be used due to possible plasticizer extraction, as a coating or adhesive layer with multiple polymers such as high density polyethylene, ionomers, etc., and as a sealant in barrier bags for primal and subprimal cuts of meat, and for medical packaging.

Gamma radiation resistance: Sterilized by gamma radiation (up to 25 kGy).

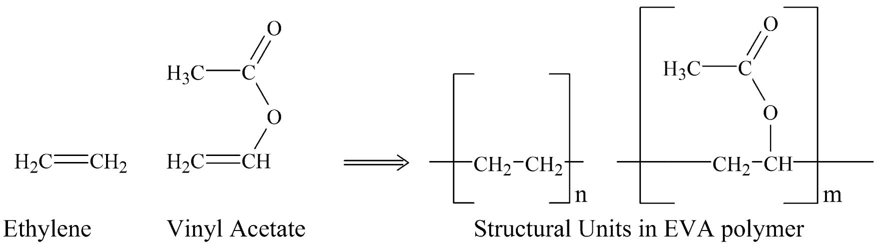
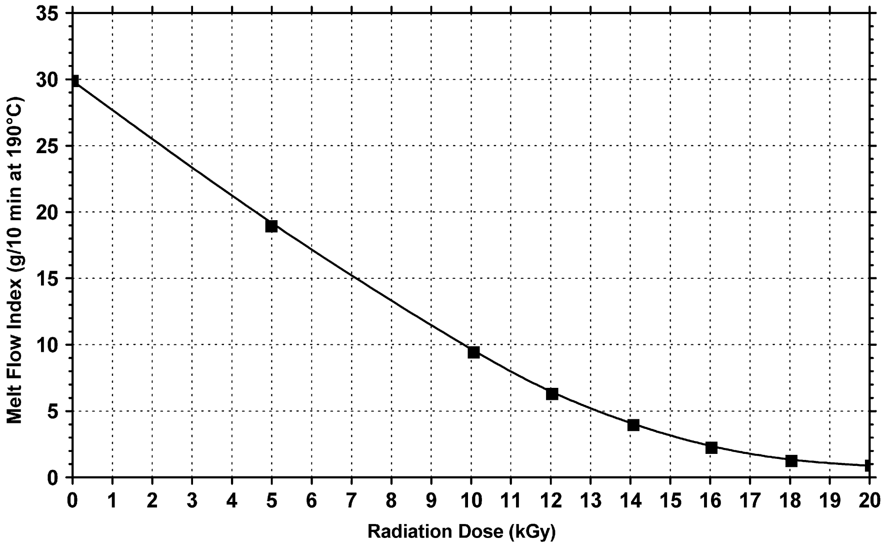


Figure 9.1 Structure of ethylene−vinyl acetate polymers.

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00009-5

Figure 9.2 Melt flow index as a function of electron beam dose in ethylene–vinyl acetate.[1]



Ethylene oxide (EtO) resistance: EVA may be EtO sterilized.

Data for EVA plastics are found in Fig. 9.2.

9.2 Ethylene–Vinyl Alcohol Copolymer

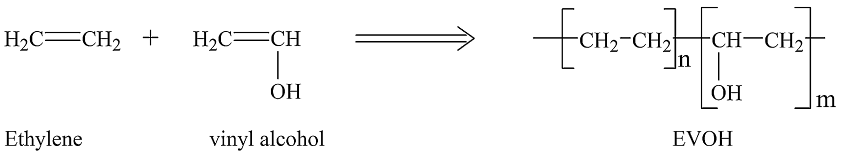
Ethylene–vinyl alcohol (EVOH) is a copolymer of ethylene and vinyl alcohol. The structure is shown in Fig. 9.3 and EVOH has a CAS number of 26221-27-2. These materials are highly crystalline and are produced with various levels of ethylene content.

The predominant product line is Eval Company of America (Kuraray) EVAL™. The general classes of the EVAL™ product line are show in Table 9.1. The films are often heat treated and oriented. These processes can dramatically affect the properties.

EVOH film has many desirable properties that are summarized as follows:

- Antistatic properties: Since EVOH resin is a highly antistatic polymer, dust is prevented from building up on the package when used as a surface layer.
- Luster and transparency: EVOH resins produce a high gloss and low haze, resulting in outstanding clarity characteristics. The use of EVOH resin as the outer surface of a package provides excellent sparkle for improved package appearance.
- Printability: With an –OH group in its molecular chain, the EVOH resin surface can be easily printed without special treatment.
- Resistance to oil and organic solvents: EVOH resins resist oils and organic solvents, making them particularly suitable for packaging oily foods, edible oils, mineral oils, agricultural pesticides, and organic solvents.
- Weather resistance: EVOH resins display excellent weatherability. Even when exposed to outdoor conditions, the polymer retains its color and does not turn yellow or become opaque. Mechanical property changes are minimal, demonstrating an overall high resistance to weather effects.
- Permeability: EVOH resins offer outstanding gas (oxygen, carbon dioxide, nitrogen, and helium) barrier properties and maintain their barrier property over a wide range of humidity. The

Figure 9.3 The formation and structure of ethylene–vinyl alcohol copolymer.



$$H_2C{=}CH_2 + H_2C{=}\underset{\displaystyle OH}{\underset{|}{CH}} \Longrightarrow \left[\left[CH_2{-}CH_2 \right]_n \left[\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2 \right] \right]_m$$

Table 9.1 EVAL™ Ethylene–Vinyl Alcohol (EVOH) Copolymer Polymer Grade Series[2]

EVAL™ Series	Ethylene Content (mol %)	General Characteristics
L Series	27	Has the lowest ethylene content of any EVOH and is suitable as an ultra high-barrier grade in several applications.
F Series	32	Offers superior barrier performance and is widely used for automotive, bottle, film, tube, and pipe applications.
T Series	32	Specially developed to obtain good layer distribution in thermoforming and has become the industry standard for multilayer sheet applications.
J Series	32	Offers thermoforming results even superior to those of T and can be used for unusually deep draw or sensitive sheet-based applications.
H Series	38	Has a balance between high-barrier properties and long-term run stability. Especially suitable for blown film, special "U" versions exist to allow improved processing and longer running times even on less sophisticated machines.
E Series	44	Has a higher ethylene content that allows for greater flexibility and even easier processing. Different versions have been especially designed for cast and blown film as well as for pipe.
G Series	48	Has the highest ethylene content, making it the best candidate for stretch and shrink film applications.

oxygen-barrier properties of EVOH will vary according to the ethylene content in the polymer. Packages containing EVOH resins can effectively retain fragrances and preserve the aroma of the contents within the package. At the same time, undesirable odors are prevented from entering or leaving the package.

Manufacturers and trade names: Eval Company of America (Kuraray) EVAL™ and Soarus LLC Soarnol®.

Sterile applications: Pharmaceutical and food packaging.

Gamma radiation resistance: EVAL EVOH resins maintain their physical properties after being irradiated by a 5-Mrad dose of gamma or beta rays, the only appreciable effect being a reduction in elongation at break. No discoloration after irradiation was noticed.

EVOH copolymers listed in 21 CFR 177.1360 are widely used as a nonfood contact barrier layer in food packaging. They significantly improve the gas and vapor barrier properties of multilaminate food packages. EVOH copolymers are not currently approved for use in contact with food during irradiation. Komolprasert et al. (2003b) and McNeal et al. (2004) studied the effects of 5–50 kGy e-beam irradiation on an EVOH copolymer powder (38 mol % ethylene, 1.17 g/cc) manufactured with and without α-methyl styrene dimer as an inhibitor.[3]

For volatiles, e-beam radiation produced many low molecular weight aliphatic hydrocarbons and oxidation products in EVOH powder without inhibitor, while fewer polymer breakdown products were detected in EVOH powder with inhibitor. For EVOH powder containing inhibitor, the major volatiles were breakdown products of the inhibitor, including alkyl aromatics such as tert-butyl benzene and isobutyl benzene, and oxygenated aromatics such as acetophenone and 2-phenyl isopropanol. The results, contained in Table 9.2, indicate that e-beam irradiation also produced propanal, methyl ethyl ketone, 2-butanol, tert-butyl benzene, and 2-methylpropylbenzene in measurable amounts. Volatiles detected in both nonirradiated and irradiated test specimens were acetic acid, cumene, α-methyl styrene, acetophenone, and 2-phenyl isopropanol. The concentrations of most volatile substances in the EVOH powder samples increased with the irradiation dose, but the increase in concentration was nonlinear.

Data for EVOH plastics are found in Tables 9.2–9.6.

For nonvolatiles, the percent extractable soluble solid from EVOH powder was greater with 50%

Table 9.2 Concentrations (μg/g) of Volatiles Present in Nonirradiated (NIR) Ethylene–Vinyl Alcohol (with α-methyl styrene dimer inhibitor) Powders and after 5, 25, and 50 kGy E-Beam Irradiation (IR)[3]

Volatile	#Rep	NIR	5 kGy	25 kGy	50 kGy
Propanal	4–6	<0.2	(0.28 ± 0.05)S	(0.5 ± 0.08)*	(0.54 ± 0.07)*
Methyl ethyl ketone	4–6	<0.2	(3.0 ± 0.23)*	(2.9 ± 0.21)*	(5.1 ± 0.79)*
2-Butanol	4–6	<0.1	(4.1 ± 0.35)*	(6.1 ± 0.61)*	(7.0 ± 0.85)*
Acetic acid (irradiated/ nonirradiated)	4–6	1	1.33	1.97	2.75
Cumene	4–6	0.72 ± 0.06	(7.5 ± 0.56)*	(7.2 ± 0.51)*	(4.8 ± 0.41)*
α-Methyl styrene	4–6	2.1 ± 0.07	(1.3 ± 0.1)*	(0.59 ± 0.06)*	(0.45 ± 0.06)*
Tert-butyl benzene	4–6	< 0.1	(4.4 ± 0.44)*	(2.3 ± 0.21)*	(1.4 ± 0.19)*
2-Methyl propyl benzene	4–6	< 0.1	(1.3 ± 0.11)*	(0.64 ± 0.07)*	(0.37 ± 0.06)*
Acetophenone	4–6	0.68	(7.6 ± 0.83)*	(5.6 ± 0.40)*	(3.8 ± 0.55)*
2-Phenyl-2-propanol	4–6	1.08 ± 0.07	(4.6 ± 0.45)*	(6.1 ± 1.1)*	(4.9 ± 0.65)*

Note: Acetic acid concentrations represented in ratios (IR/NIR); 1 = no change nor increase.

**Significant at* $P < 0.05$ *(IR versus NIR).*

Table 9.3 Percent Soluble Solids Extracted from Nonirradiated (NIR) Ethylene–Vinyl Alcohol (with inhibitor) Powders and after E-Beam Irradiation at 5, 25, and 50 kGy, using Aqueous 10% Ethanol and 50% Ethanol Solution Maintained at 40 °C for 2, 5, and 10 Days[3]

Food Simulant	Day	NIR	5 kGy	25 kGy	50 kGy
10% ETOH	2	0.43 ± 0.20	(0.36 ± 0.09)**	(0.24 ± 0.03)*	(0.47 ± 0.21)**
	5	0.45 ± 0.10	(0.47 ± 0.08)**	(0.50 ± 0.17)**	(0.41 ± 0.10)**
	10	0.64 ± 0.09	(0.74 ± 0.06)**	(0.52 ± 0.21)**	(0.62 ± 0.03)**
50% ETOH	2	1.07 ± 0.04	(1.15 ± 0.15)**	(1.79 ± 0.54)**	(1.79 ± 0.05)**
	5	1.97 ± 0.39	(1.90 ± 0.75)**	(1.36 ± 0.66)**	(1.79 ± 0.54)**
	10	2.75 ± 0.32	(2.15 ± 0.33)**	(2.23 ± 0.45)**	(2.52 ± 0.72)**

Insignificant at* $P < 0.05$ *(IR versus NIR);Significant at* $P < 0.05$ *(IR versus NIR).*

Table 9.4 Percent Soluble Solids Extracted from Nonirradiated (NIR) Ethylene–Vinyl Alcohol (without inhibitor) Powders and after E-Beam Irradiation at 5, 25, and 50 kGy, Using Aqueous 10% Ethanol and 50% Ethanol Solution Maintained at 40 °C for 2, 5, and 10 Days[3]

Food Simulant	Day	NIR	5 kGy	25 kGy	50 kGy
10% ETOH	2	0.27 ± 0.05	(0.29 ± 0.03)*	(0.33 ± 0.02)*	(0.37 ± 0.01)**
	5	0.30 ± 0.02	(0.35 ± 0.01)**	(0.37 ± 0.02)**	(0.41 ± 0.01)**
	10	0.30 ± 0.01	(0.33 ± 0.02)*	(0.35 ± 0.01)**	(0.39 ± 0.02)**
50% ETOH	2	1.12 ± 0.06	(1.25 ± 0.16)**	(1.54 ± 0.06)**	(1.56 ± 0.15)**
	5	1.22 ± 0.11	(1.32 ± 0.20)*	(1.76 ± 0.25)**	(1.72 ± 0.20)**
	10	1.24 ± 0.06	(1.53 ± 0.20)**	(1.84 ± 0.18)**	(1.94 ± 0.20)**

**Insignificant at* $P < 0.05$ *(IR versus NIR); **Significant at* $P < 0.05$ *(IR versus NIR),*

Table 9.5 Effect of Gamma Ray and Beta Ray Sterilization on Kuraray EVAL™ EP-F Type Ethylene−Vinyl Alcohol[4]

Exposure Type	**Unexposed**	**Gamma Radiation**		**Beta Radiation**
Radiation dose (Mrad)	–	2	5	5
Properties Retained				
Tensile strength at break, MD (MPa)	95.15	87.29	78.46	87.29
Tensile strength at break, TD (MPa)	39.23	41.19	62.77	37.27
Tensile strength at yield, MD (MPa 56.88)	62.78	59.81	57.85	
Tensile strength at yield, TD (MPa)	59.81	66.67	–	60.81
Elongation at break, MD (%)	230	210	160	220
Elongation at break, TD (%)	220	250	17	90

Note: MD, machine direction; TD, transverse direction.

Table 9.6 Effect of Gamma Ray and Beta Ray Sterilization on Kuraray EVAL™ EP-E Type Ethylene−Vinyl Alcohol[3]

Exposure Type	**Unexposed**	**Gamma Radiation**		**Beta Radiation**
Radiation dose (Mrad)	–	2	5	5
Properties Retained				
Tensile strength at break, MD (Mpa)	78.49	57.84	45.12	61.78
Tensile strength at break, TD (MPa)	35.30	32.37	51.02	31.37
Tensile strength at yield, MD (MPa 56.88)	51.98	50.02	32.37	49.04
Tensile strength at yield, TD (MPa)	53.95	49.02	–	49.02
Elongation at break, MD (%)	230	270	130	260
Elongation at break, TD (%)	280	100	10	120

Note: MD, machine direction; TD, transverse direction.

ethanol than with 10% ethanol (Tables 9.3 and 9.4). For EVOH powder with inhibitor, e-beam irradiation at 5−50 kGy doses did not significantly increase the levels of extractable solids soluble in 10% and 50% ethanol (Table 9.3). On the other hand, for EVOH powder without inhibitor, e-beam radiation significantly increased the levels of extractable soluble solids in both 10% and 50% ethanol (Table 9.4). EVOH powder containing α-methyl styrene dimer was chemically more stable than EVOH without when exposed to e-beam radiation up to 50 kGy.[3]

9.3 Polyvinyl Chloride

PVC is a flexible or rigid material that is chemically nonreactive. Rigid PVC is easily machined, heat formed, welded, and even solvent cemented. PVC can also be machined using standard metal working tools and finished to close tolerances and finishes without great difficulty. PVC resins are normally mixed with other additives such as impact modifiers and stabilizers, providing hundreds of PVC-based materials with a variety of engineering properties.

There are three broad classifications for rigid PVC compounds: Type II, Chlorinated polyvinyl chloride (CPVC), and Type I. Type II differs from Type I due to greater impact values, but lower chemical resistance. CPVC is PVC that has been chlorinated via a free radical chlorination reaction. CPVC has greater high temperature resistance. These materials are considered “unplasticized” because they are less flexible than the plasticized formulations. PVC has a broad range of applications, from high-volume construction-related products to simple electric wire insulation and coatings. CAS No 9002-86-2, 8063-94-3, 51248-43-2, and 93050-82-9.

PVC is the most widely used resin in medical devices. Approximately 25% of all plastic medical products are made of PVC, according to most market estimates. The main reason is the resin's low cost, ease of processing, and the ability to tailor its properties to a wide range of applications. The following is a more through list of reasons for the popularity of PVC in medical devices:

- It has been used successfully for over 50 years in various medical devices with no known adverse or toxic effects.
- Plasticized PVC has good clarity so that tubes and other products retain their transparency to allow for continual monitoring of fluid flow.
- PVC can be manufactured in a range of flexibilities and its resistance to kinking in tubing reduces the risk of fluid flow being interrupted.
- PVC can be used in a wide range of temperatures, and it retains its flexibility, strength, and durability at low temperatures.
- PVC formulations exhibit excellent strength and toughness.
- PVC exhibits very good chemical resistance and stability and is also biocompatible for applications in blood bags and drug delivery.
- Plasticized PVC maintains its product integrity under various sterilization environments like steam, radiation, and ethylene oxide.
- PVC can be easily welded to various other plastics by a wide range of methods.
- Its relatively lower cost and high-performance value maintains its position as the number one plastic used in medical devices.
- PVC meets safety and cost criteria for a wide variety of medical applications, especially for single-use disposable devices.

A large number of plasticizers have been used with PVC to reduce rigidity, the most common family being the phthalates, especially di(2-ethylhexyl) phthalate (DEHP). It is sometimes called dioctyl phthalate and abbreviated to DOP. These plasticizers are incorporated in amounts ranging from 40% to 65%. Its structure is shown in Fig. 9.4. The effect of DEHP loading on Shore A hardness is shown in Fig. 9.5.

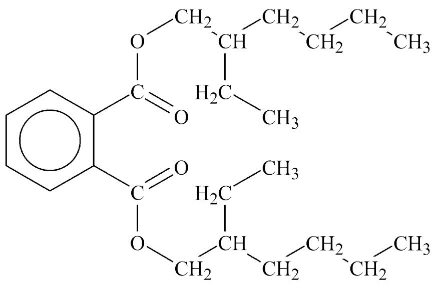


Figure 9.4 Structure of di(2-ethyl hexyl) phthalate.

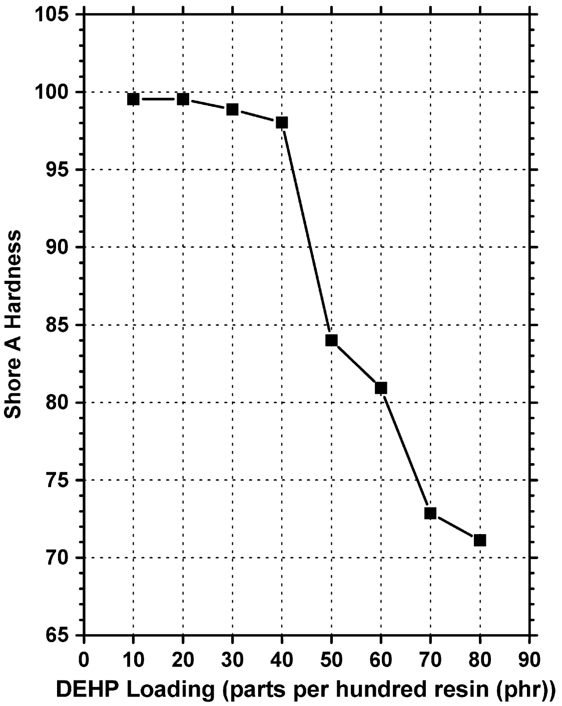


Figure 9.5 Effect of di(2-ethyl hexyl) phthalate loading on the Durometer Shore A hardness of polyvinyl chloride.

Some of the other plasticizers used in medical applications are the following:

- Diisobutyl phthalate
- Trioctyl trimellitate
- Viernol — polymeric plasticizer
- Dioctyl phthalate
- Di-*n*-decyl phthalate
- Acetyl *n*-tributyl citrate
- Acetyl *n*-trihexyl citrate
- Butyryl-*n*-trihexyl citrate
- Epoxidized soybean oil and epoxidized linseed oil.

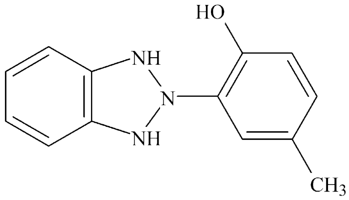


Figure 9.6 Structure of ®Tinuvin-P, 2-(2H-benzotriazol-2-yl)-*p*-cresol.

Heat stabilizers are typically used in medical-grade PVC, not only to protect it against the high temperatures the resin might see during processing but also the high heat it may encounter in storage or autoclaving. Barium—zinc additives are very effective heat stabilizers for PVC but are restricted for medical applications in some countries. Alternatives like calcium—zinc formulations are often used to stabilize medical-grade PVC. Heat stabilizers trap the hydrogen chloride that is generated when PVC decomposes at high temperatures. That prevents discoloration and degradation. Rigid PVC may contain up to 15% by weight of thermal stabilizers. Another additive, ®Tinuvin-P, 2-(2H-benzotriazol-2-yl)-*p*-cresol, is used to provide stability / exposure to ultraviolet light. Its structure is shown in Fig. 9.6. The effect of DEHP and Tinuvin-P and radiation dose is shown in Fig. 9.7.

Manufacturing and trade names: Polyone Geon™, Fiberloc™, and VPI LLC Mirrex®.

Sterile applications:

- Rigid PVC: Luer connectors and Y-sites
- Flexible PVC: secondary packaging, blister packs, solution containers, fluid transport tubes, drip chambers, diaphragms, pull rings, oxygen face-masks, and gloves.

Gamma radiation resistance: Gamma ray sterilization generally uses an energy dose of about 2.5 Mrad. Sterilization at excessive dosage rates or with excessive sterilization times can result in discoloration or odor. Rigid PVC suffers more severe adverse effects than flexible PVC when inappropriate procedures of this type are used. Specific gamma radiation-resistant PVC blends are commercially available.[5]

PVC degrades by chain scission when exposed to high-energy radiation. This degradation occurs in a three-step process:

1. Initially active radicals (a radical is shown as a "●"on an atom in a chemical structure) are formed from C—Cl or C—H bond scission reactions, though a C—C bond scission can also occur
2. The radicals propagate, during which hydrogen chloride (HCl) is produced
3. The radicals are deactivated when they react with another radical.

Figure 9.8 diagrams the degradation mechanism. The radiation forms a pair of radicals, but there is a high probability that the two radicals will recombine with each other due to the restricted mobility of the polymer chains in the solid state. Among the three radiation-induced polymeric radicals shown, "A" and "B" would continue the reaction in which

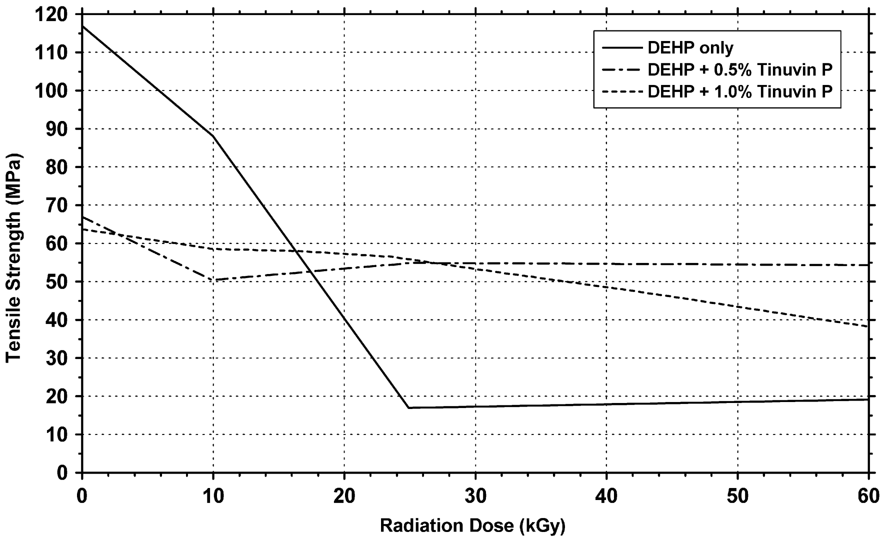


Figure 9.7 Effect of di(2-ethyl hexyl) phthalate and Tinuvin-P loading on the tensile strength after ionizing radiation exposure of polyvinyl chloride.

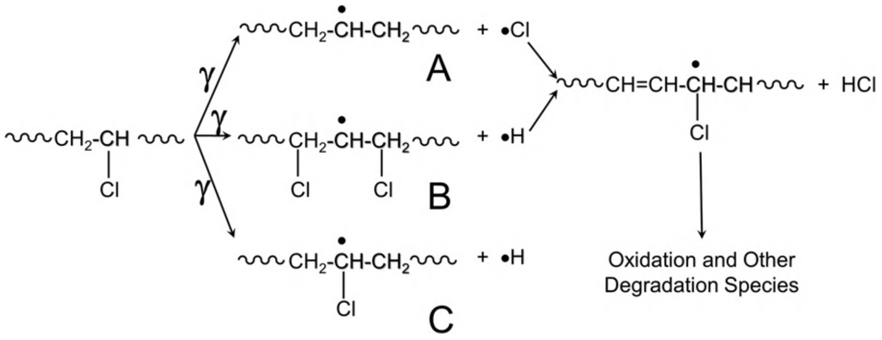


Figure 9.8 Polyvinyl chloride degradation mechanisms.

HCl is formed and acts as a catalyst. Chain scission can follow causing degradation or the radicals can react with oxygen to form oxidized products leading to discoloration.

Ethylene oxide (EtO) resistance: Ethylene oxide sterilization is recommended for PVC. When choosing ethylene oxide gas sterilization, a 7- to 14-day quarantine period is necessary to assure that there is no EtO residue.[6]

Sterilization using ethylene oxide gas is a method that has proven particularly useful for PVC products having a large number of cavities or capillaries.[5]

Autoclave sterilization: Steam sterilization in autoclaves is conducted at temperatures from 121 °C to 134 °C. The temperature used is above the glass transition temperature of PVC. Rigid unplasticized PVC is unsuitable for use in steam and autoclave sterilizations as the material and parts will warp and distort in when exposed to that temperature range. The temperature range poses no problem for flexible PVC, which is a rubbery material. Plasticized, flexible PVC can be sterilized using steam or autoclave. Low-temperature steam sterilization (conducted at 60–80 °C) can be used for both rigid and flexible PVC.

Low-temperature plasma sterilization: PVC products can also be sterilized using newly developed low-temperature plasma technology (Sterrad® plasma sterilization).[5]

Data for PVC plastics are found in Tables 9.7–9.12 and Figs 9.9–9.18.

9.4 Polyvinylidene Chloride

Polyvinylidene chloride (PVDC) resin, the structure of which is shown in Fig. 9.19, is usually a copolymer of vinylidene chloride with vinyl chloride or other monomers. Dow Plastics vinyl chloride and vinylidene chloride, Saran™, is usually supplied as a white, free-flowing powder. PVDC has a CAS number of 9002-85-1.

Manufacturers and trade names: Dow Saran™.

Table 9.7 Effect of Gamma Radiation Sterilization on Colorite Polyvinyl Chloride Shore A Hardness 65 and 75[7]

Material Note	Shore A Hardness: 65; Transparent		Shore A Hardness: 75; Transparent	
Exposure Conditions				
Radiation dose (Mrad)	2.5	4	2.5	4
Properties Retained (%)				
Tensile strength	102.5	104.4	102	107
Elongation	104.7	110.8	90.9	84.7
Surface and Appearance				
Δ*b* Color	0.31	0.41	0.47	0.93

Table 9.8 .Effect of 2.5 Mrad Gamma Radiation Sterilization on AlphaGary Polyvinyl Chloride Shore A Hardness 80[8]

Sterilization							
Times Reprocessed	1	2	3	4	5	6	6*
Properties Retained (%)							
Tensile strength	95.8	99.5	104.2	103.7	101.9	89.8	96
Elongation	90.6	103.4	100	93.3	100	116	147.4
Surface and Appearance							
ΔE Color	3.7	3.5	3.2	3.1	2.9	4	3.8
Δb Color	3.6	3.4	3.2	3	2.8	3.9	3.8

Note: (1) Type: reprocessing; regrind level: 20%.
**Enhanced stabilizer system used.*

Table 9.9 Effect of 3.5 Mrad Gamma Radiation Sterilization on AlphaGary Polyvinyl Chloride Shore A Hardness 80[8]

Sterilization							
Times reprocessed	1	2	3	4	5	6	6*
Properties Retained (%)							
Tensile strength	102.3	96.7	100	100.5	102.8	88.1	91.2
Elongation	87.5	103.4	100	93.3	86.2	108	136.8
Surface and Appearance							
ΔE Color	6.3	5.7	5.6	5.7	6	5.9	6.6
Δb Color	6.2	5.5	5.5	5.6	5.8	5.8	6.5

Note: (1) Sterilization conditions: 3.5 Mrad.
**Enhanced stabilizer system used.*

Table 9.10 Effect of 2.5 Mrad Gamma Radiation Sterilization on AlphaGary Polyvinyl Chloride Shore A Hardness 84[8]

Sterilization						
Times reprocessed	1	2	3	4	5	6
Properties Retained (%)						
Tensile strength	106.1	91	107.8	90.2	97.2	96.3
Elongation	88.5	104.2	92.6	100	108.3	96.3
Surface and Appearance						
ΔE Color	3.3	2.1	1.5	1.5	1.5	1.6
Δb Color	3.1	2	1.3	1.4	1.5	1.5

Table 9.11 Effect of 3.5 Mrad Gamma Radiation Sterilization on AlphaGary Polyvinyl Chloride Shore A Hardness 84[8]

Sterilization						
Times reprocessed	1	2	3	4	5	6
Properties Retained (%)						
Tensile strength	92.5	89.1	102.4	89.8	92.1	96.3
Elongation	96.2	104.2	92.6	96.2	108.3	92.6
Surface and Appearance						
ΔE Color	6.3	5.4	4.9	5.2	5.1	5.1
Δb Color	6.2	5.3	5.3	6.2	6.3	5.9

Table 9.12 Effect of Ethylene Oxide (EtO) Sterilization on Polyvinyl Chloride[11]

Gas Composition	**12% EtO and 88% Freon 8.6%**				**EtO and 91.4% HCFC-124**				
Number of cycles	1	1	2	2	1	1	2	2	
Postexposure Conditioning II									
Time (h)	168	1344	168	1344	168	1344	168	1344	
	Properties Retained (%)								**Test Method**
Tensile strength at yield	100.1	96.7	99.6	96.4	95.6	94.5	99.6	97.3	ASTM D638
Elongation	100	92.3	92.3	84.6	96.2	88.5	96.2	80.8	ASTM D638
Tensile modulus	114.4	82.9	100.7	97.7	87.2	80.5	110.1	100	ASTM D638
Dart impact (total energy)	95.8	95.8	97.9	102.1	97.9	102.1	100	104.2	ASTM D3763
Dart impact (peak energy)	75	72.5	72.5	80	72.5	75	75	80	ASTM D3763
Surface and Appearance									
ΔE Color	0.1	0.13	0.15	0.15	0.11	0.17	0.18	0.14	–

Note: (1) Preexposure conditioning: 18 h; 37.8 °C; 60% Relative Humidity. (2) Sterilization details: gas composition in table, 60% RH, 48.9 °C, 6 h. (3) Postexposure conditioning I: aeration, 127 mmHg, 32.2 °C; Postexposure conditioning II: ambient conditions, time noted in table.

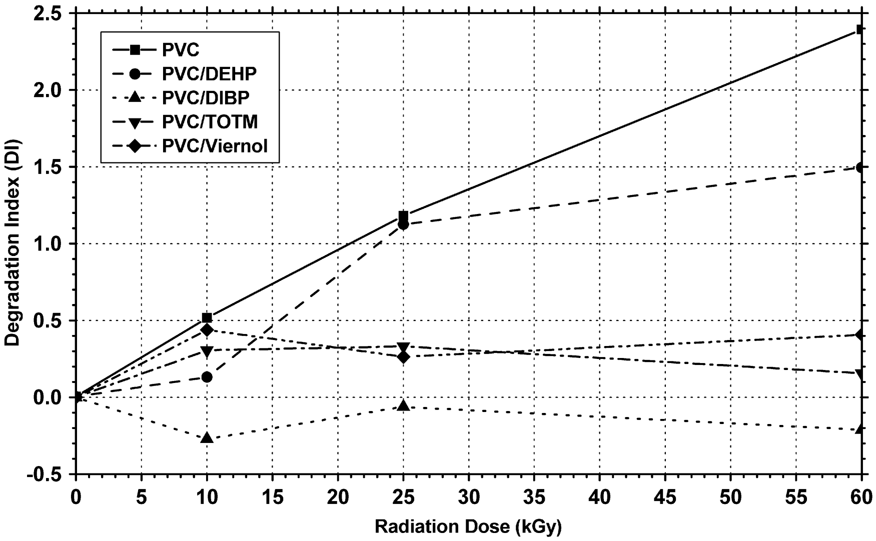


Figure 9.9 Degradation indexes of pure polyvinyl chloride and plasticized polyvinyl chloride-irradiated films as a function of radiation dose.[9]

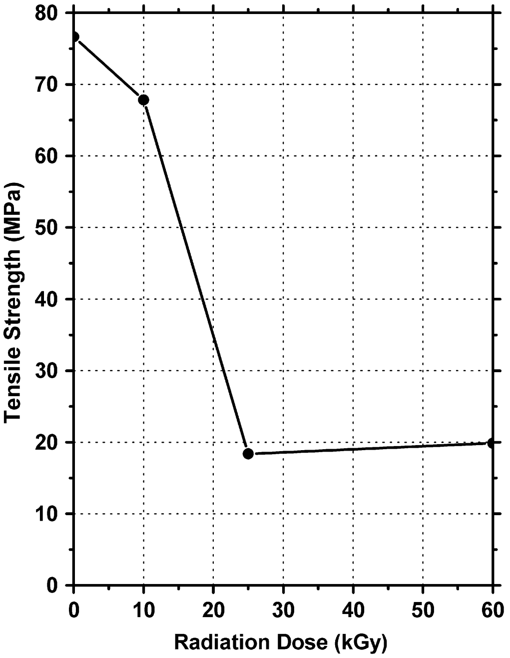


Figure 9.10 Effect of gamma radiation sterilization on tensile strength of polyvinyl chloride-based/di(2-ethyl hexyl) phthalate compounds.[9]

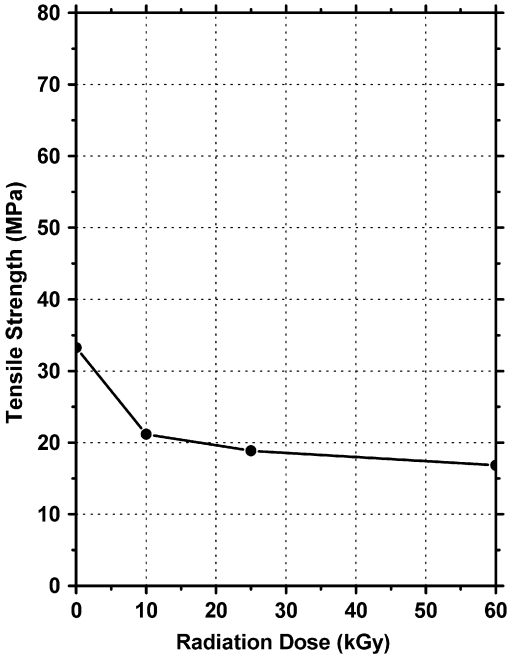


Figure 9.11 Effect of gamma radiation sterilization on tensile strength of polyvinyl chloride-based/diisobutyl phthalate compounds.[9]

Sterile applications and uses: Monolayer films (Saran™) for food wrap and medical packaging, and coextruded films and sheet structures as a barrier layer in medical and packaging including fresh red meats, cheese, and sausages. Coatings are applied to containers to prevent gas transmission.

Gamma sterilization: Maximum dose is 100 kGy, however PVDC yellows and releases hydrogen chloride.

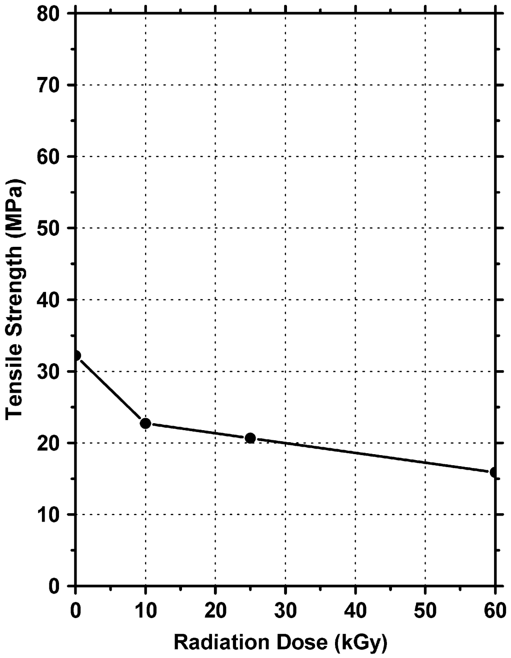


Figure 9.12 Effect of gamma radiation sterilization on tensile strength of polyvinyl chloride-based/trioctyl trimellitate compounds.[9]

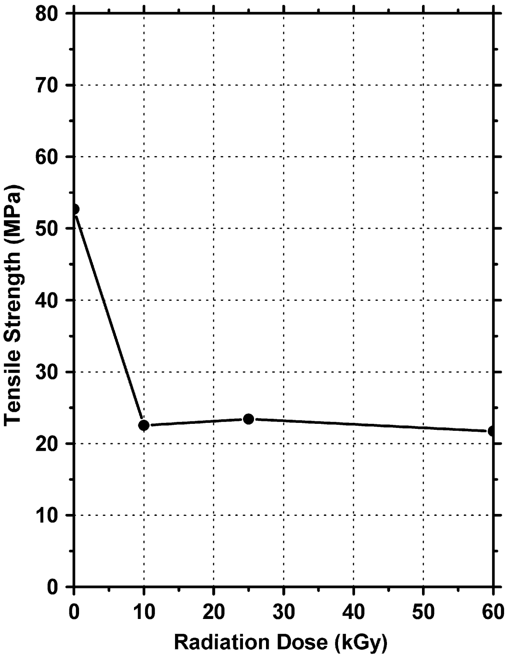


Figure 9.13 Effect of gamma radiation sterilization on tensile strength of polyvinyl chloride-based/Veirnol compounds.[9]

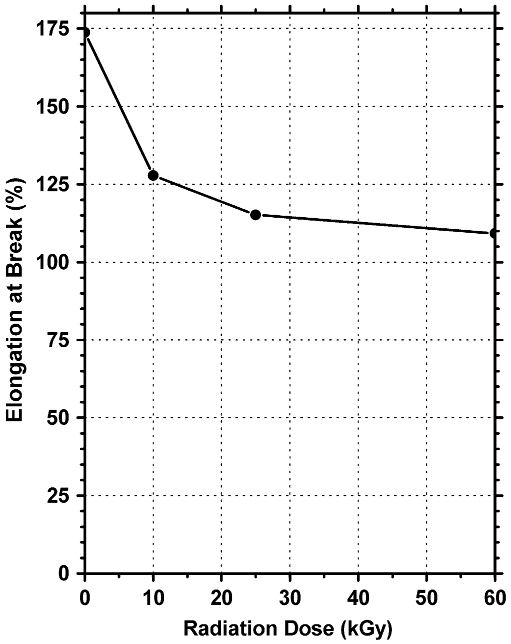


Figure 9.14 Effect of gamma radiation sterilization on elongation at break of polyvinyl chloride-based/ di(2-ethyl hexyl) phthalate compounds.[9]

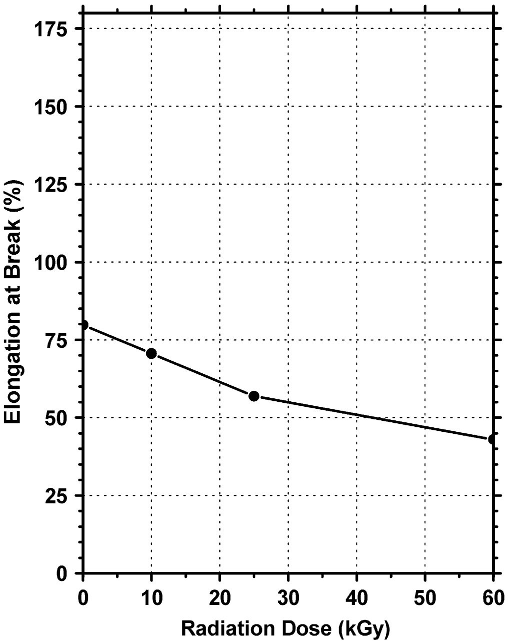


Figure 9.15 Effect of gamma radiation sterilization on elongation at break of polyvinyl chloride-based/ diisobutyl phthalate compounds.[9]

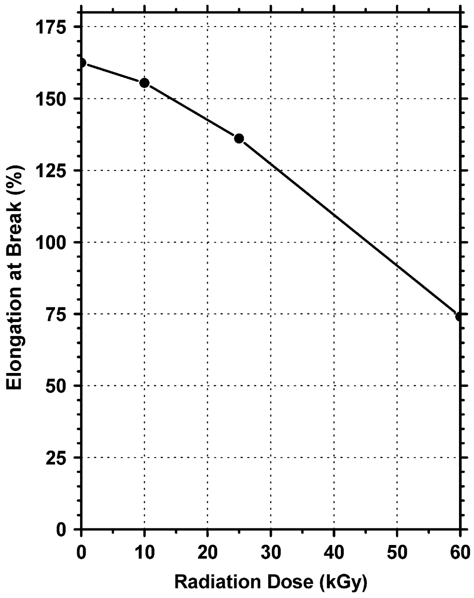


Figure 9.16 Effect of gamma radiation sterilization on elongation at break of polyvinyl chloride-based/trioctyl trimellitate compounds.[9]

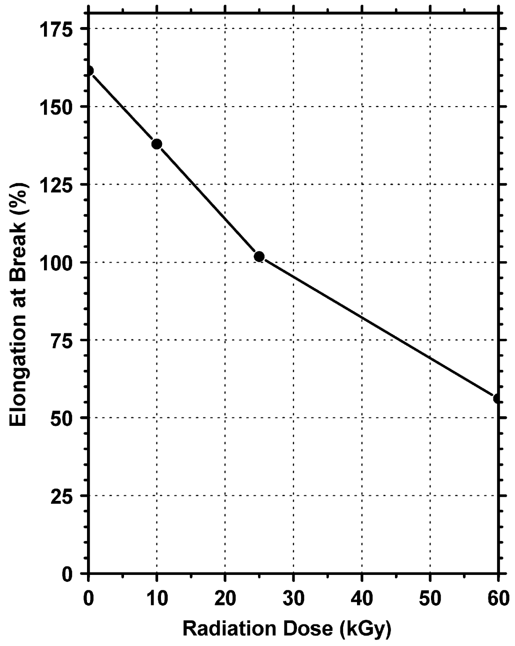


Figure 9.17 Effect of gamma radiation sterilization on elongation at break of polyvinyl chloride-based/Viernol compounds.[9]

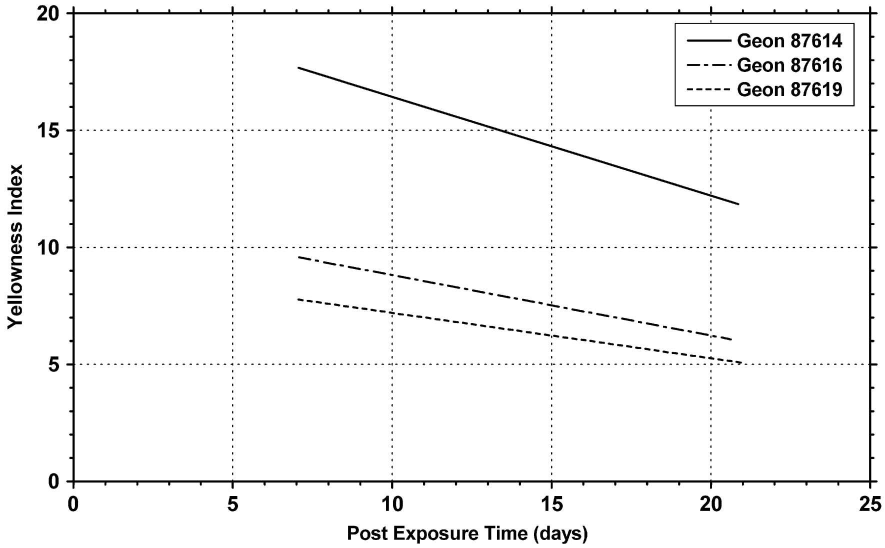
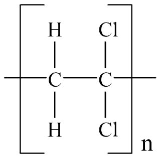


Figure 9.18 Post-gamma radiation exposure time versus Δ yellowness index of polyvinyl chloride.[10]



$$-\left[CH_2-CCl_2\right]_n-$$

Figure 9.19 Structure of polyvinylidene chloride homopolymer.

9.5 Polyacrylics

While a large number of acrylic polymers are manufactured, polymethyl methacrylate (PMMA) is by far the most common. The structure of PMMA is shown in Fig. 9.20. Nearly everyone has heard of Plexiglas®. PMMA has two very distinct properties that set the products apart from

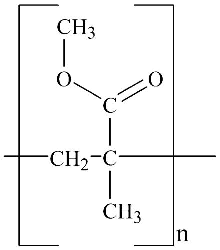


Figure 9.20 Structure of polymethyl methacrylate.

others. First it is optically clear and colorless. It has a light transmission of 92%. The 4% reflection loss at each surface in unavoidable. Second its surface is extremely hard. It is also highly weather resistant. PMMA has a CAS number of 9011-14-7.

PMMA films show very good abrasion resistance, weather resistance (with a UV absorber), and are absolutely colorless.

Acrylic resins are available as homopolymer (primarily PMMA), copolymer, and terpolymer. Each of these is discussed separately in the following sections.

Manufacturers and trade names: Lucite International, Lucite Diakon and Perspex®; Evonik Industries LLC Plexiglas®, Acrylite®, Europlex® and Rohaglas®; Arkema Oroglas; Rowland Technologies, Inc. SolaTuf®; Mitsubishi Rayon Co., Ltd, and Shinkolite®.

Sterile applications and uses: Clear, disposable plastics – only glass transmits light as well.

Parts made from Plexiglas® can be sterilized by means of gamma radiation or ethylene oxide gas. However, in the event of repeated sterilization, the following disadvantages are known to occur:

- Gamma radiation: yellowing of moldings
- Ethylene oxide gas: stress cracking.

9.5.1 Homopolymer

Manufacturers and trade names: Altuglas International Plexiglas, Novacor, and Evonik Industries Acrylite®.

Sterilization resistance: Wet ethylene oxide and steam sterilization methods are not recommended for acrylic.[12]

Gamma radiation resistance: Plexiglas SG-7 exposed to 5.0 Mrad of gamma radiation experiences virtually no yellowing or discoloration. Properties such as impact, tensile, and flexural strength, modulus of elasticity, and percent elongation are constant.[13] Gamma sterilization has a tendency to yellow most acrylics. This yellowing is often temporary and recovery can be complete, with the parts retaining their original integrity. The higher the radiation dosage, the greater the yellowing and the longer the required recovery time. Current techniques have cut recovery time to a week for some grades.[12]

E-beam radiation resistance: Plexiglas maintains constant impact, tensile, and flexural strength, modulus of elasticity, and percent elongation properties.[13]

Ethylene oxide (EtO) resistance: Acrylics and impact-modified acrylics are compatible with ethylene oxide gas and can be EtO sterilized without adversely affecting the medical device.

Data for acrylic homopolymer plastics are found in Tables 9.13–9.16 and Fig. 9.21–9.28.

9.5.2 Acrylic Copolymer

Manufacturers and trade names: INEOS Nova Zylar®.

Sterile applications and uses: Medical Devices.

Data for acrylic copolymer plastics are found in Tables 9.17–9.18 and Figs 9.29–9.39.

INEOS Nova Zylar® 330 (formerly 94–568) impact-modified styrene methylmethacrylate copolymer.

INEOS Nova Zylar® 220 (formerly 93–546) impact-modified styrene methylmethacrylate copolymer.

9.5.3 Acrylic Terpolymer

Degussa Cyro Industries CYROLITE® acrylic terpolymer compounds are methyl methacrylate/styrene/ethyl acrylate terpolymers with an added impact modifier.[21]

Manufacturers and trade names: Degussa Cyro Industries CYROLITE® and CYREX®.

Sterile applications: Chest drainage units, medical spikes, breathing apparatus accessories, urological accessories, Y-sites, check valves, filter housings, intravenous (IV) adaptors, IV pump housings, medical cassettes, blood handling components, and catheter accessories.

Table 9.13 Effects of Gamma Radiation on Altuglas International Plexiglas SG-7 and Plexiglas SG-10 Radiation-resistant Grade Acrylic[14–16]

Exposure Conditions					
Radiation dose (Mrad)	Unexposed	5	Unexposed	5	
Properties Retained					**Test method**
Tensile strength (MPa)	49		37	37	ASTM D638
Elongation at break (%)	4.3		6.9	6.7	–
Flexural modulus (MPa)	2400		1760	1790	–
Flexural yield strength (MPa)	80		59	60	ASTM D790
Izod impact (J/cm)	0.3		0.5	0.4	ASTM D256
Charpy impact (J/cm^2)	6.3		9.7	4.4	ASTM D256
Optical Properties					
Haze	Max 2%				ASTM D1003
Transmission, visible	92%				ASTM D1003

Table 9.14 Effect of Gamma Radiation Sterilization on Yellowness Index of Novacor Acrylic Resin[17]

Exposure Conditions								
Radiation dose (Mrad)	1.27	2.8	3.55	5.43	1.27	2.8	3.55	5.43
Postexposure Conditioning								
Time (h)	0				840			
Surface and Appearance								
Yellowness index note	Yellow	Dark yellow	Dark yellow	Yellow orange	Light yellow	Light yellow	Light yellow	Dark yellow

Table 9.15 Effect of Gamma Radiation Sterilization on Yellowness Index of Acrylic[17]

Material Note	**Transparent, General-Purpose Grade**		**Transparent, Impact Modified**	
Exposure Conditions				
Radiation dose (Mrad)	3	5	3	5
Postexposure Conditioning				
Tensile strength	80	58	100	100
Modulus	100	100	100	100
Notched Izod impact	–	–	96	89
Surface and Appearance				
Δ Yellowness index	20	24.5	14	19

Table 9.16 Qualitative Review of Effects of Low-Temperature Hydrogen Peroxide Gas Plasma (LTHPGP) Sterilization on Cyro Industries' Acrylite H15-003 Acrylic Resins[20]

Type	**Unexposed**	**LTHPGP Sterilized**	
Properties Retained			**Test Method**
Tensile strength (MPa)	80.25	78.6	ASTM D638
Tensile modulus (MPa)	3240	3261	ASTM D638
Elongation at break (%)	10.3	5.5	ASTM D638
Elongation at yield (%)	5.7	5.5	ASTM D638
Notched Izod impact (fppi, 1/8 in)	0.36	0.31	ASTM D256
Optical Properties			
Gloss, 60 °C	137	138	ASTM D523
Haze (%)	0.7	0.9	ASTM D1003
Refractive index	1.49	1.49	ASTM D542
Transmittance (%)	93	93	ASTM D1003
Yellowness index	0.4	0.3	ASTM D1003

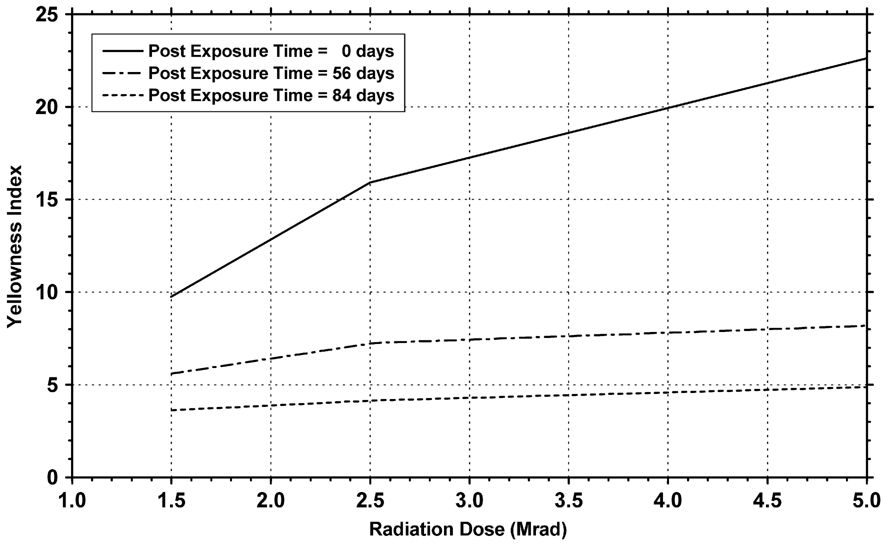


Figure 9.21 Gamma radiation dose versus yellowness index of Altuglas International Plexiglas V-Grade acrylic resin.[18]

Gamma radiation resistance: CYROLITE® compounds are generally used when gamma sterilization is required; they exhibit no significant loss in key mechanical properties such as elongation at break and notched Izod impact after exposures of up to 7.5 Mrad.

E-beam radiation resistance: All grades of CYROLITE® compounds are suitable for e-beam sterilization and exhibit no significant loss in key mechanical properties such as elongation at break and notched Izod impact after exposures of up to 7.5 kGy.

Ethylene oxide (EtO) resistance: The use of EtO sterilization results in no significant property deterioration or yellowing in CYROLITE® compounds or Cyrex® alloys. EtO sterilization results in little or no color shift in CYROLITE® compounds.

Dry heat sterilization: This is generally conducted at 160−170 °C for a minimum of two hours. Specific exposures are dictated by the

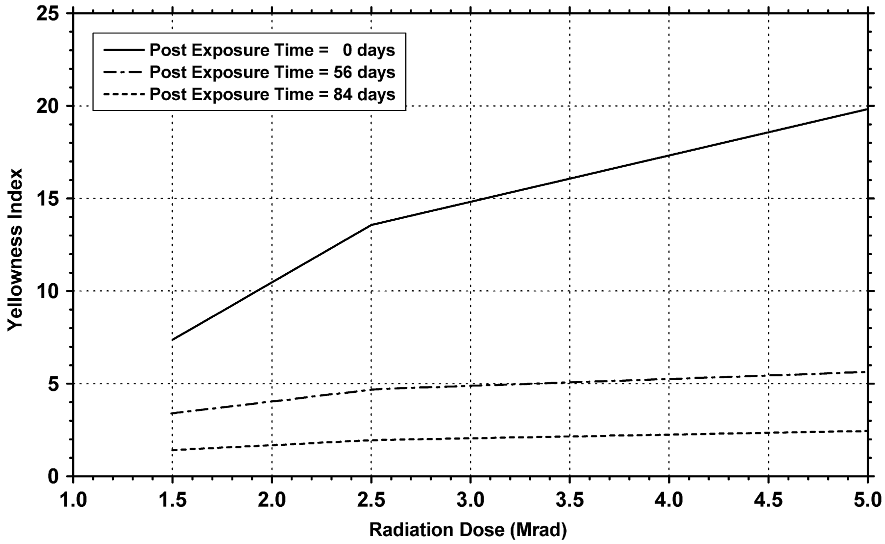


Figure 9.22 Gamma radiation dose versus yellowness index of Altuglas International Plexiglas DR-G Grade acrylic resin.[18]

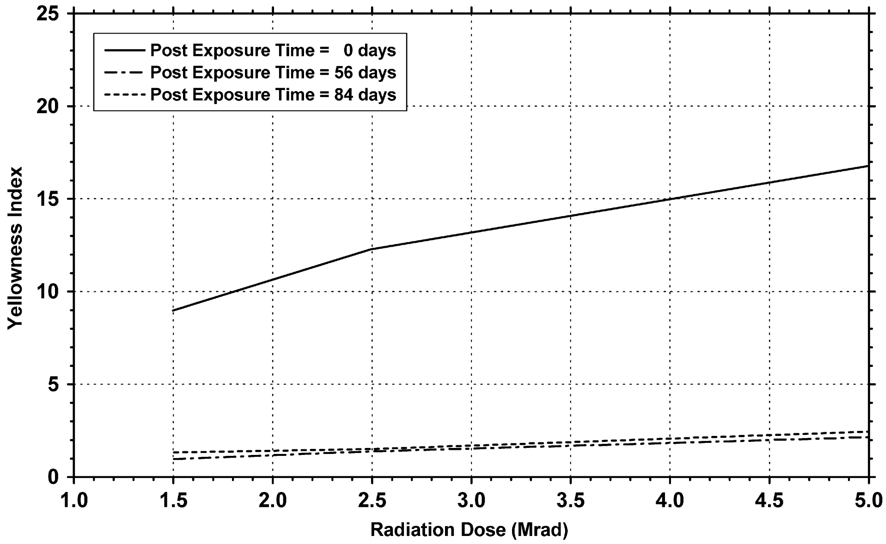


Figure 9.23 Gamma radiation dose versus yellowness index of Altuglas International Plexiglas HFI-10 G acrylic resin.[18]

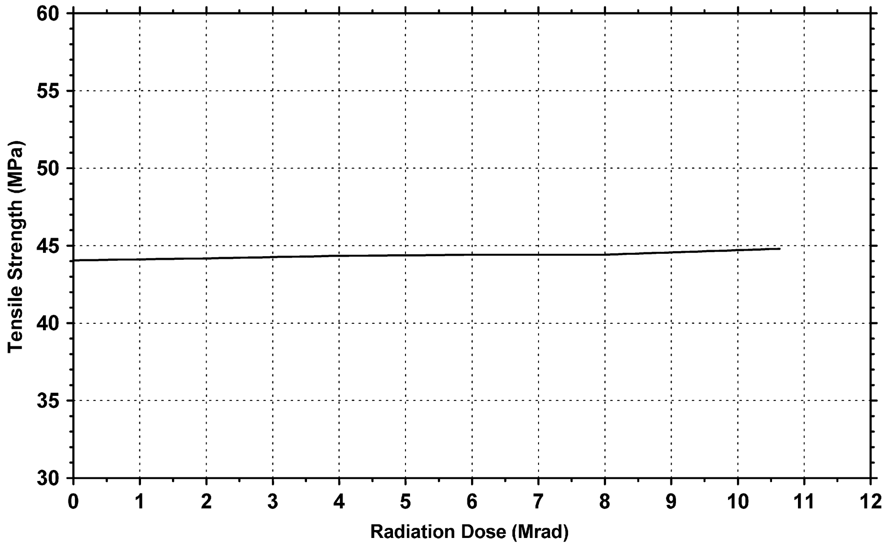


Figure 9.24 Beta radiation dose versus tensile strength of acrylic resin.[19]

Figure 9.25 Beta radiation dose versus tensile modulus of acrylic resin.[19]

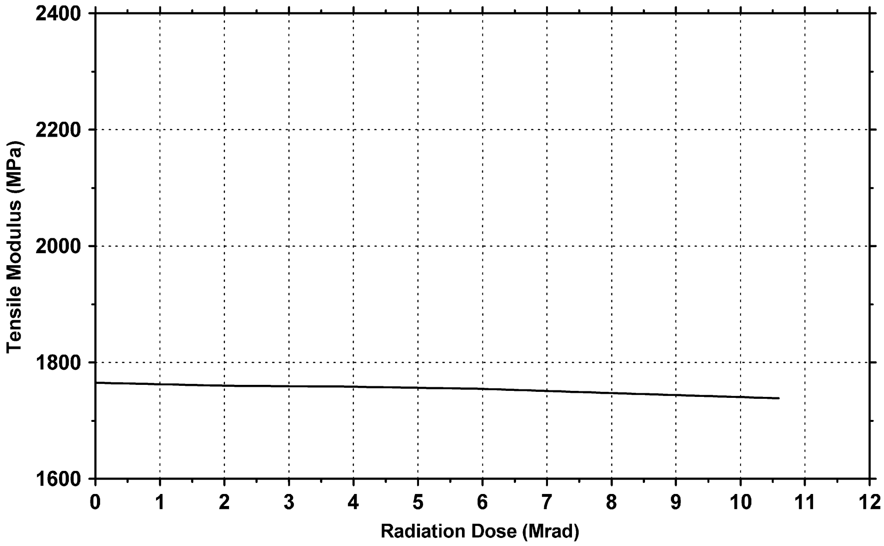


Figure 9.26 Beta radiation dose versus notched Izod impact strength of acrylic resin.[19]

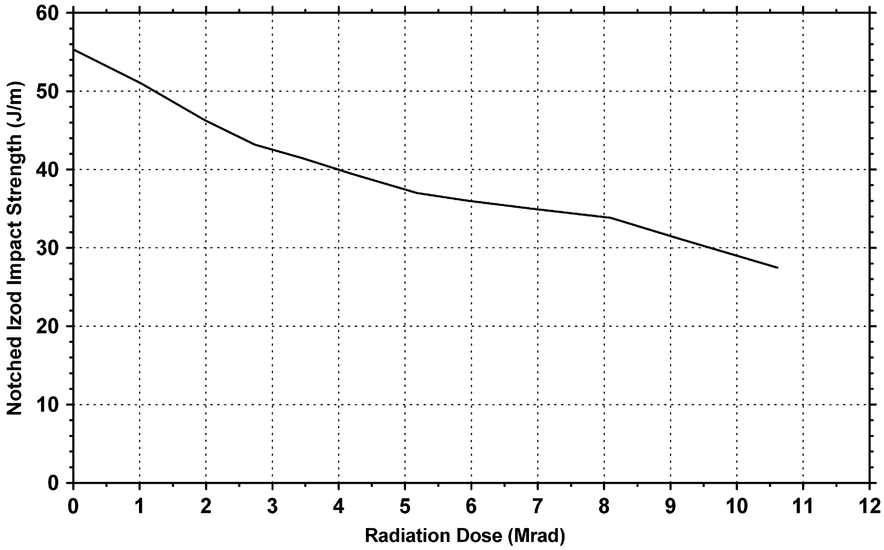
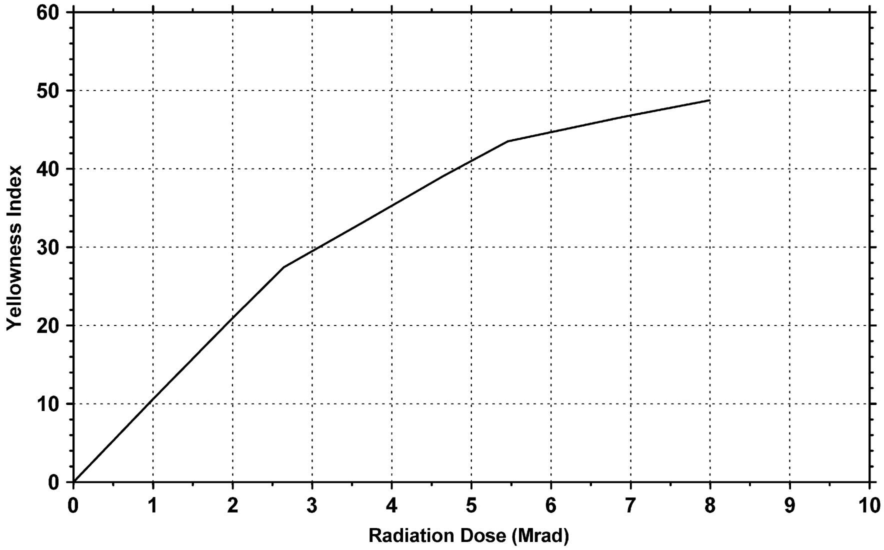


Figure 9.27 Beta radiation dose versus yellowness index of acrylic resin.[19]



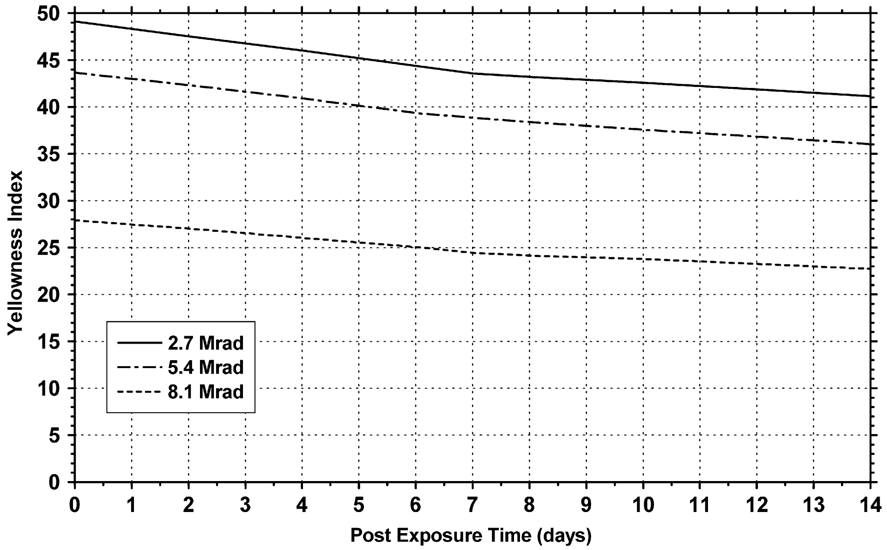


Figure 9.28 Post-beta radiation exposure time versus yellowness index of acrylic resin.[19]

Table 9.17 Effect of Gamma Radiation Sterilization on INEOS Nova Zylar® 220 and Zylar® 330 Transparent and Impact-Modified Acrylic Copolymers[19]

Product Code	**INEOS Nova Zylar® 220**		**INEOS Nova Zylar® 330**	
Exposure Conditions				
Radiation dose (Mrad)	3.5	7	3.5	7
Properties Retained (%)				
Tensile strength	100	96	96	96
Elongation	92	90	86	82
Notched Izod impact	95	100	83	86
Surface and Appearance				
Δ Yellowness index	1.5	2.6	1.2	2.4

Table 9.18 Effect of Ethylene Oxide Sterilization on INEOS Nova Zylar® 220 and Zylar® 330 Transparent and Impact-Modified Acrylic Copolymers[19]

Product Code	**Zylar® 220**	**Zylar® 330**	**Zylar® 220**	**Zylar® 330**
Exposure Conditions				
Details	100% EtO		12% EtO and 88% Freon	
Number of cycles	1		1	
Properties Retained (%)				
Notched Izod impact	90	100	75	100

Figure 9.29 Gamma radiation dose versus tensile strength of INEOS Nova Zylar® 330 acrylic copolymer.[19]

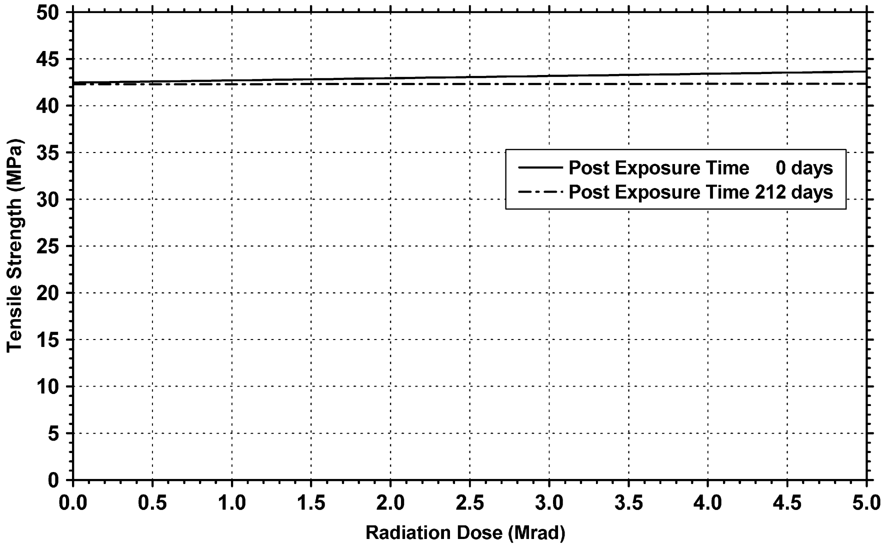


Figure 9.30 Gamma radiation dose versus elongation of INEOS Nova Zylar® 330 acrylic copolymer.[19]

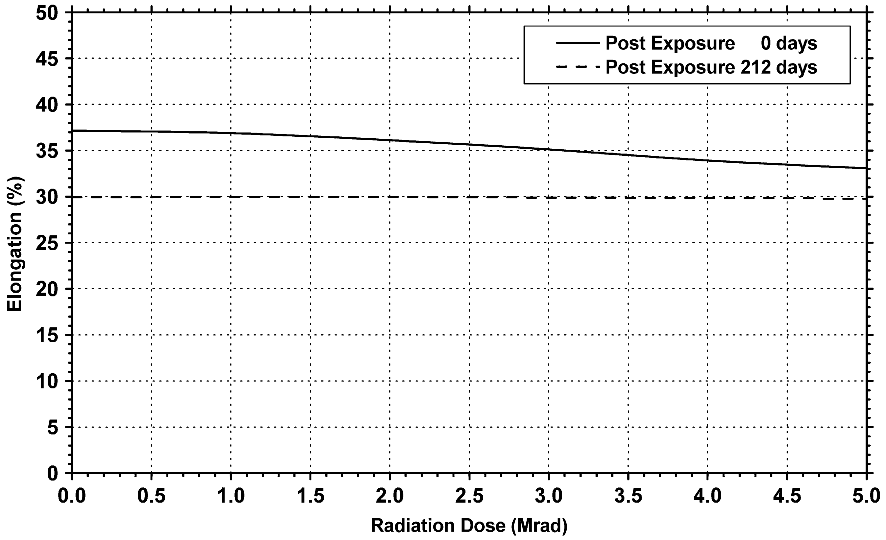
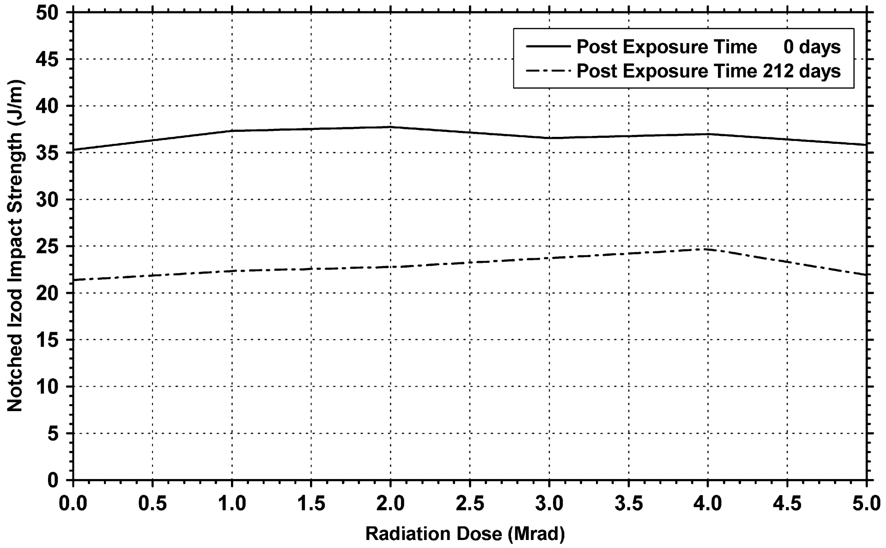


Figure 9.31 Gamma radiation dose versus notched Izod impact strength of INEOS Nova Zylar® 330 acrylic copolymer.[19]



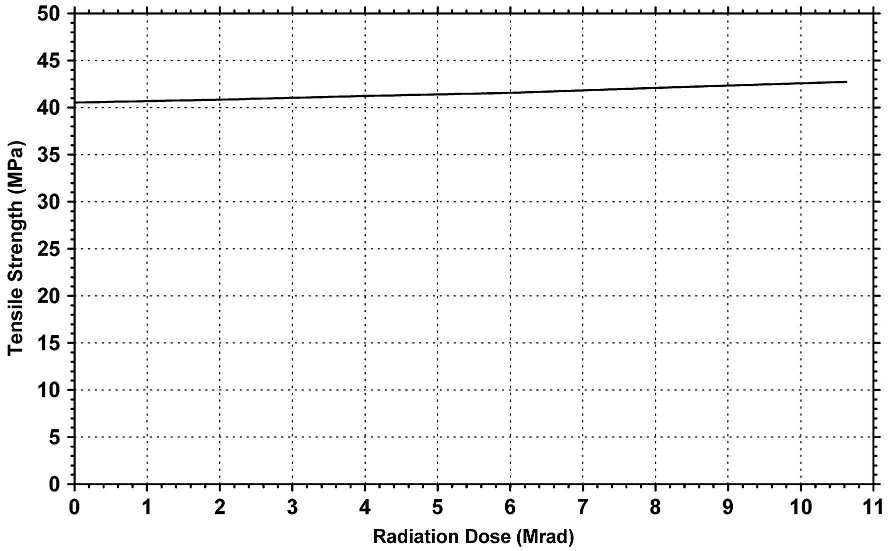


Figure 9.32 Beta radiation dose versus tensile strength of INEOS Nova Zylar® 330 acrylic copolymer.[19]

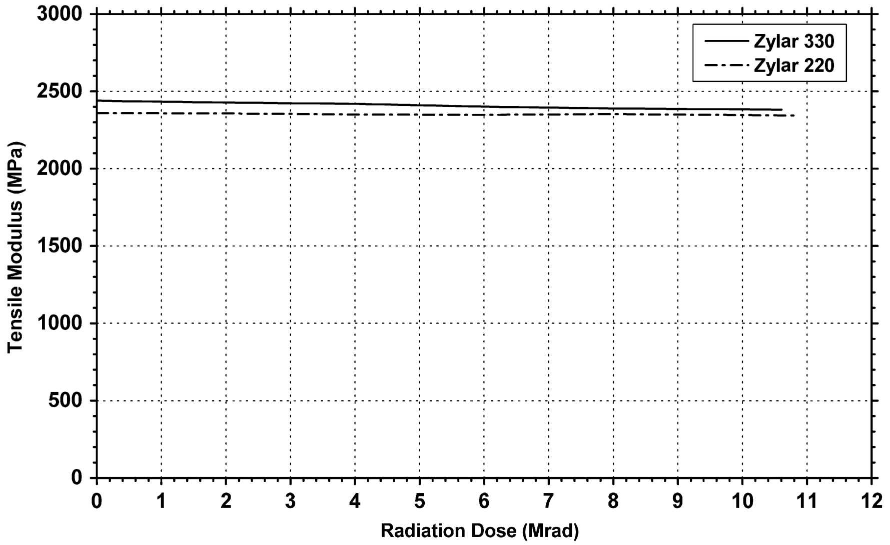


Figure 9.33 Beta radiation dose versus tensile modulus of INEOS Nova Zylar® 330 and Zylar® 220 acrylic copolymers.[19]

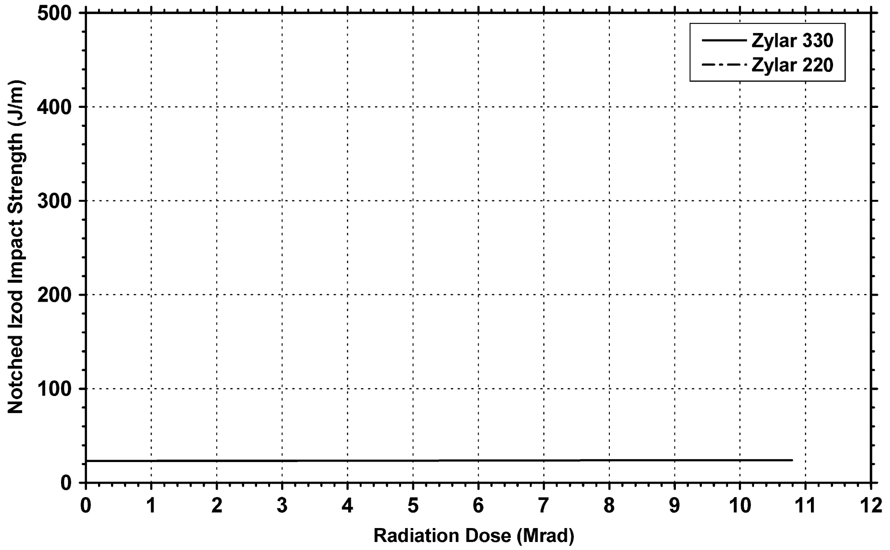


Figure 9.34 Beta radiation dose versus notched Izod impact strength of INEOS Nova Zylar® 330 and Zylar® 220 acrylic copolymers.[19]

Figure 9.35 Beta radiation dose versus yellowness index of INEOS Nova Zylar® 330 and Zylar® 220 acrylic copolymers.[19]

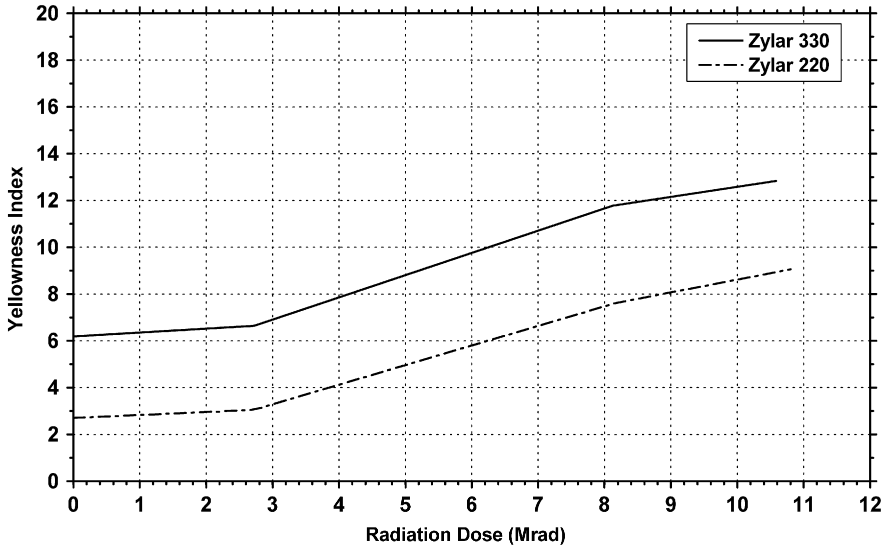


Figure 9.36 Post-beta radiation (2.7 Mrad) exposure time versus yellowness index of INEOS Nova Zylar® 330 and Zylar® 220 acrylic copolymers.[19]

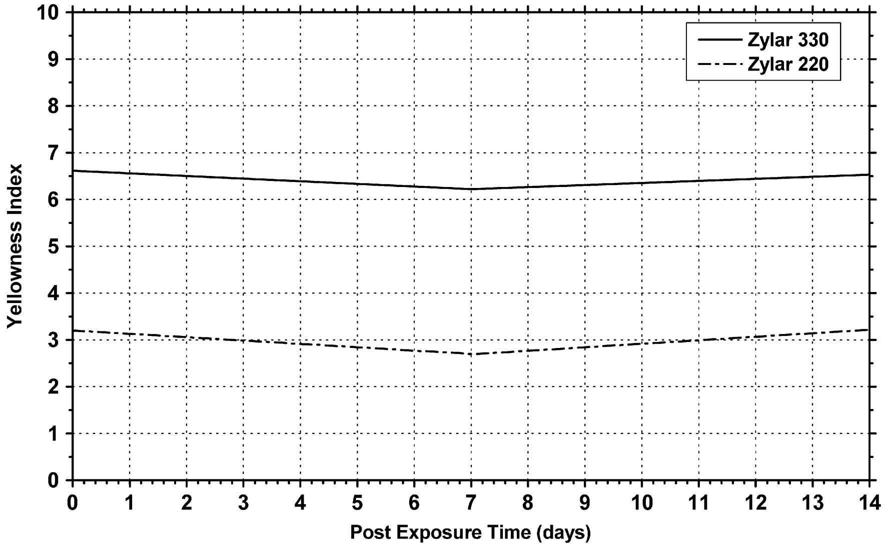
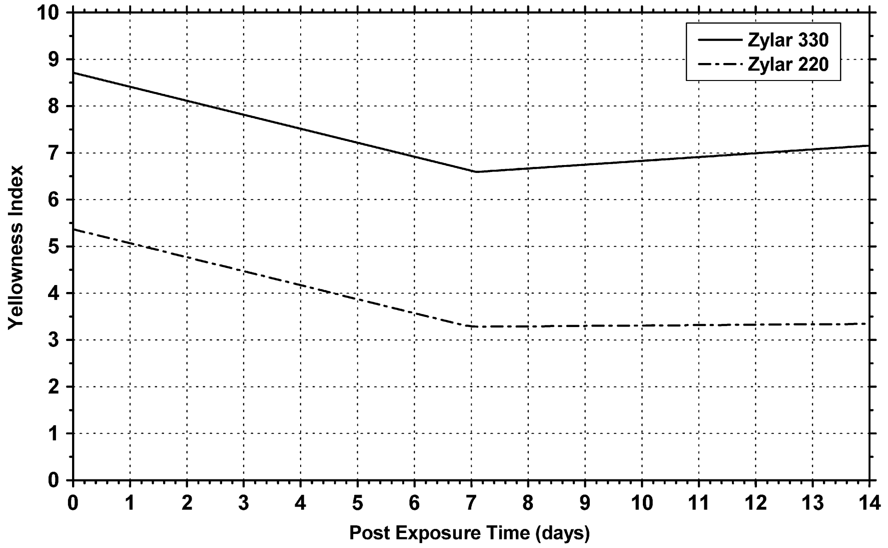


Figure 9.37 Post-beta radiation (5.4 Mrad) exposure time versus yellowness index of INEOS Nova Zylar® 330 and Zylar® 220 acrylic copolymers.[19]



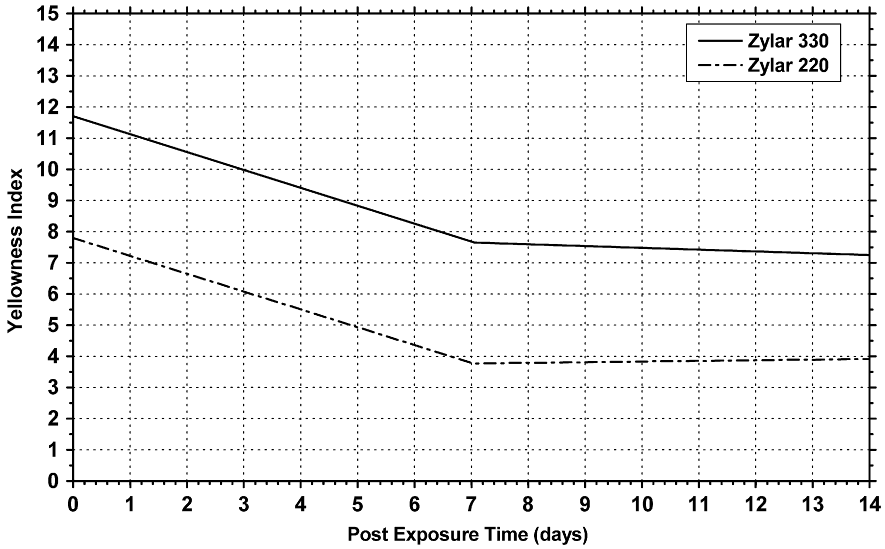


Figure 9.38 Post-beta radiation (8.1 Mrad) exposure time versus yellowness index of INEOS Nova Zylar® 330 and Zylar® 220 acrylic copolymers.[19]

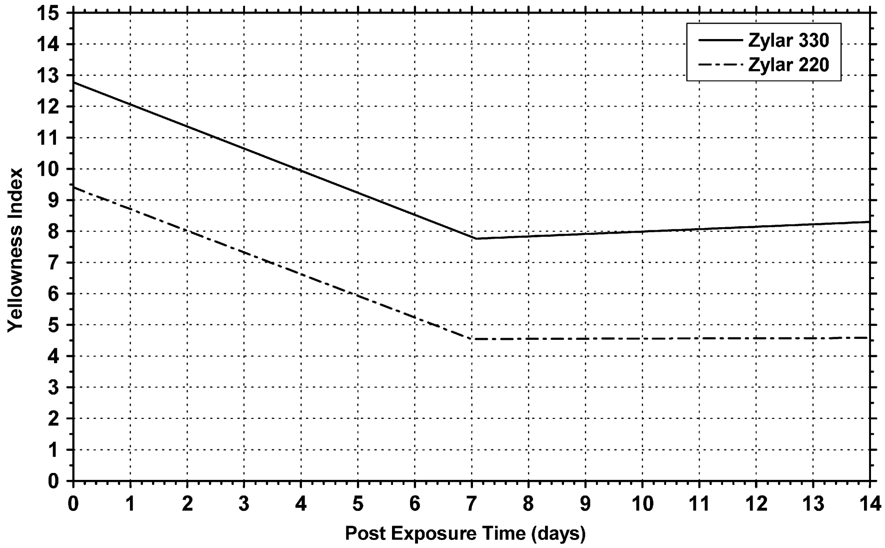


Figure 9.39 Post-beta radiation (10.8 Mrad) exposure time versus yellowness index of INEOS Nova Zylar® 330 and Zylar® 220 acrylic copolymers.[19]

bioburden concentration and the temperature tolerance of the products. Appropriate conditions must be determined throughout the material being sterilized. The equipment used is a forced-air type oven with temperature recording. This type of sterilization is not recommended for use with CYRO materials because of the high temperatures required.[21]

Steam sterilization: The process is carried out in autoclaves using saturated steam. Temperatures range from 115 °C to 121 °C and higher. Critical parameters are temperature, time, air elimination, steam quality, and absence of superheating. There must be direct steam contact that can be prevented by the presence of air; its absence is therefore considered an absolute requirement. The selection of an appropriate steam sterilization cycle must be made after careful study of the nature of the articles being sterilized, the type and number of organisms present, type and size of each package, type of packaging material used, and other factors that may influence the performance in the application. This method is not recommended for use with CYRO products because of the high temperatures involved.[21]

Regulatory status: Cyro Industries' CYROLITE®, XT Polymer, and CYREX® meet FDA food contact, USP Class VI and Tripartit (ISO 10993) standards.

Data for acrylic terpolymer plastics are found in Figs 9.40–9.48.

Figure 9.40 Effect of gamma irradiation on elongation of CYROLITE® G20-100 and GS-90 compound.[21]

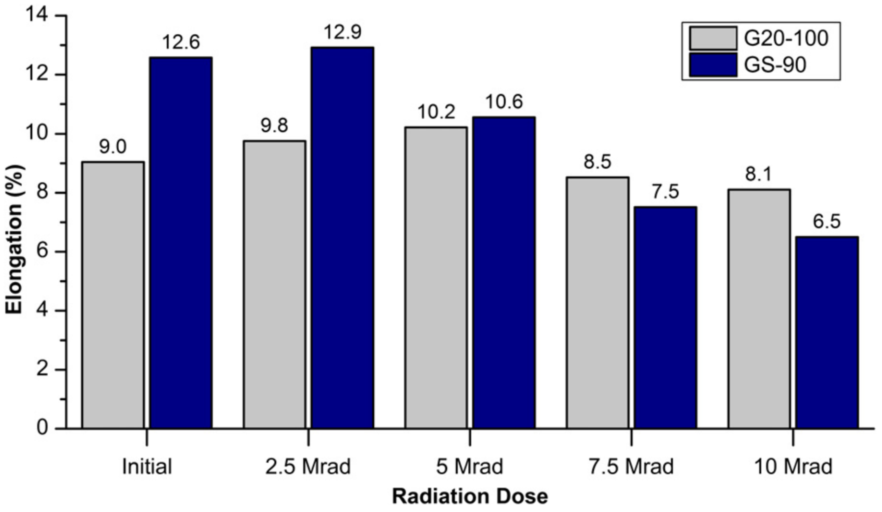


Figure 9.41 Effect of gamma irradiation on impact properties of CYROLITE® G20-100 and GS-90 compound.[21]

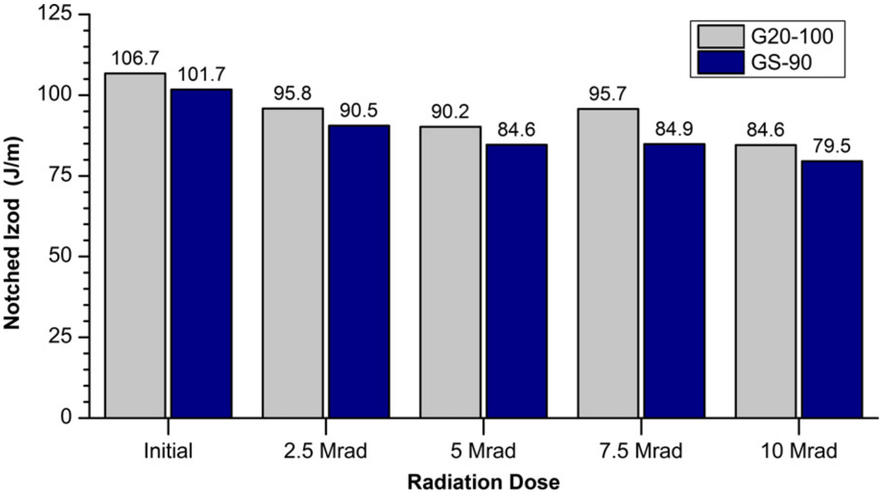
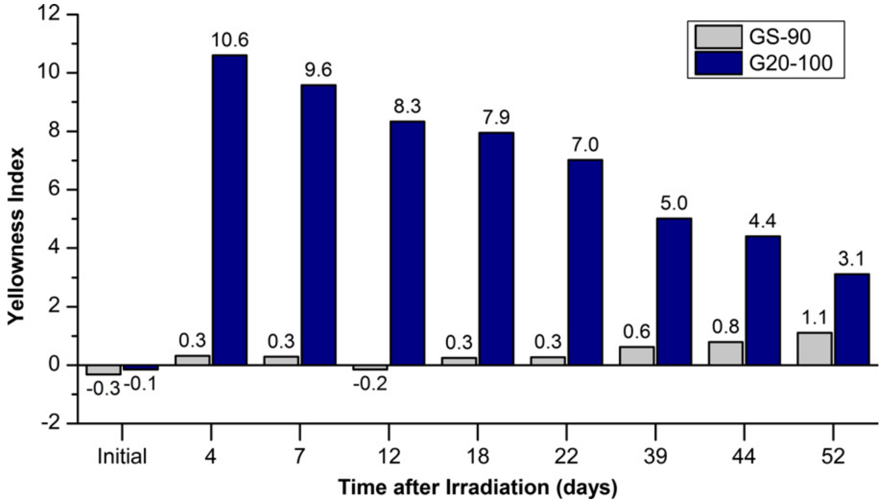


Figure 9.42 Yellowness index versus time after gamma irradiation of CYROLITE® G20-100 and GS-90 compound @ 2.5 Mrad.[21]



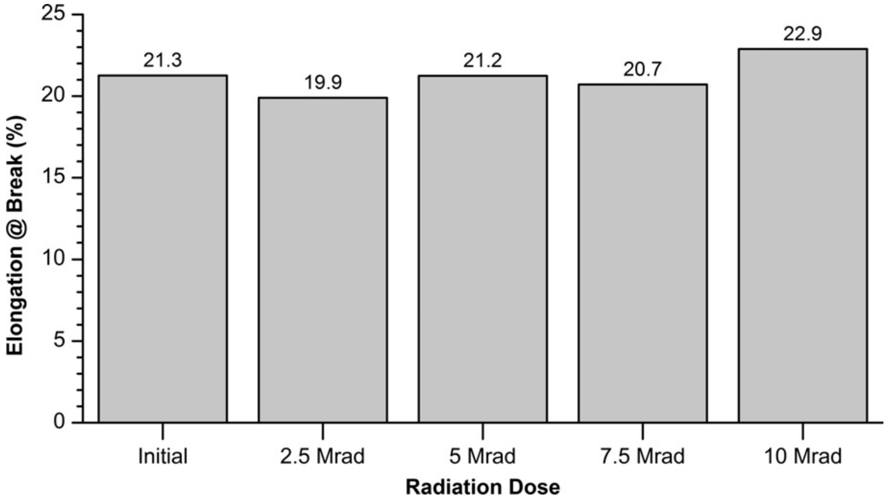


Figure 9.43 Effect of gamma irradiation on the elongation of CYREX® 200-8005 alloy.[21]

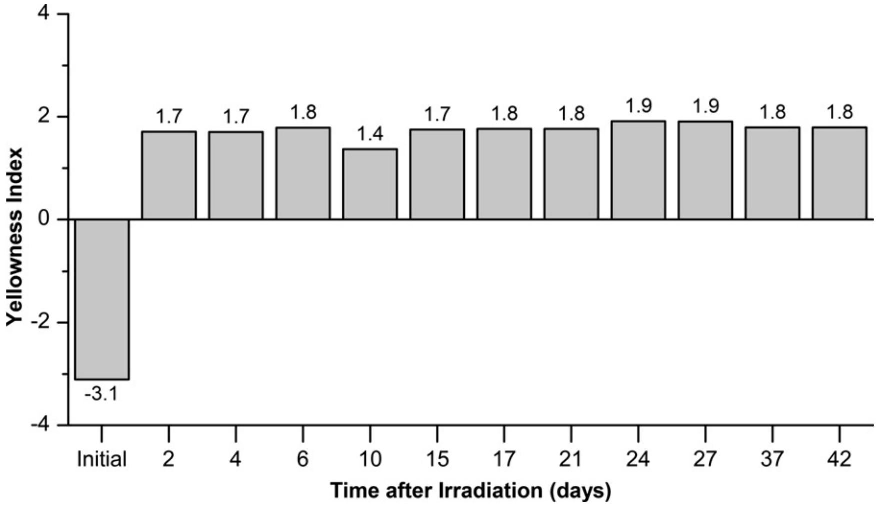


Figure 9.44 Effect of gamma irradiation on yellowness index of CYREX® 200-8005 alloy @ 2.5 Mrad.[21]

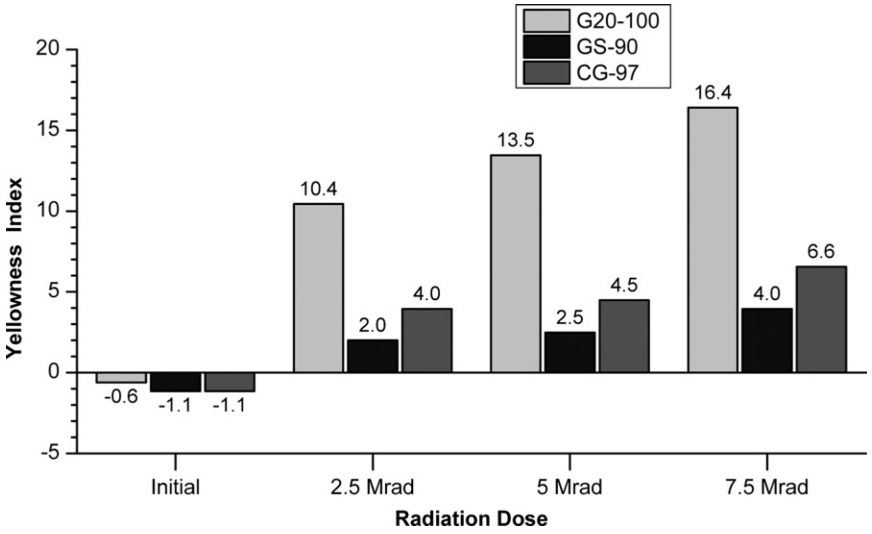


Figure 9.45 Effect of e-beam on the yellowness index of CYROLITE® G20-100, GS-90, and CG-97 compound.[21]

Figure 9.46 Effect of e-beam on the impact properties of CYROLITE® G20-100, GS-90, and CG-97 compound.[21]

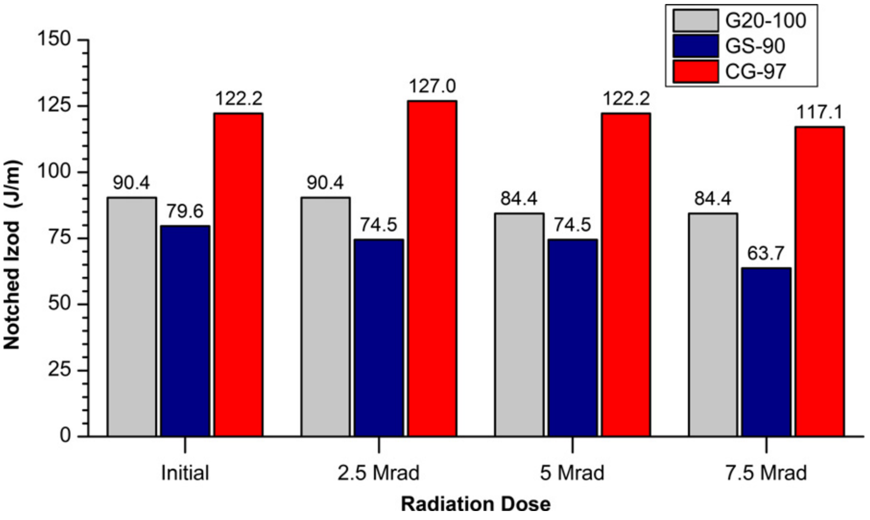


Figure 9.47 Effect of e-beam on the elongation of CYROLITE® G20-100, GS-90, and CG-97 compound.[21]

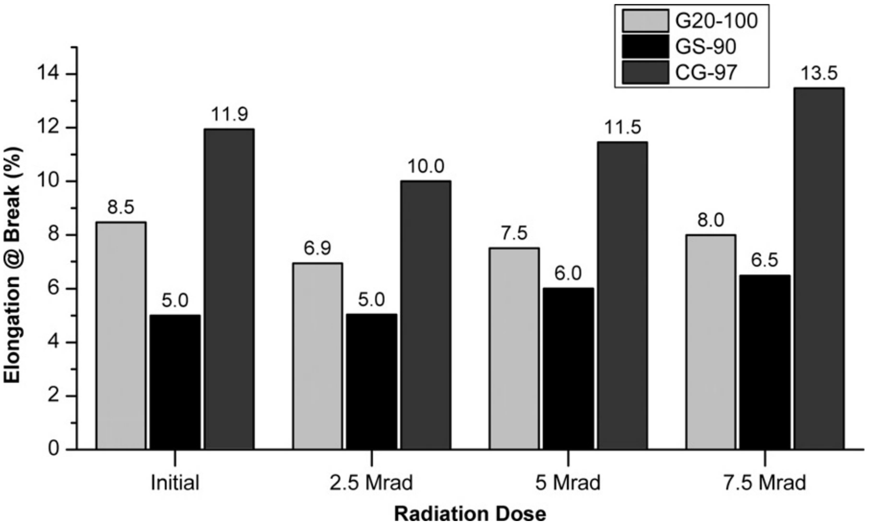
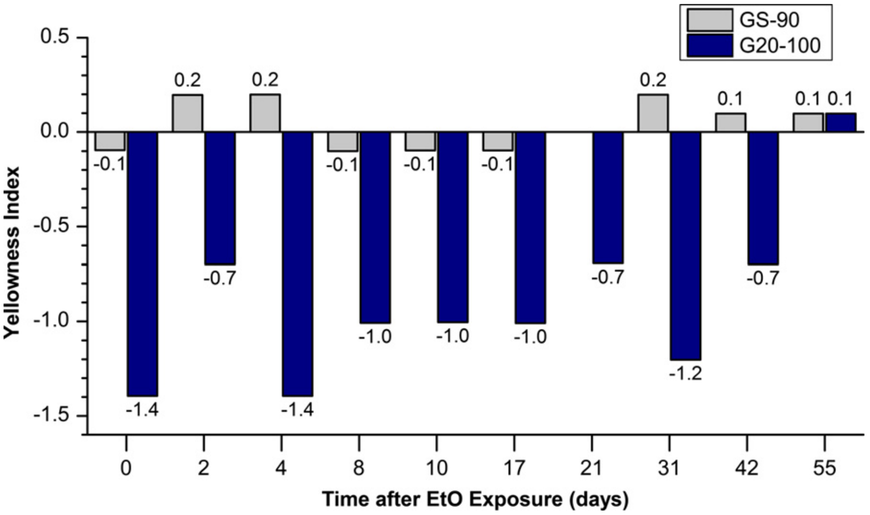


Figure 9.48 Effect of EtO on the yellowness index of CYROLITE® GS-90 and G20-100 compound.[21]



9.6 Acrylonitrile–Methyl Acrylate Copolymer

Acrylonitrile–methyl acrylate (AMA) copolymer is a copolymer of acrylonitrile and methyl acrylate. The generalized structure of AMA is shown in Fig. 9.49. It is a mixture of the acrylonitrile group and methyl group, with the ratio of the two groups affecting the properties. AMA has a CAS number of 24968-79-4.

Manufacturers and trade names: INEOS Barex®.

Sterile applications:

- Food packaging: Processed meats, fish, cheese, spices, sauces, extracts, and juice concentrates.
- Medical packaging: Pharmaceutical, transdermal patches.
- Personal care: Cosmetic packs, mouth wash, perfume.

There are several INEOX Barex® film grades:

- Barex® 210 Film Grade resin is an impact-modified AMA copolymer with excellent gas barrier and a wide range of chemical resistance.
- Barex® 214 Calender Grade resin is an impact-modified AMA copolymer with excellent gas barrier and a wide range of chemical resistance.
- Barex® 218 Extrusion Grade resin is an impact-modified AMA copolymer with increased flexibility and higher impact resistance than the standard Barex 210 resins.

Barex film grades are exceptionally resistant to gamma radiation. Barex film does yellow slightly when irradiated, but this discoloration does not affect performance or transparency.[22] Klöckner Pentaplast BAREX® thin films, made from BAREX® 210, are gamma, e-beam, and EtO sterilizable.[23]

9.7 Ionomers

An ionomer is a polymer that comprises repeat units of both electrically neutral repeating units and a fraction of ionized units. Only ethylene–acrylic acid (EAA) copolymer is discussed in this section.

Starting with selected various grades of copolymers such as ethylene–methacrylic acid, manufacturers add zinc, sodium, lithium, magnesium, or other metal salts. Acid neutralization (for instance of the methacrylic acid in an ethylene–methacrylic acid copolymer) results in the formation of ion clusters (hence the general term, "ionomer") within the resulting polymer matrix. The chemical structure of this process is shown in Fig. 9.50.

The ionomer resins incorporate many of the performance features of the original ethylene-based copolymers, such as chemical resistance, melting range, density, and basic processing characteristics. However, with the alteration forming the ionomer resin, the performance is significantly enhanced in such areas as:

- Low temperature impact toughness
- Abrasion/scuff resistance
- Chemical resistance
- Transparency/clarity
- Melt strength
- Direct adhesion of epoxy and polyurethane finishes, to metal, glass, and natural fibers by heat lamination.

Manufacturers and trade names: DuPont™ Surlyn® and Bexloy® (ethylene–methacrylic acid), Exxon Iotek™ (EAA), Goodrich Hycar®

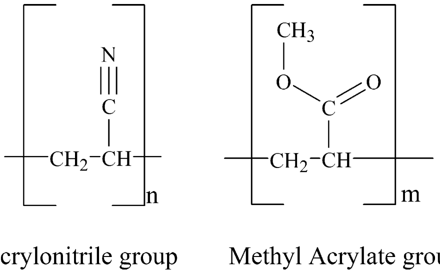
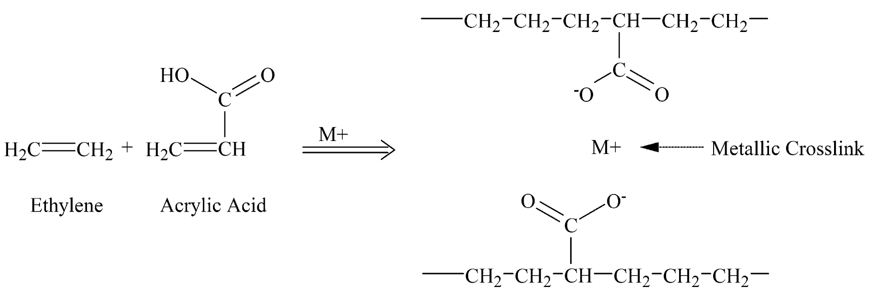


Figure 9.49 Structure of acrylonitrile–methyl acrylate segments.

Figure 9.50 Structure of ethylene—acrylic acid copolymer ionomers.



(butadiene—acrylic acid)-discontinued, and Dow Amplify™ (EAA).

Sterile applications and uses: Packaging films and sealants.

Data for ionomer plastics are found in Tables 9.19—9.41 and Fig. 9.51—9.53.

DuPont™ Surlyn® ionomer resins, some of which are listed below, are crystal clear and are used alone or in combination with other resins:

- Surlyn® 1601. Blown film with superior optical properties.
- Surlyn® 1605. Extrusion coating and blown film; high grease resistance and low-temperature sealability.
- Surlyn® 1650. Blown film coextrusion; good blend of toughness and low-temperature sealability.
- Surlyn® 1652. General-purpose extrusion coating; also blown film.
- Surlyn® 1702. Extrusion coating; excellent low-temperature sealability and hot tack.
- Surlyn® 1705-1. Extrusion coating; excellent low-temperature sealability and hot tack.
- Surlyn® 1802. Blown film; superior low-temperature sealability and toughness.
- Surlyn® 1855. Terionomer for blown film; superior low-temperature sealability and high stress crack.
- Surlyn® 1857. Terionomer for blown film and extrusion coating; superior low-temperature sealability and adhesion to nylon in coextrusion.
- Surlyn® 1901. For blown film; terionomer version of 1601 for lower temperature sealing.
- Surlyn® AD-8273. A zinc ionomer, gives both interfacial peelable and fusion seals depending on sealing temperature.

Table 9.19 The Effect of Gamma Radiation and Aging on the Tensile Strength of a 51-μm Film of DuPont Surlyn® 1601 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Tensile Strength (MPa)		
0	25.2	21.4	18.5
25	22.9	25.3	18.3
50	29.2	28.6	23.1

Table 9.20 The Effect of Gamma Radiation and Aging on the Tensile Strength of a 51-μm Film of DuPont Surlyn® 1652 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Tensile Strength (MPa)		
0	23.4	22.6	18.1
25	24.5	24.6	19.8
50	27.2	26.8	23.4

Table 9.21 The Effect of Gamma Radiation and Aging on the Tensile Strength of a 51-μm Film of DuPont Surlyn® AD 8273 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Tensile Strength (MPa)		
0	25.6	26.9	22.8
25	26.7	25.9	23.9
50	31.3	27.5	28.3

Table 9.22 The Effect of Gamma Radiation and Aging on the Elongation of a 51-μm Film of DuPont Surlyn® 1601 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Elongation (%)		
0	292	261	231
25	251	321	215
50	290	329	300

Table 9.23 The Effect of Gamma Radiation and Aging on the Elongation of a 51-μm Film of DuPont Surlyn® 1652 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Elongation (%)		
0	390	352	291
25	371	371	320
50	370	370	300

Table 9.24 The Effect of Gamma Radiation and Aging on the Elongation of a 51-μm Film of DuPont Surlyn® AD 8273 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Elongation (%)		
0	481	471	440
25	450	451	431
50	460	421	409

Table 9.25 The Effect of Gamma Radiation and Aging on the Secant Modulus of a 51-μm Film of DuPont Surlyn® 1601 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Secant Modulus (MPa)		
0	168	175	199
25	167	210	196
50	172	231	203

Table 9.26 The Effect of Gamma Radiation and Aging on the Secant Modulus of a 51-μm Film of DuPont Surlyn® 1652 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Secant Modulus (MPa)		
0	140	185	155
25	116	180	103
50	128	167	123

Table 9.27 The Effect of Gamma Radiation and Aging on the Secant Modulus of a 51-μm Film of DuPont Surlyn® AD 8273 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Secant Modulus (MPa)		
0	84	97	81
25	78	104	77
50	77	105	74

Table 9.28 The Effect of Electron Beam and Aging on the Tensile Strength of a 76-μm Film of DuPont Surlyn® 1601 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Tensile Strength (MPa)		
0	23.7	27.1	30.2
25	30.4	31.3	33.0
50	32.0	34.1	34.5

Table 9.29 The Effect of Electron Beam and Aging on the Tensile Strength of a 76-μm Film of DuPont Surlyn® 1652 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Tensile Strength (MPa)		
0	23.0	25.5	23.4
25	22.6	23.5	25.8
50	26.9	24.7	27.6

Table 9.30 The Effect of Electron Beam and Aging on the Elongation of a 76-μm Film of DuPont Surlyn® 1601 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Elongation (%)		
0	375	380	381
25	466	390	391
50	447	411	369

Table 9.31 The Effect of Electron Beam and Aging on the Elongation of a 76-μm Film of DuPont Surlyn® 1652 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Elongation (%)		
0	474	404	409
25	379	404	389
50	420	439	445

Table 9.32 The Effect of Electron Beam and Aging on the Secant Modulus of a 76-μm Film of DuPont Surlyn® 1601 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Secant Modulus (MPa)		
0	184	220	265
25	219	234	267
50	212	228	266

Table 9.33 The Effect of Electron Beam and Aging on the Secant Modulus a of 76-μm Film of DuPont Surlyn® 1652 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Secant Modulus (MPa)		
0	190	215	170
25	172	194	206
50	173	190	203

Table 9.34 The Effect of Electron Beam and Aging on the Elmendorf Tear of a 76-μm Film of DuPont Surlyn® 1601 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Elmendorf Tear (g/μm)		
0	0.70	1.07	1.48
25	0.95	0.78	0.83
50	1.00	0.77	0.89

Table 9.35 The Effect of Electron Beam and Aging on the Elmendorf Tear of a 76-μm Film of DuPont Surlyn® 1652 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Elmendorf Tear (g/μm)		
0	3.4	3.9	3.9
25	3.4	3.6	3.6
50	3.0	3.0	2.9

Table 9.36 The Effect of Electron Beam and Aging on the 20° Gloss of a 76-μm Film of DuPont Surlyn® 1601 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	20° Gloss		
0	104	95	111
25	139	96	84
50	139	95	65

Table 9.37 The Effect of Electron Beam and Aging on the 20° Gloss of a 76-μm Film of DuPont Surlyn® 1652 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	20° Gloss		
0	44.2	44.1	49.1
25	29.9	49.1	53.1
50	34.0	36.0	35.0

Table 9.38 The Effect of Electron Beam and Aging on the Haze of a 76-μm Film of DuPont Surlyn® 1601 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Haze (%)		
0	1.5	1.8	2.2
25	1.5	1.7	2.4
50	1.6	1.6	2.6

Table 9.39 The Effect of Electron Beam and Aging on the Haze of a 76-μm Film of DuPont Surlyn® 1652 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Haze (%)		
0	4.8	4.6	4.6
25	4.8	5.0	5.8
50	5.0	4.8	6.8

Table 9.40 The Effect of Electron Beam and Aging on the Transparency of a 76-μm Film of DuPont Surlyn® 1601 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Transparency (%)		
0	72	71	75
25	73	74	74
50	75	75	74

Table 9.41 The Effect of Electron Beam and Aging on the Transparency of a 76-μm Film of DuPont Surlyn® 1652 Ionomer[24]

Radiation Dose (kGy)	Months of Aging		
	0	6	12
	Transparency (%)		
0	36.9	37.7	39.7
25	29.7	33.6	29.5
50	29.6	30.4	33.5

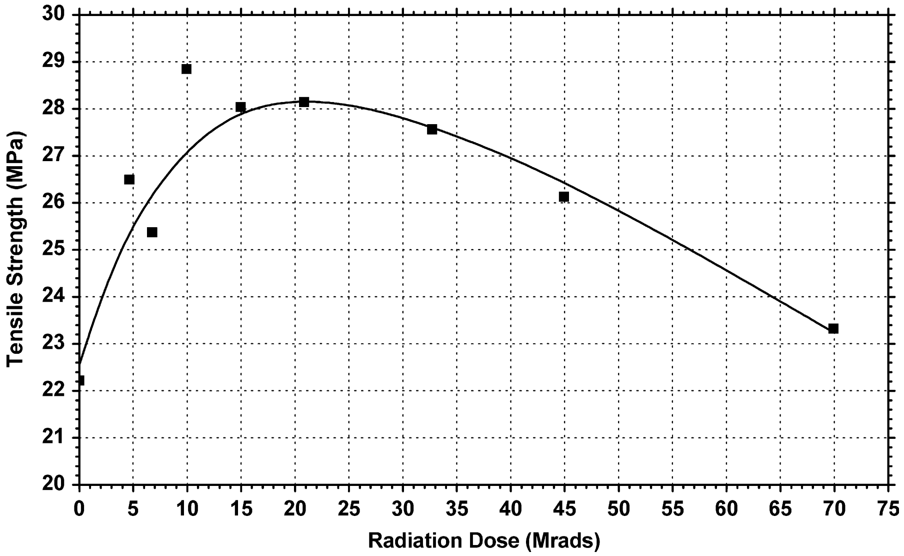


Figure 9.51 The effect of electron beam radiation on the tensile strength of DuPont Surlyn® ionomer.[25]

Figure 9.52 The effect of electron beam radiation on the elongation at break of DuPont Surlyn® ionomer.[25]

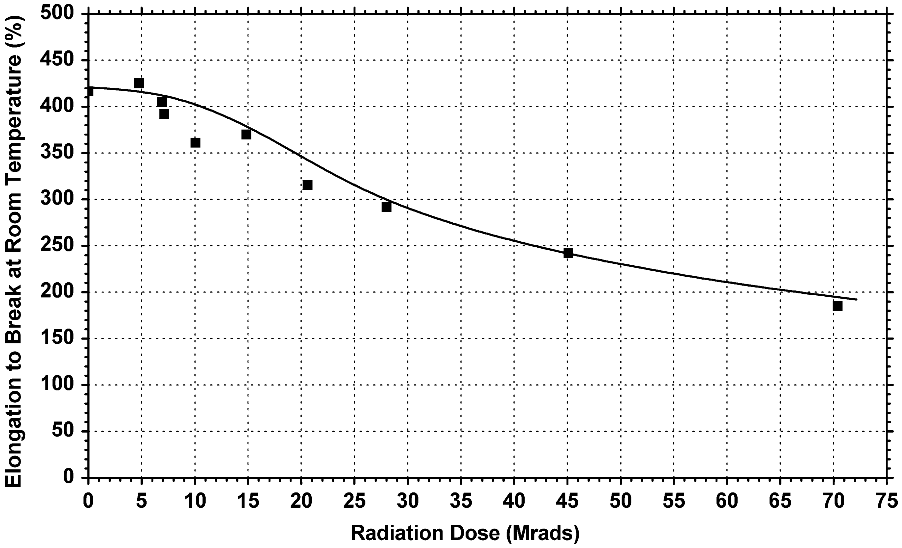
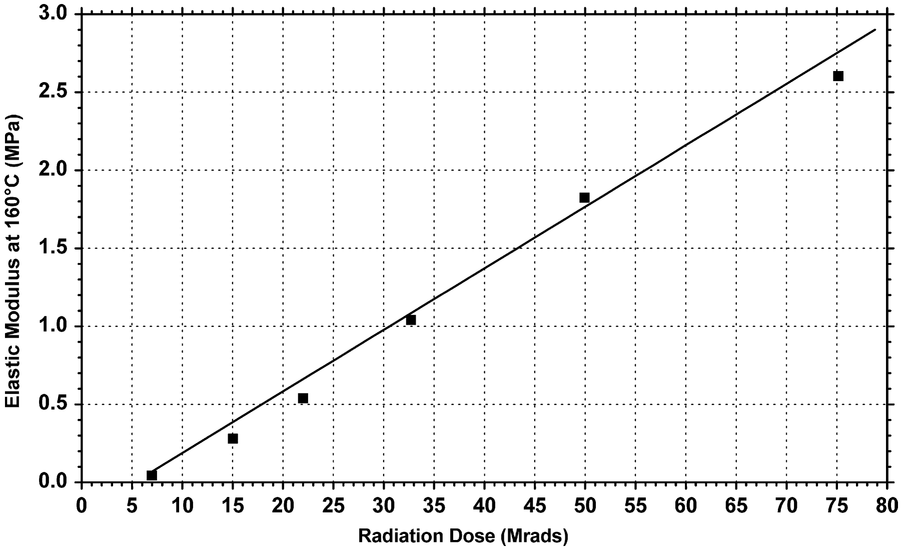


Figure 9.53 The effect of electron beam radiation on the elastic modulus at 160 °C of DuPont Surlyn® ionomer.[25]



Surlyn® cannot be heat sterilized because of its low softening point. It may be sterilized using radiation, gamma or electron beam, with a maximum of 5.0 Mrad, or ethylene oxide (used in a 12%/88% ethylene oxide/Freon gas mix). Ionizing radiation leads to cross-linking.

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10 Fluoropolymers

Traditionally, a fluoropolymer or fluoroplastic is defined as a polymer consisting of carbon (C) and fluorine (F). Sometimes these are referred to as perfluoropolymers to distinguish them from partially fluorinated polymers, fluoroelastomers, and other polymers that contain less fluorine in their chemical structure. For example, fluorosilicone and fluoroacrylate polymers are not referred to as fluoropolymers. The monomers used to make the various fluoropolymers are shown in Fig. 10.1.

Details of each of the fluoropolymers are in the following sections. The melting points are all compared in Table 10.1.

An overview of the effect of various sterilization processes on fluoropolymers is given in Tables 10.2 and 10.3.

High-energy radiation (X-ray, gamma ray, and electron beam) has two effects on fluoroplastics, molecular weight reduction and degradation, and cross-linking by forming intermediate free radicals. The degradation effect is more severe in the presence of oxygen (in air) than in vacuum and is further intensified at elevated temperatures. Oxygen allows the formation of unstable peroxide bonds in the polymer backbone. Each peroxide bond breaks and generates two shorter chains from the original

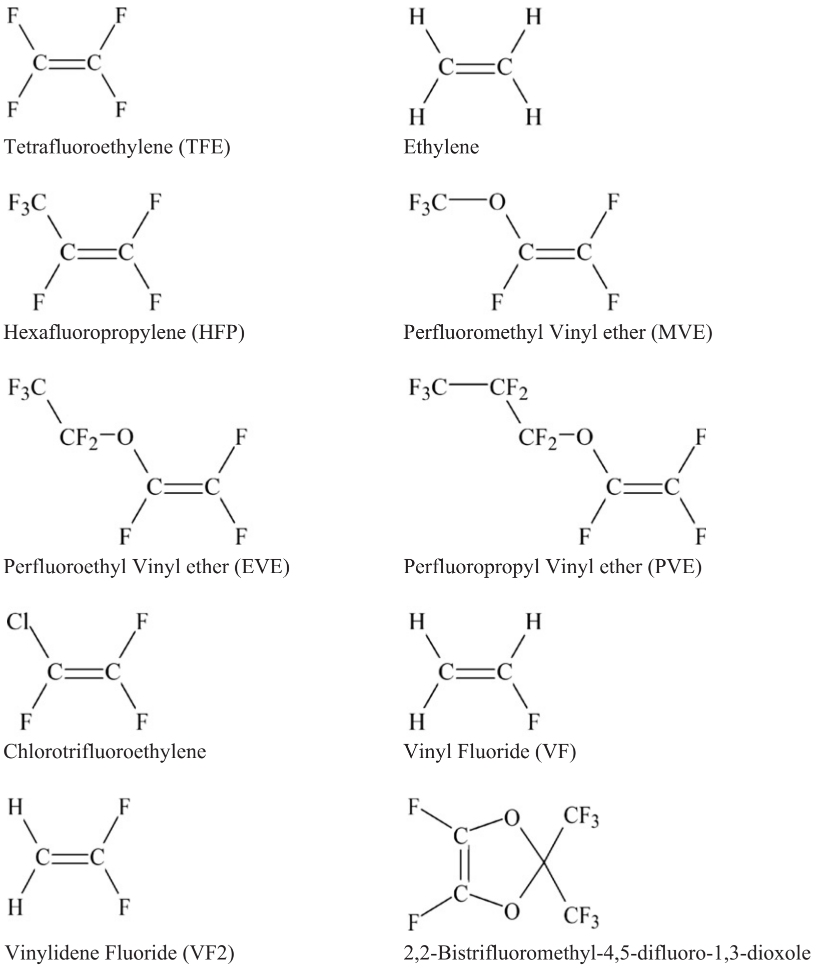

Tetrafluoroethylene (TFE)
Ethylene
Hexafluoropropylene (HFP)
Perfluoromethyl Vinyl ether (MVE)
Perfluoroethyl Vinyl ether (EVE)
Perfluoropropyl Vinyl ether (PVE)
Chlorotrifluoroethylene
Vinyl Fluoride (VF)
Vinylidene Fluoride (VF2)
2,2-Bistrifluoromethyl-4,5-difluoro-1,3-dioxole

Figure 10.1 Structures of many monomers used to make fluoropolymers.

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00010-1

Table 10.1 Melting Point Ranges of Various Fluoroplastics

Fluoroplastic	Melting Point (°C)
Polytetrafluoroethylene (PTFE)	320–340
Polyethylene chlorotrifluoroethylene (ECTFE)	240
Polyethylene tetrafluoroethylene (ETFE)	255–280
Fluorinated ethylene propylene (FEP)	260–270
Perfluoroalkoxy (PFA)	302–310
Perfluoroalkoxy (MFA)	280–290
Polychlorotrifluoroethylene (PCTFE)	210–212
Polyvinylidene fluoride (PVDF)	155–170
THV™	115–235
HTE*	155–215

**HTE is a Dyneon™ proprietary fluoropolymer.*

polymer chain. In the vacuum, cross-linking and recombination of free radicals offset some of the chain scission effect of radiation.[3]

Perfluorinated fluoropolymers, such as polytetrafluoroethylene (PTFE), are more susceptible to degradation by radiation than partially fluorinated fluoropolymers, especially in air.

10.1 Polytetrafluoroethylene

PTFE polymer is an example of a linear fluoropolymer. Its structure in simplistic form is shown in Fig. 10.2. The CAS number for PTFE is 9002-84-0.

Formed by the polymerization of tetrafluoroethylene (TFE), the (—CF_2—CF_2—) groups repeat many thousands of times. The fundamental properties of fluoropolymers evolve from the atomic structure of fluorine and carbon and their covalent bonding in specific chemical structures. The backbone is formed of carbon—carbon bonds and the pendant groups are carbon—fluorine bonds. Both are extremely strong bonds. The basic properties of PTFE stem from these two very strong chemical bonds. The size of the fluorine atom allows the

Table 10.2 Performance of Fluoropolymers Poststerilization[1]

Sterilization Method	PTFE	FEP	PFA	ETFE	PVDF
Ethylene oxide	Excellent	Excellent	Excellent	Excellent	Excellent
Autoclave	Average	Excellent	Excellent	Excellent	Excellent
Gamma	Poor	Good	Excellent	Excellent	Excellent

Note: PTFE, polytetrafluoroethylene; FEP, fluorinated ethylene propylene; PFA, perfluoro alkoxy; ETFE, ethylene—tetrafluoroethylene; PVDF, polyvinylidene fluoride.

Table 10.3 Sterilization Capabilities of Fluoropolymers[2]

Fluoropolymers	Steam	Dry Heat	Ethylene Oxide	Gamma Radiation	E-Beam
PTFE*	Fair	Fair	Good	Poor	Poor
FEP	Good	Good	Good	Fair	Fair
PFA	Good	Good	Good	Good	Good
ECTFE/ETFE	Good	Good	Good	Good	Good
PVF/PVDF	Good	Good	Good	Good	Good

Note: PTFE, polytetrafluoroethylene; FEP, fluorinated ethylene propylene; PFA, perfluoroalkoxy; ECTFE, ethylene—chlorotrifluoroethylene; ETFE, ethylene—tetrafluoroethylene; PVF, polyvinyl fluoride; PVDF, polyvinylidene fluoride.
**Radiation-stable grades should be considered for gamma and e-beam radiation sterilization.*

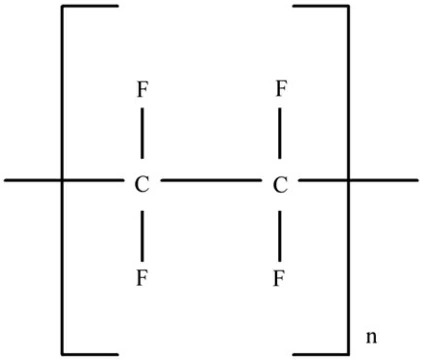


Figure 10.2 Chemical structure of polytetrafluoroethylene.

formation of a uniform and continuous covering around the carbon—carbon bonds and protects them from chemical attack, thus imparting chemical resistance and stability to the molecule. PTFE is rated for use up to (260 °C). PTFE does not dissolve in any known solvent. The fluorine sheath is also responsible for the low surface energy (18 dynes/cm) and low coefficient of friction (0.05—0.08, static) of PTFE. Another attribute of the uniform fluorine sheath is the electrical inertness (or nonpolarity) of the PTFE molecule. Electrical fields impart only slight polarization in this molecule, so volume and surface resistivity are high.

The PTFE molecule is simple and is quite ordered. This is shown in the three-dimensional models of Figs 10.3 and 10.4. PTFE can align itself with other molecules or other portions of the same molecule. Disordered regions are called *amorphous* regions. This is important because polymers with high crystallinity require more energy to melt. In other words, they have higher melting points. When this happens, it forms what is called a crystalline region. Crystalline polymers have a substantial fraction of their mass in the form of parallel, closely packed molecules. High molecular weight PTFE resins have high crystallinity and therefore high melting points, typically as high as 320—342 °C (608—648 °F). The crystallinity of as-polymerized PTFE is typically 92—98%. Further, the viscosity in the molten state (called melt creep viscosity) is so high that high molecular weight PTFE particles do not flow even at temperatures above its melting point. They sinter much like powdered metals; they stick to each other at the contact points and combine into larger particles.

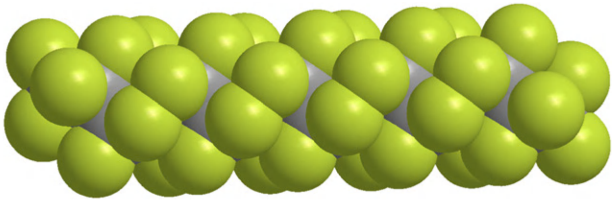


Figure 10.3 Three-dimensional representation of polytetrafluoroethylene.

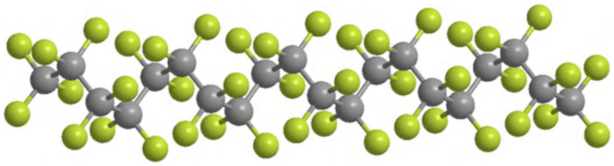


Figure 10.4 Ball-and-stick three-dimensional representation of polytetrafluoroethylene.

PTFE is called a *homopolymer*, a polymer made from a single monomer. Recently, many PTFE manufacturers have added minute amounts of other monomers to their PTFE polymerizations to produce alternate grades of PTFE designed for specific applications. Fluoropolymer manufacturers continue to call these grades modified homopolymers at below 1% by weight of comonomer. DuPont grades of this type are called Teflon® NXT resins. Dyneon™ TFM™ modified PTFE incorporates less than 1% of the comonomer perfluoropropyl vinyl ether (PPVE). Daikin's modified grade is Polyflon™ M-111. These modified granular PTFE materials retain the exceptional chemical, thermal, anti-stick, and low-friction properties of conventional PTFE resin, but offer some improvements:

- Weldability
- Improved permeation resistance
- Less creep
- Smoother, less porous surfaces
- Better high-voltage insulation.

The copolymers described in the next sections contain significantly more of the non-TFE monomers.

Manufacturers and trade names: DuPont™ Teflon® PTFE, Dyneon PTFE, Daikin Polyflon™ and many others.

Applications and uses: Pipe liners, fittings, valves, pumps, and other components used for transferring aggressive, ultrapure fluids.

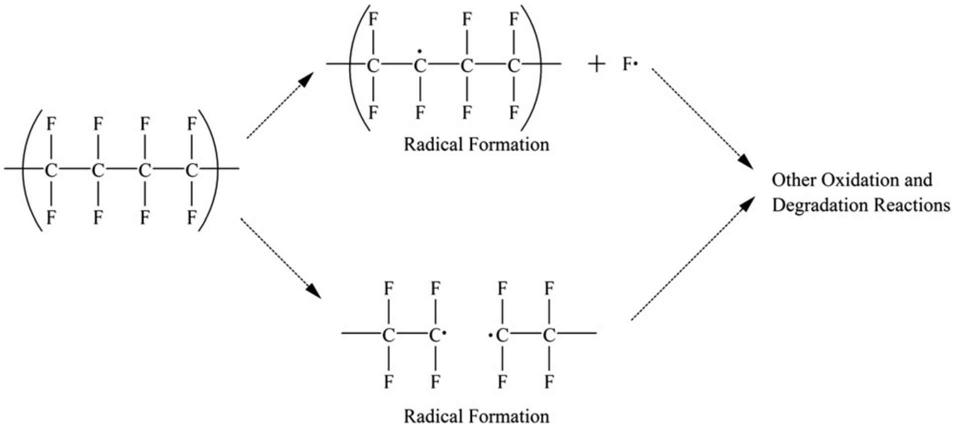


Figure 10.5 Radiation degradation mechanisms of polytetrafluoroethylene.[2]

Exposure to high-energy (ionizing) radiation, regardless of the source, degrades PTFE by breaking down the molecules and reducing its molecular weight, resulting in a marked decrease in melt viscosity. The degradation mechanism is outlined in Fig. 10.5. As in thermal degradation, radiation stability of PTFE is much better under vacuum compared to air. For example, exposure of PTFE film to a dose of 1 Mrad of gamma rays from a Cobalt-60 in air resulted in 87% loss of initial elongation and 54% loss of tensile strength as shown in Table 10.4. A significantly less loss of tensile properties occurs when PTFE is exposed to the same radiation dose in a vacuum.

Data for PTFE plastics are found in Table 10.4 and Figs 10.6 and 10.7.

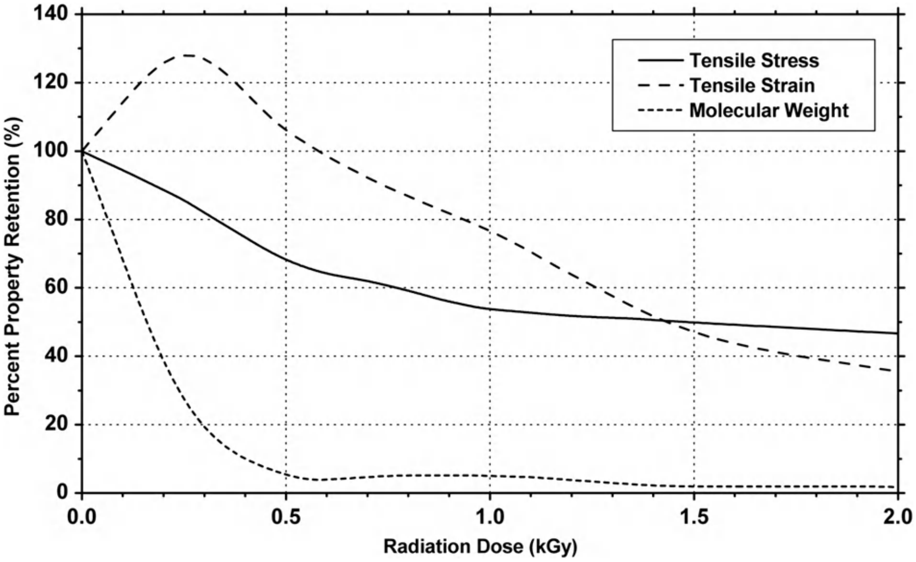
Table 10.4 Effect of Radiation (1 Mrad) on Polytetrafluoroethylene[4]

Environment	Elongation Loss (%)	Tensile Strength Loss (%)
Air	87	54
Vacuum	44	17

10.2 Fluorinated Ethylene Propylene

If one of the fluorine atoms on TFE is replaced with a trifluoromethyl group ($-CF_3$), then the new monomer is called hexafluoropropylene (HFP). Polymerization of monomers HFP and TFE yield a fluoropolymer, fluorinated ethylene propylene,

Figure 10.6 Effect of gamma sterilization on some retention of properties of polytetrafluoroethylene.[2]



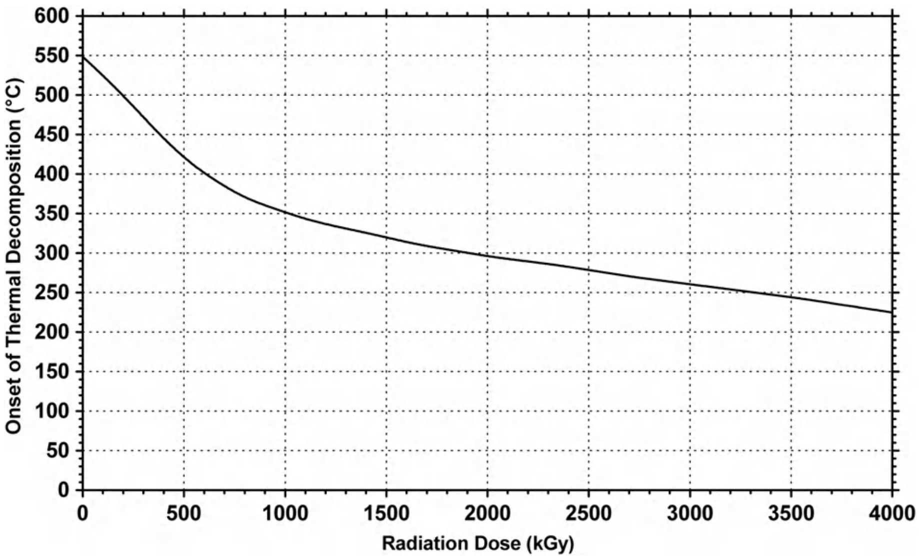
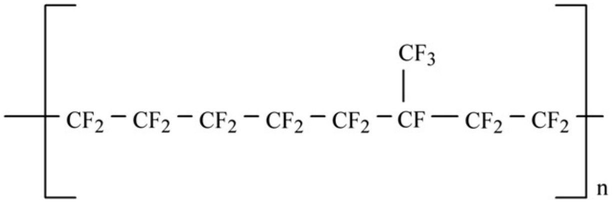


Figure 10.7 Effect of e-beam sterilization on the onset of thermal decomposition of polytetrafluoroethylene.[2]



$$\left[-CF_2-CF_2-CF_2-CF_2-CF_2-\overset{\overset{CF_3}{|}}{CF}-CF_2-CF_2- \right]_n$$

Figure 10.8 Chemical structure of fluorinated ethylene propylene.

FEP. The number of HFP groups is typically 13% by weight or less, and its structure is shown in Fig. 10.8. The CAS number for FEP is 25067-11-2.

The effect of using HFP is to put a "bump" along the polymer chain as shown in the three-dimensional models in Figs 10.9 and 10.10. This bump disrupts the crystallization of the FEP, which has a typical as-polymerized crystallinity of 70% versus 92–98% for PTFE. It also lowers its melting point. The reduction of the melting point depends on the amount of trifluoromethyl groups added and secondarily on the molecular weight. Most FEP resins melt around 274 °C (525 °F), although lower melting points are possible. Even high molecular weight FEP will melt and flow. The high chemical resistance, low surface energy, and good electrical insulation properties of PTFE are retained.

Manufacturers and trade names: DuPont™ Teflon® FEP, Dyneon™ THV FEP, and Daikin Neoflon™.

Applications and uses: Applications requiring excellent chemical resistance, superior electrical properties, and high service temperatures: release films, tubing, cable insulation, and jacketing.

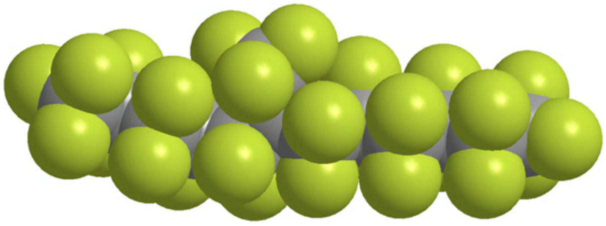


Figure 10.9 Three-dimensional representation of fluorinated ethylene propylene.

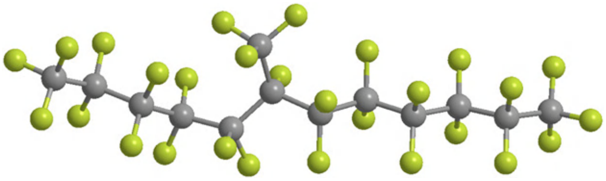


Figure 10.10 Ball-and-stick three-dimensional representation of fluorinated ethylene propylene.

FEP is somewhat more resistant to high-energy radiation than PTFE.

Data for FEP plastics are found in Table 10.5 and Figs 10.11 and 10.12.

10.3 Perfluoroalkoxy

Making a more dramatic change in the side group than that done in making FEP, chemists put

Table 10.5 Effect of Radiation on Fluorinated Ethylene Propylene (courtesy DuPont Fluoroproducts)

Exposure (Mrad)	Break Elongation (%)	Tensile Strength (%)
0	113	33.1
1.0	88	27.3
2.5	71	24.3
3.5	66	24.1
5	53	23.3

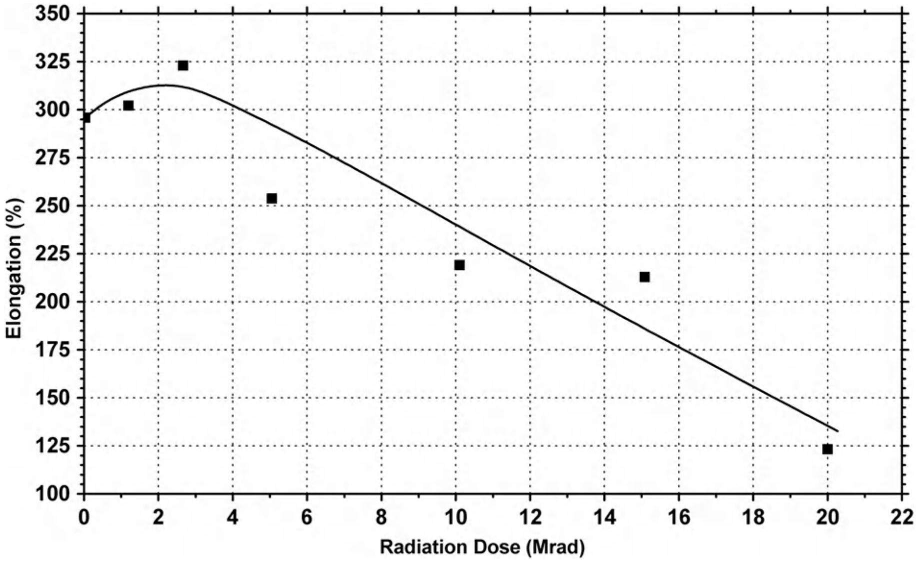


Figure 10.11 Effect of gamma radiation dose on the break elongation of fluorinated ethylene propylene.[5]

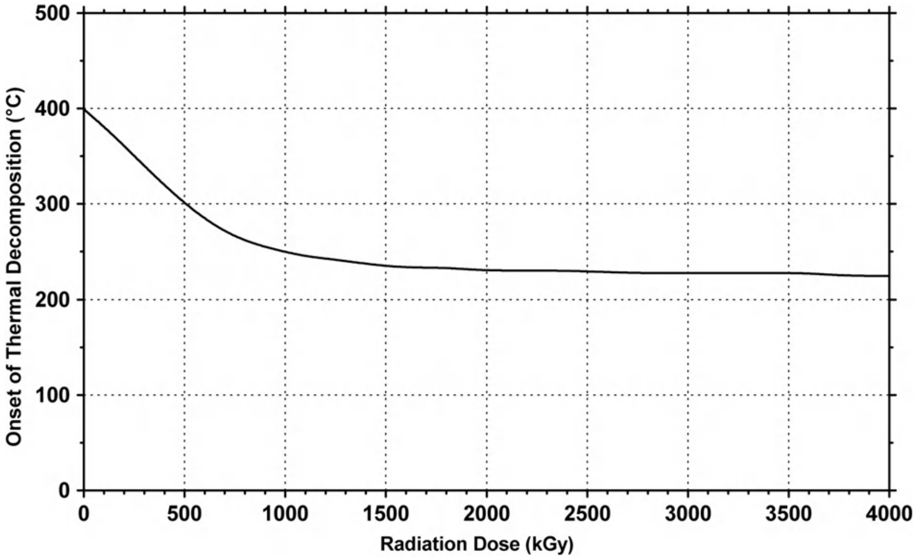


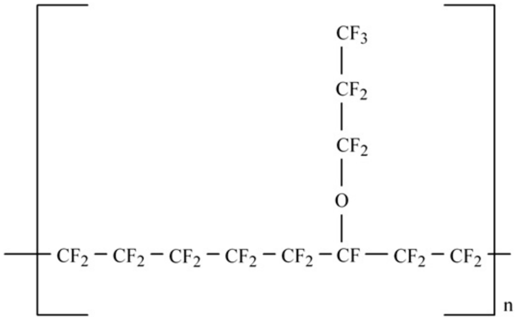
Figure 10.12 Effect of e-beam sterilization dose on the onset of thermal decomposition of fluorinated ethylene propylene.[2]

a perfluoroalkoxy group on the polymer chain. This group is signified as $-O\text{-}R_f$, where R_f can be any number of totally fluorinated carbons. The most common comonomer is perfluoropropyl ($-O-CF_2-CF_2-CF_3$). However, other comonomers are shown in Table 10.6.

The polymers based on perfluoroalkylvinyl ether (PVE) are called PFA and the perfluoroalkylvinyl

Table 10.6 Perfluoroalkoxy Comonomers

Comonomer	Structure
Perfluoromethyl vinyl ether (MVE)	$CF_2{=}CF{-}O{-}CF_3$
Perfluoroethyl vinyl ether (EVE)	$CF_2{=}CF{-}O{-}CF_2\text{-}CF_3$
Perfluoropropyl vinyl ether (PVE)	$CF_2{=}CF{-}O{-}CF_2{-}CF_2{-}CF_3$



$$\left[-CF_2-CF_2-CF_2-CF_2-CF_2-\overset{\displaystyle CF_3-CF_2-CF_2-O}{\overset{|}{CF}}-CF_2-CF_2-\right]_n$$

Figure 10.13 Chemical structure of perfluoroalkoxy.

ether group is typically added at 3.5% or less. When the comonomer is MVE, the polymer is called MFA. A structure of PFA is shown in Fig. 10.13. The CAS Number of PFA using PPVE as comonomer is 26655-00-5.

The large side group as shown in Figs 10.14 and 10.15 reduces the crystallinity drastically. The melting point is generally between 305−310 °C (581−590 °F) depending on the molecular weight. The melt viscosity is also dramatically dependent on the molecular weight. Since PFA is still perfluorinated, as with FEP, the high chemical resistance, low surface energy, and good electrical insulation properties are retained.

Solvay Solexis Hyflon® MFA and PFA are semicrystalline fully fluorinated melt-processible fluoropolymers. Hyflon® PFA belongs to the class of PFA (perfluoroalkoxy) having a lower melting point than standard PFA grades.

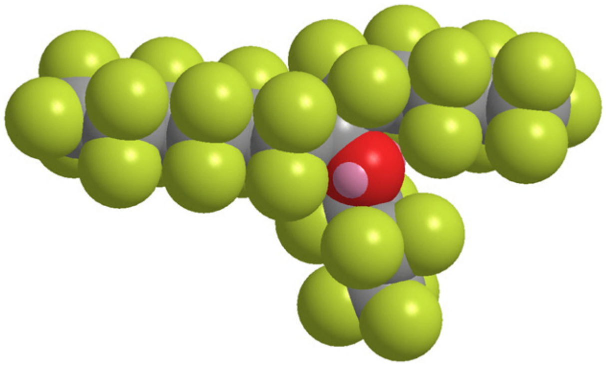


Figure 10.14 Three-dimensional representation of perfluoroalkoxy.

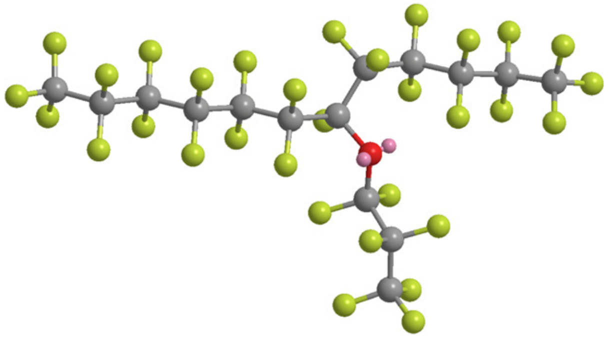


Figure 10.15 Ball-and-stick three-dimensional representation of perfluoroalkoxy.

Manufacturers and trade names: DuPont™ Teflon®, Solvay Solexis Hyflon®, Dyneon™ (a 3M company), and Daikin.

Applications and uses: Lined and coated processing equipment, vessels and housings, high-purity chemical storage.

10.3.1 PFA

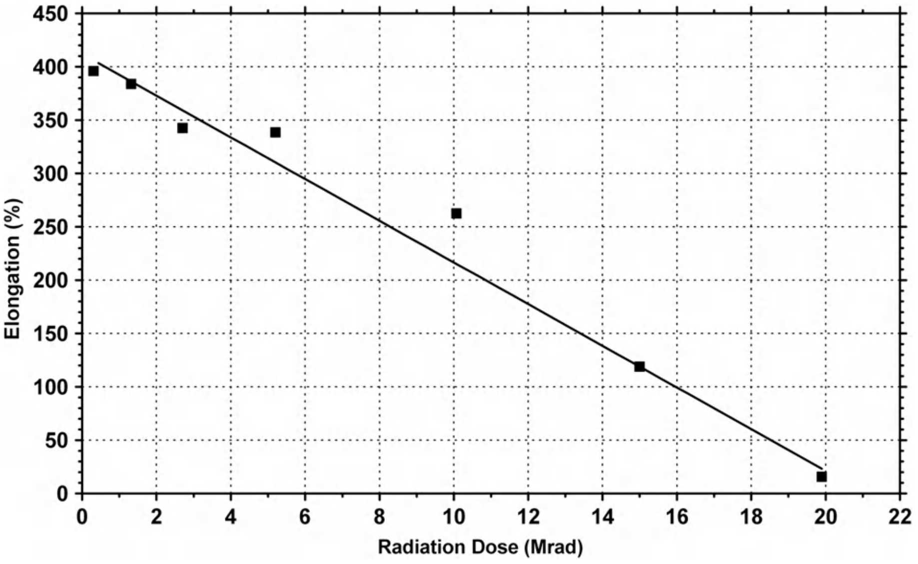
PFA is somewhat more resistant to high-energy radiation than PTFE.

Data for PFA plastics are found in Table 10.7 and Fig. 10.16.

Table 10.7 Effect of Radiation on Perfluoroalkoxy[6]

Exposure (Mrad)	Break Elongation (%)	Tensile Strength (%)
0	358	30
0.5	366	28
1.0	333	25
2.0	302	21
5.0	35	15
20	<5	–
50	<5	–

Figure 10.16 Effect of gamma radiation dose on the break elongation of perfluoroalkoxy.[5]



10.3.2 MFA

Resistance to high-energy radiation: Like PTFE, perfluoroalkoxy resins have limited resistance to high-energy ionizing radiation. Further to exposure, MFAs undergo a reduction of their tensile strength and elongation at break. For example, a 5 MRad will cause a 95% reduction of the resin's elongation at break. A 50 MRad exposure will cause complete polymer degradation.[7]

10.4 Amorphous Fluoropolymer – Teflon AF®

A perfluorinated polymer made by DuPont™ called Teflon AF® breaks down the crystallinity completely, hence its designation AF (Amorphous Fluoropolymer). It is a copolymer made from 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole and TFE. The structure of Teflon AF® is shown in Fig. 10.17.

The Teflon AF® family of amorphous fluoropolymers is similar to Teflon® PTFE and PFA in many of the usual properties but is unique in the following ways. It:

1. Is a true amorphous fluoropolymer
2. Has a somewhat higher coefficient of friction than Teflon® PTFE and PFA
3. Has excellent mechanical and physical properties at end-use temperatures up to 300 °C (572 °F)

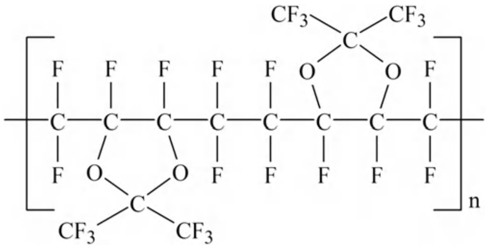


Figure 10.17 Structure of Teflon® AF.

4. Has excellent light transmission from ultraviolet (UV) through a good portion of infrared (IR)
5. Has very low refractive index
6. Has the lowest dielectric constant of any plastic even at gigahertz frequencies
7. Has solubility to a limited extent in selected perfluorinated solvents.

Teflon® AF can be designed to have some solubility in selected perfluorinated solvents but remains chemically resistant to all other solvents and process chemicals. The solubility is typically only 3–15% by weight, but this makes it possible one to solution-cast extremely thin coatings in the submicron thickness range.

Manufacturers and trade names: DuPont™ Teflon AF®.

Data for Teflon® AF plastics are found in Figs 10.18 and 10.19.

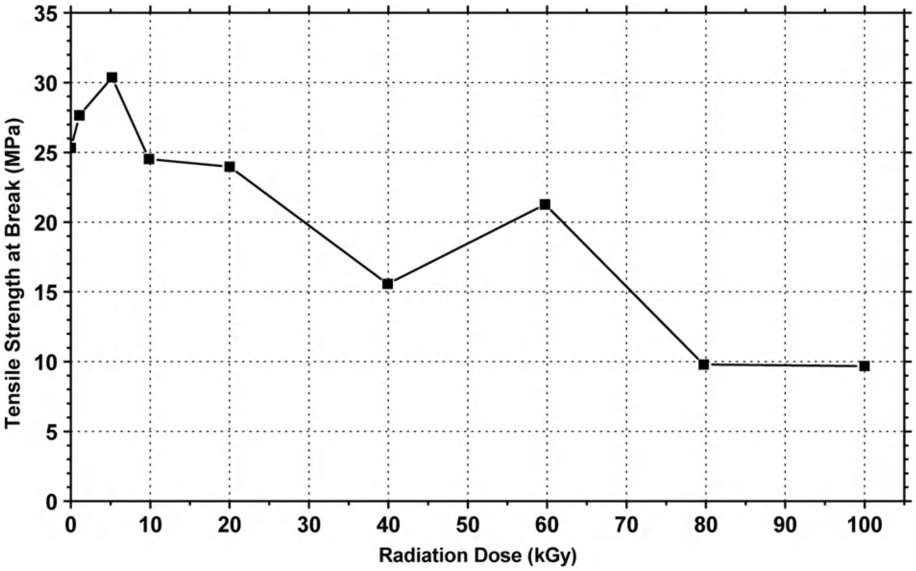


Figure 10.18 Tensile strength at break versus radiation dose of DuPont Teflon® AF1600 irradiated films.[8]

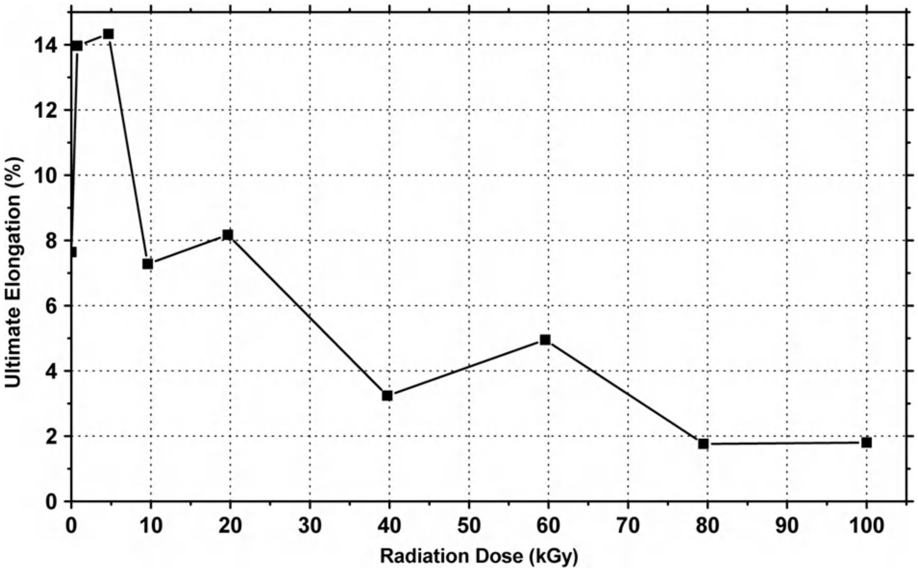


Figure 10.19 Ultimate elongation versus radiation dose of DuPont Teflon® AF1600 irradiated films.[8]

10.5 Polyvinyl Fluoride

Polyvinyl fluoride (PVF) is a homopolymer of vinyl fluoride. The molecular structure of PVF is shown in Fig. 10.20.

DuPont™ is the only known manufacturer of this polymer they call Tedlar®. The structure above shows a head-to-tail configuration of the CF monomer; there are no fluorines on adjacent carbons. But in reality vinyl fluoride polymerizes in both head-to-head and head-to-tail configurations. DuPont's commercial PVF contains 10−12% of head-to-head and tail-to-tail units, also called *inversions*.[9] Its CAS number is 24981-14-4.

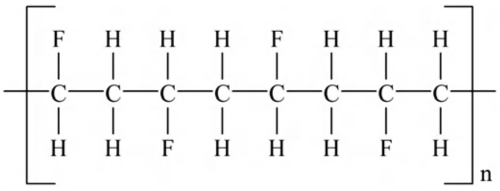


Figure 10.20 Structure of polyvinyl fluoride.

PVF has excellent resistance to weathering, staining, and chemical attack (except ketones and

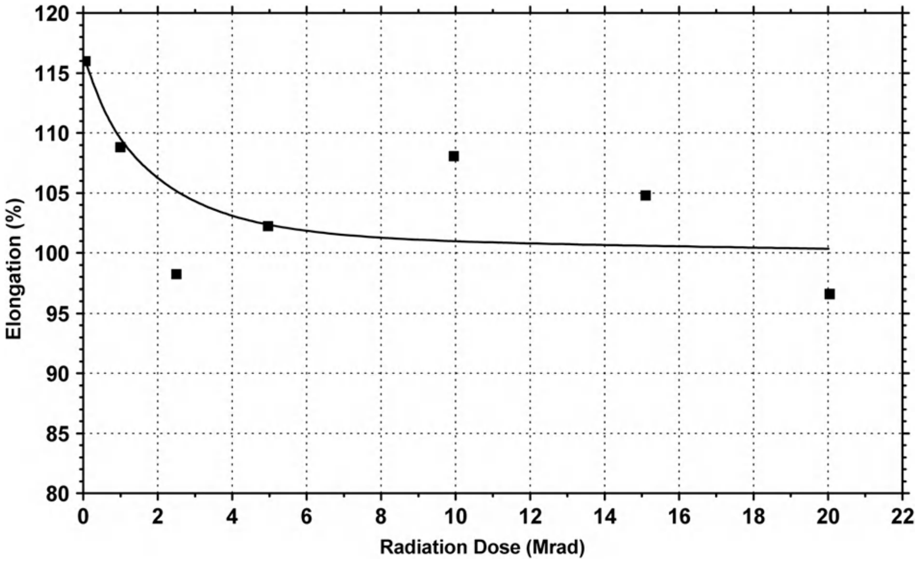


Figure 10.21 Effect of gamma radiation dose on the elongation at break of polyvinyl fluoride.[5]

esters). It exhibits very slow burning and low permeability to vapor. Its most visible use is on the interiors of the passenger compartments of commercial aircraft.

General description: PVF is available only in film form. DuPont™ Tedlar® films are available in clear, translucent, or opaque white film and in several surface finishes.

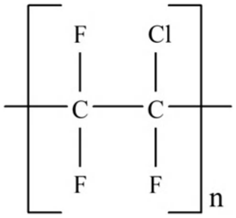
Applications and uses: Gas/breath sampling bags.

Data for PVF plastics are found in Fig. 10.21.

10.6 Polychlorotrifluoroethylene

Polychlorotrifluoroethylene (PCTFE) is a homopolymer of chlorotrifluoroethylene, characterized by the following structure shown in Fig. 10.22. The CAS number is 9002-83-9.

The addition of the one chlorine atom contributes to lowering the melt viscosity to permit extrusion and injection molding. It also contributes to the transparency, the exceptional flow, and the rigidity characteristics of the polymer. Fluorine is responsible for its chemical inertness and zero moisture absorption. Therefore, PCTFE has unique properties. Its resistance to cold flow, dimensional stability, rigidity, low gas permeability, and low moisture absorption is superior to any other fluoropolymer. It can be used at low temperatures. Some products contain a small amount of a comonomer.



$\left[-\mathrm{CF_2}-\mathrm{CFCl}- \right]_n$

Figure 10.22 Chemical structure of polychlorotrifluoroethylene.

Manufacturers and trade names: Honeywell Aclar®, Arkema VOLTALEF®, and Daikin Industries Neoflon® CTFE.

Sterile applications: Pharmaceutical packaging including bags, pouches, and blister packs; different types of diagnostic apparatus such as blood analyzers.

VOLTALEF® PCTFE's transparency to UV, near IR, and X-rays and its insensitivity and impermeability to oxygen allow it to be used for the protection of drugs or pharmaceuticals sensitive to oxygen or which need to be sterilized in their packaging.[10]

Data for PCTFE plastics are found in Table 10.8.

Table 10.8 Effect of Gamma Radiation Sterilization on 3M KEL-F 81(discontinued) PCTFE[11]

Sterilization Conditions		
Radiation dose (Mrad)	16	24
Properties Retained (%)		
Tensile strength	70	60
Tensile strength at yield	70	110
Elongation	80	80
Modulus	115	110

10.7 Polyvinylidene Fluoride

The polymers made from 1,1-di-fluoro-ethene (or vinylidene fluoride) are known as polyvinylidene fluoride (PVDF). They are resistant to oils and fats, water and steam, and gas and odors, making them of particular value for the food industry. PVDF is known for its exceptional chemical stability and excellent resistance to UV radiation. It is used chiefly in the production and coating of equipment used in aggressive environments and where high levels of mechanical and thermal resistance are required. It has also been used in architectural applications as a coating on metal siding where it provides exceptional resistance to environmental exposure. The chemical structure of PVDF is shown in Fig. 10.23. Its CAS number is 24937-79-9. Some products are comonomers.

The alternating CH_2 and CF_2 groups along the polymer chain provide a unique polarity that influences its solubility and electric properties. At elevated temperatures, PVDF can be dissolved in polar solvents such as organic esters and amines. This selective solubility offers a way to prepare corrosion resistant coatings for chemical process equipment and long-life architectural finishes on building panels.

Key attributes of PVDF include:

- Mechanical strength and toughness
- High abrasion resistance
- High thermal stability
- High dielectric strength
- High purity
- Readily melt processible
- Resistant to most chemicals and solvents
- Resistant to UV and nuclear radiation
- Resistant to weathering
- Resistant to fungi
- Low permeability to most gases and liquids
- Low flame and smoke characteristics.

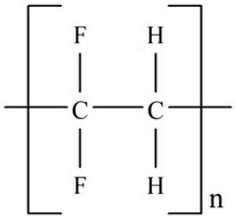


Figure 10.23 Chemical structure of polyvinylidene fluoride.

Manufacturers and trade names: Arkema Kynar®, Solvay Solexis Solef® and Hylar®.

Sterile applications: Reusable tube sets and equipment which can be disassembled, sterilized, and reassembled for reuse.

Gamma radiation resistance: PVDF can be sterilized by gamma irradiation. Kynar® is resistant to multiple radiation sterilization cycles.[12] Kynar® is highly compatible with gamma radiation, but will discolor to a brownish hue. Physical properties typically improve post-irradiation.

Ethylene oxide resistance (EtO): Kynar® exhibits excellent resistance to EtO sterilization.

Autoclaving resistance: Kynar® is resistant to multiple autoclave sterilization cycles. PVDF tolerates high temperatures and will perform consistently after repeated autoclaving.

Data for PVDF plastics are found in Table 10.9 and Figs 10.24−10.31.

Table 10.9 Effects of Electron Beam Radiation Sterilization on Polyvinylidene Fluoride Thermoplastic Elastomer[5]

Exposure Conditions					
Radiation dose (Mrad)	2	4	8	20	
Properties Retained (%)					**Test Method**
Tensile strength at break (%)	100	104.3	100	113.3	ASTM D882
Tensile modulus	106.4	106.4	101.6	104.8	ASTM D882

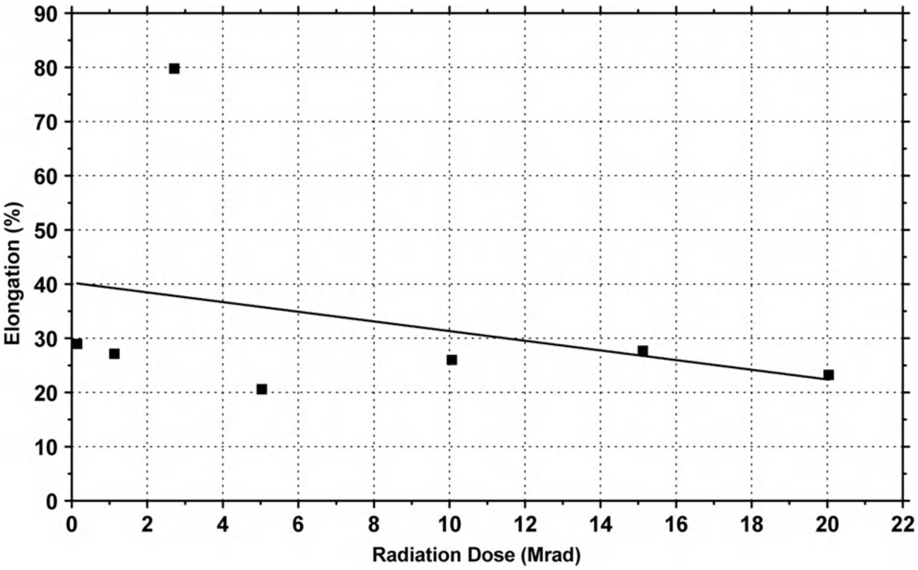


Figure 10.24 Effect of gamma radiation dose on the elongation at break of polyvinylidene fluoride.[5]

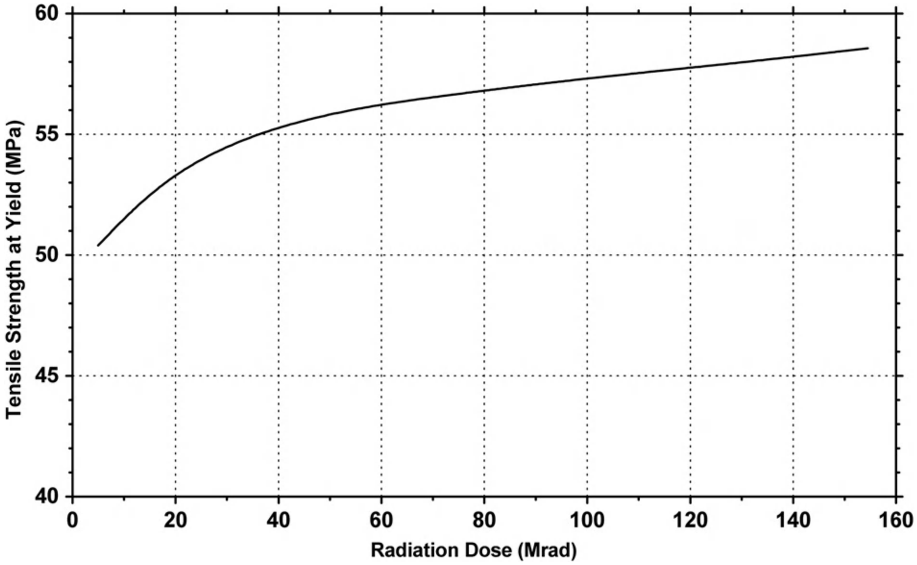


Figure 10.25 Gamma radiation dose versus tensile strength at yield of polyvinylidene fluoride.[13]

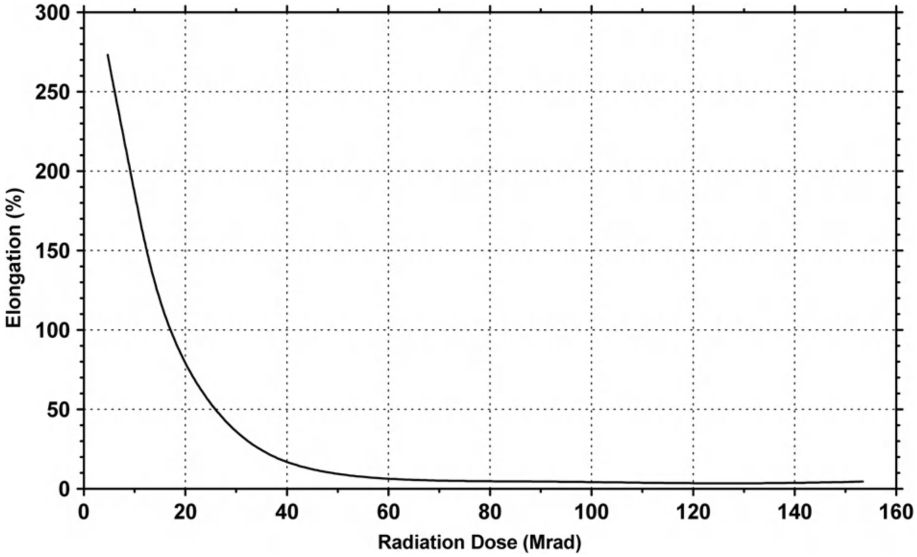


Figure 10.26 Gamma radiation dose versus elongation at break of polyvinylidene fluoride.[13]

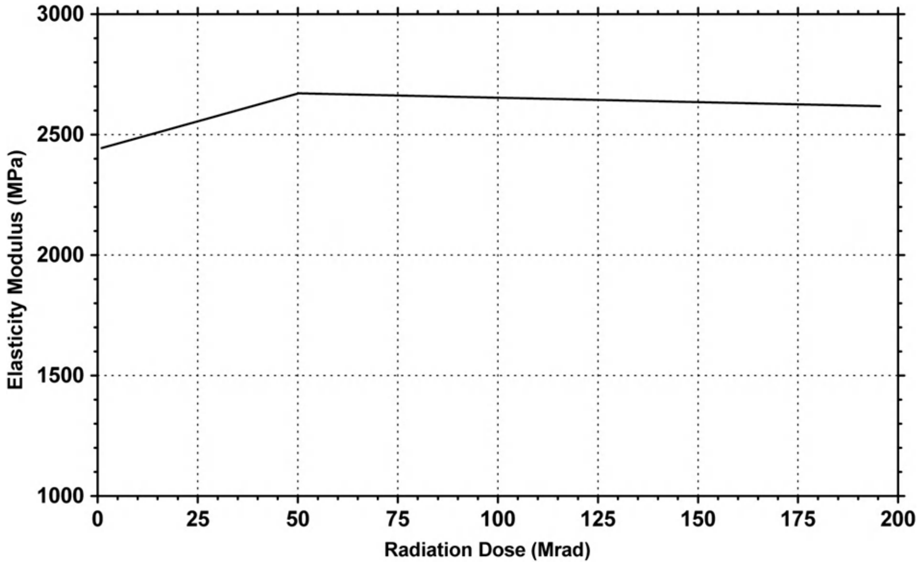


Figure 10.27 Elasticity modulus of Solef® PVDF 1010 versus doses of gamma radiation.[14]

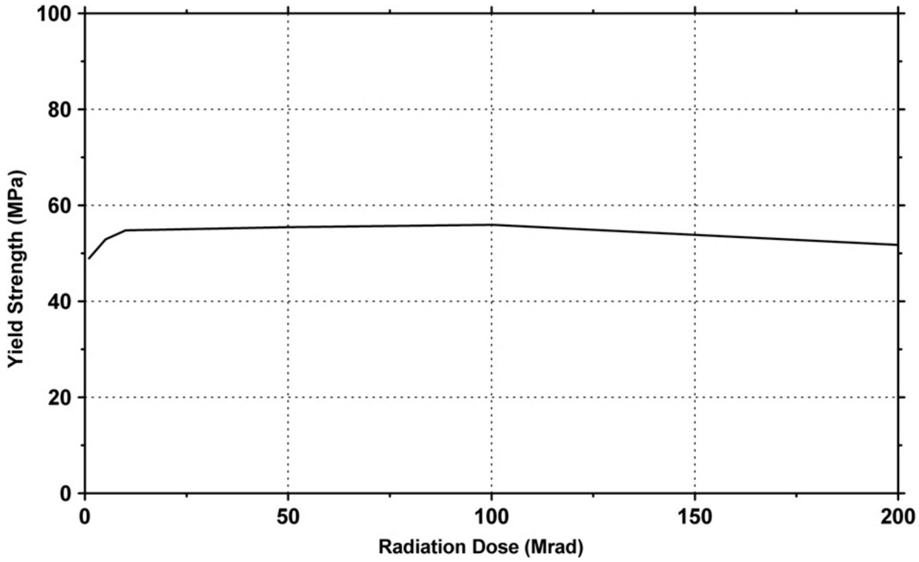


Figure 10.28 Yield strength of Solef® PVDF 1010 versus dose of gamma radiation.[14]

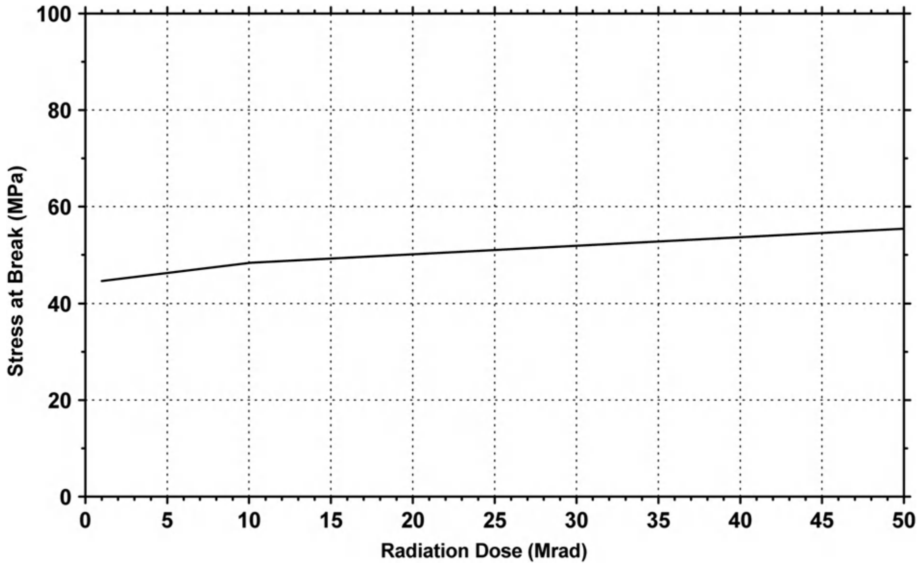


Figure 10.29 Stress at break of Solef® PVDF 1010 versus dose of gamma radiation.[14]

Figure 10.30 Tensile impact strength of Solef® PVDF 1010 versus dose of gamma radiation.[14]

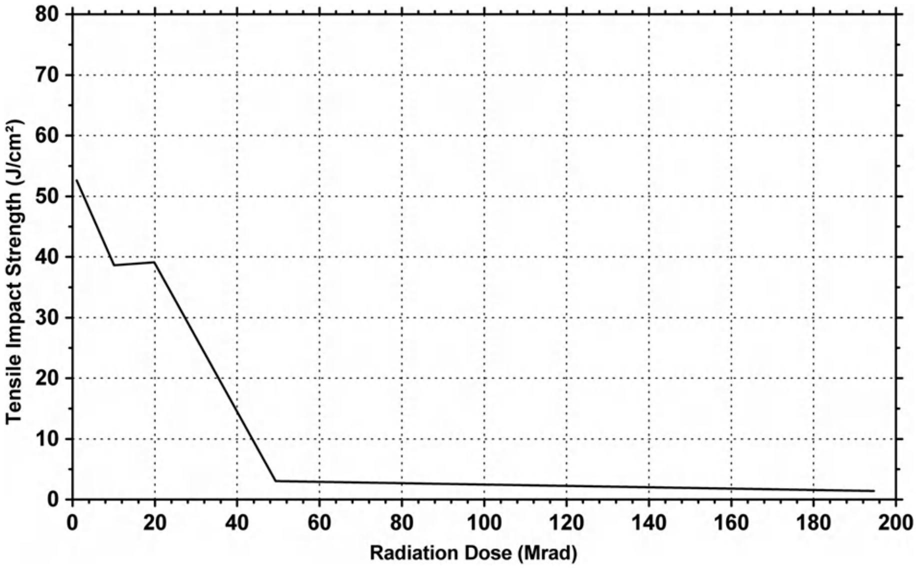
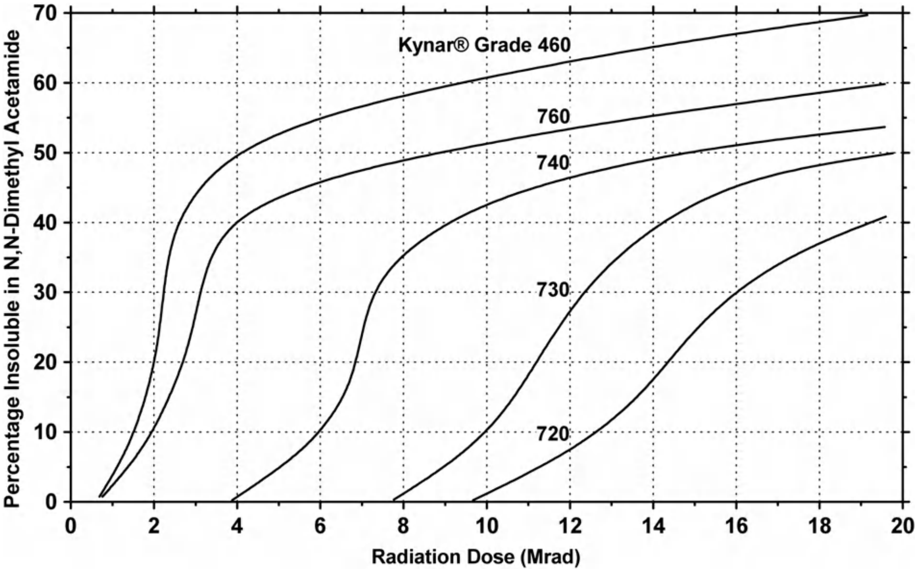


Figure 10.31 Insoluble fraction of PVDF (Kynar®) homopolymer after electron beam irradiation.[15]



10.8 Ethylene–Tetrafluoroethylene Copolymer

Ethylene–tetrafluoroethylene (ETFE) is a copolymer of ethylene and TFE. The basic molecular structure of ETFE is shown in Fig. 10.32.

It is sometimes called polyethylene tetrafluoroethylene. The depicted structure in Fig. 10.32 shows alternating units of TFE and ethylene. While this can be readily made, many grades of ETFE vary the ratio of the two monomers slightly to optimize properties for specific end uses. Its CAS number is 25038-71-5.

ETFE is a fluoroplastic with excellent electrical and chemical properties. It also has excellent mechanical properties. ETFE is especially suited for uses requiring high mechanical strength, chemical, thermal, and/or electrical properties. The mechanical properties of ETFE are superior to those of PTFE and FEP. ETFE has:

- Excellent resistance to extremes of temperature, with a working temperature range of −200 °C to 150 °C
- Excellent chemical resistance.
- Good mechanical strength with excellent tensile strength and elongation and superior physical properties compared to most fluoropolymers.

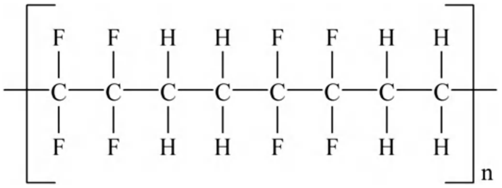

$$-\!\!\left[CF_2-CF_2-CH_2-CH_2-CF_2-CF_2-CH_2-CH_2\right]_n\!\!-$$

Figure 10.32 Chemical structure of polyethylene tetrafluoroethylene (ETFE).

- Low smoke and flame characteristics, it is rated 94 V-0 by the Underwriters Laboratories Inc. It is odorless and nontoxic.
- Outstanding resistance to weather and aging.
- Excellent dielectric properties.
- Nonstick characteristics.

Manufacturers and trade names: DuPont™ Tefzel®, Asahi Glass Fluon®, and 3M Dyneon™.

Applications and uses: Liquid pouches and other applications demanding high flex life/crack resistance, exposure to high temperatures, and wear.

Data for ETFE plastics are found in Fig. 10.33.

10.9 Ethylene–Chlorotrifluoroethylene Copolymer

Ethylene–chlorotrifluoroethylene (ECTFE) copolymer, also called polyethylene chlorotrifluoroethylene or ECTFE, is a copolymer of ethylene and chlorotrifluoroethylene. Its CAS number is 25101-45-5. Figure 10.34 shows the molecular structure of ECTFE.

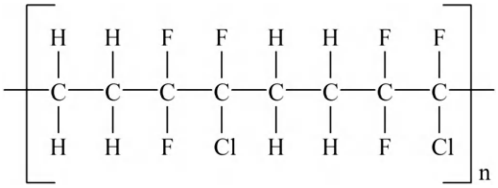

$$-\!\!\left[CH_2-CH_2-CF_2-CFCl-CH_2-CH_2-CF_2-CFCl\right]_n\!\!-$$

Figure 10.34 Chemical structure of polyethylene chlorotrifluoroethylene (ECTFE).

This simplified structure shows the ratio of the monomers being 1-1 and strictly alternating, which is the desirable proportion. Commonly known by the trade name, Halar®, ECTFE is an expensive, melt-processable, semicrystalline, whitish semi-opaque thermoplastic with good chemical resistance and barrier properties. It also has good tensile and creep properties and good high-frequency electrical characteristics.

Processing methods include extrusion, compression molding, rotomolding, blow molding, and liquid and powder coating.

Manufacturers and trade names: Solvay Solexis Halar®.

Applications and uses: Chemically resistant linings and coatings, valve and pump components, hoods, tank and filter house linings, nonwoven filtration fibers, barrier films, and release/vacuum bagging films. It is used in food processing particularly involving acidic food and fruit juice processing.

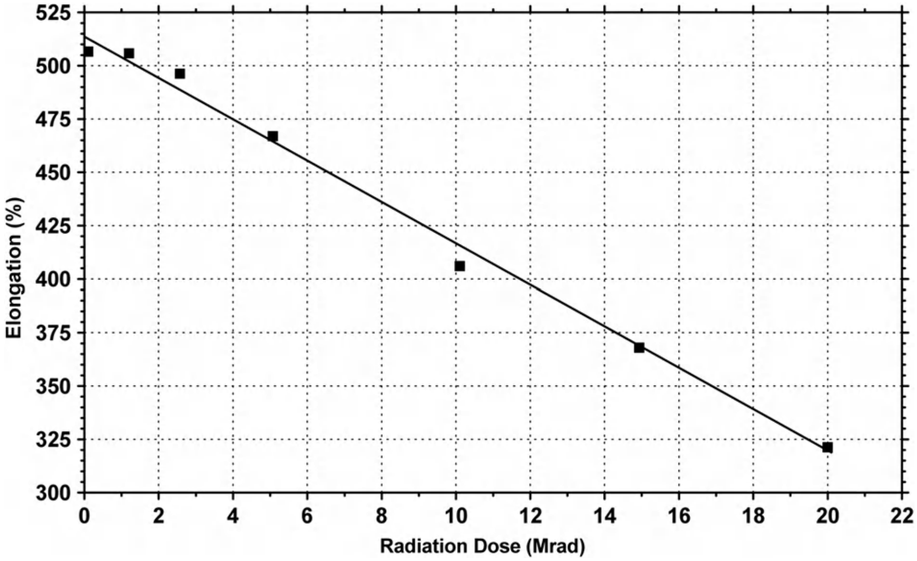


Figure 10.33 Effect of gamma radiation dose on the elongation at break of ethylene–tetrafluoroethylene.[5]

Table 10.10 Effect of Gamma Radiation on Ethylene–Chlorotrifluoroethylene[17]

Exposure (Mrad)	Break Elongation (%)	Tensile Strength (%)
0	210	48
50	105	32
100	65	30
500	20	28
1000	10	19

Halar® ECTFE has demonstrated excellent resistance to many sources of radiation up to 200 Mrad.[16]

Data for ECTFE plastics are found in Table 10.10.

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11 High-Temperature/High-Performance Polymers

This chapter covers several high-temperature, high-performance plastics. They might have been classified differently and included in another chapter, but they are grouped in this chapter because of their performance levels.

11.1 Polyether Ether Ketone

Polyether ether ketones (PEEKs) are also referred to as polyketones. The most common structure is given in Fig. 11.1. The CAS number is 31694-16-3.

PEEK is a thermoplastic with extraordinary mechanical properties. The Young's modulus of elasticity is 3.6 GPa and its tensile strength 170 MPa. PEEK is partially crystalline, melts at around 350 °C, and is highly resistant to thermal degradation. The material is also resistant to both organic and aqueous environments and is used in bearings, piston parts, pumps, compressor plate valves, and cable insulation applications. It is one of the few plastics compatible with ultra-high vacuum applications. In summary, the properties of PEEK include:

- Outstanding chemical resistance
- Outstanding wear resistance
- Outstanding resistance to hydrolysis
- Excellent mechanical properties
- Outstanding thermal properties
- Very good dielectric strength, volume resistivity, tracking resistance
- Excellent radiation resistance.

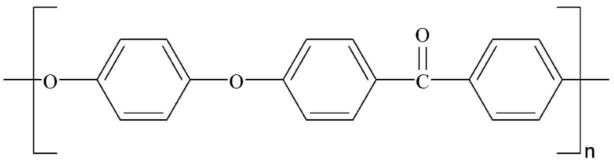


Figure 11.1 The structure of polyether ether ketone.

Manufacturers and trade names: Victrex PLC Victrex® and APTIV®, Greene, Tweed & Co. Arlon®, Solvay Advanced Polymers GATONE™, and KetaSpire®.

Sterile applications: Reusable medical components including dental syringes and keyhole surgery devices.

Gamma radiation resistance: Victrex® PEEK shows excellent resistance to hard (gamma) irradiation, absorbing over 1000 Mrad of radiation without suffering significant damage and showing no embrittlement of the polymer. It is believed that PEEK will resist dose levels of well over 10,000 Mrad of particle (alpha or beta) irradiation without significant degradation of properties. Fiber-reinforced grades are expected to show even better performance than this.

Ethylene oxide (EtO) resistance: PEEK polymers can be sterilized by ethylene oxide (EtO) methods.

Steam sterilization resistance: PEEK maintains high mechanical strength, stress-cracking resistance, and hydrolytic stability in the presence of pressurized steam (200 °C, 14 bar), dry heat (170−180 °C), hot water, solvents, and chemicals. PEEK can withstand high temperatures and pressures for extended periods of time.

Autoclave: Parts made from PEEK can undergo 3000 autoclave cycles at temperatures of up to 134 °C, which is well beyond the typical life expectancy of metal components.

Data for PEEK plastics are found in Tables 11.1−11.2 and Fig. 11.2−11.10.

11.2 Polyaryletherketone

Polyaryletherketone (PAEK) is a family of semicrystalline thermoplastics with high-temperature stability and high mechanical strength. The structure of PAEK varies but one of which is shown in Fig. 11.11. Commercial plastics that fall within this family include:

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00011-3

Table 11.1 Effects of Gamma Sterilization on PEEK-Optima® Implant Grade PEEK[1]

Property	Test Method	Units	Control	After 75 kGy
Tensile strength	ISO 527	MPa	100	100
Tensile elongation	ISO 527	%	32	34
Flexural strength	ISO 178	MPa	164	164
Flexural modulus	ISO 178	GPa	4	4
Impact strength	ISO 180	kJ/m^2	7	7
Density	ASTM D792	g/cc	1.30	1.30
Glass transition temperature (T_g)	DSC	°C	146.8	144.3
Melting point (T_m)	DSC	°C	341.3	339.5
Crystallization temperature (T_c)	DSC	°C	289.8	290.3

Table 11.2 Effect of Steam Sterilization on Victrex PEEK 450GL30 (30% glass fiber reinforced) Polyether ether ketone[3]

Sterilization Conditions					
Time (h)	75	350	1000	2000	2500
Properties Retained (%)					
Tensile strength	73.1	69.4	67.2	68.7	66.4
Elongation at break	93.3	—	86.7	106.7	86.7

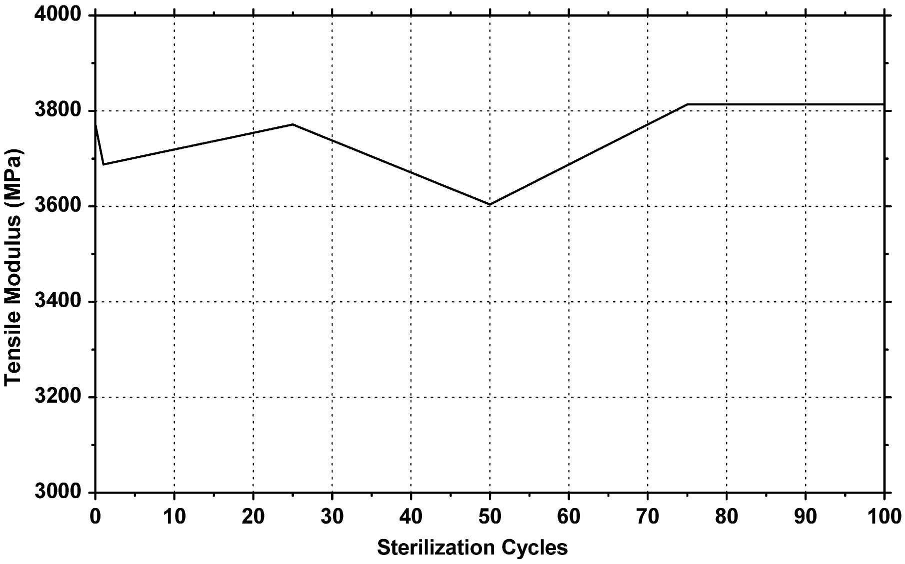


Figure 11.2 Tensile modulus versus EtO sterilization cycles of Solvay Solexis KetoSpire® PEEK.[2] Note: Cycle = 55 °C, 60 min, 70% RH, aeration 60 min.

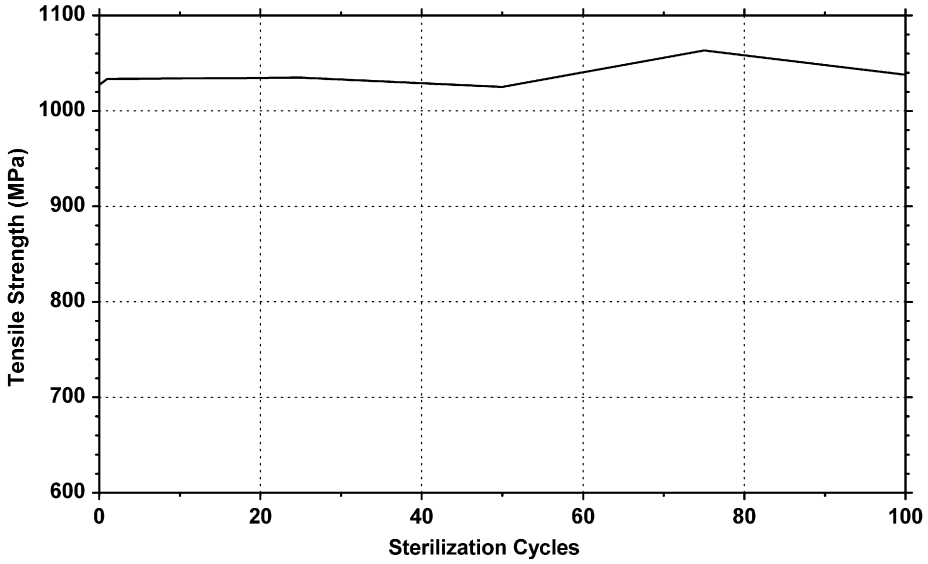


Figure 11.3 Tensile strength versus EtO sterilization cycles of Solvay Solexis KetoSpire® PEEK.[2] Note: Cycle = 55 °C, 60 min, 70% RH, aeration 60 min

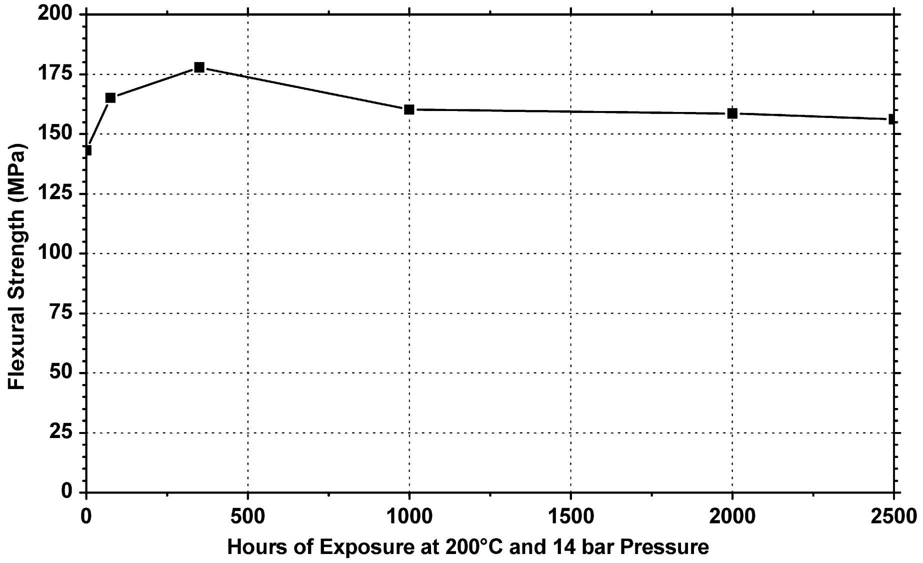


Figure 11.4 Flexural strength after steam exposure of Victrex PEEK.[4]

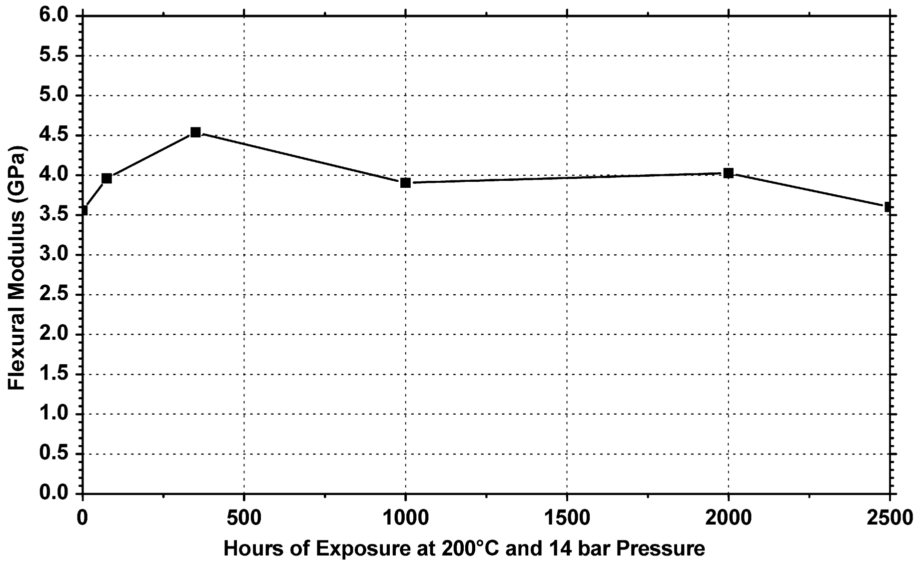


Figure 11.5 Flexural modulus after steam exposure of Victrex PEEK.[4]

Figure 11.6 Property retention of PEEK after steam sterilization.[5]

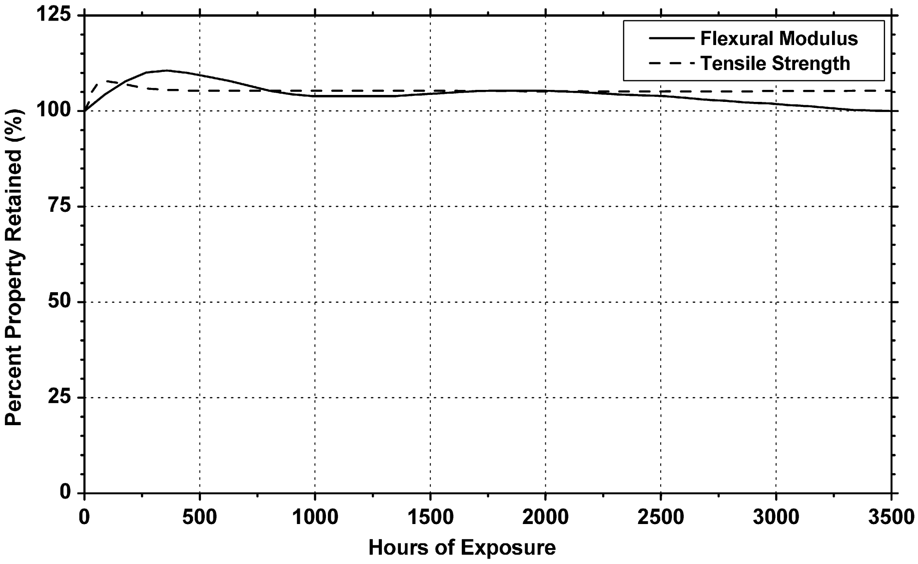


Figure 11.7 Tensile modulus versus steam sterilization cycles of Solvay Solexis KetoSpire® PEEK.[2] Note: 135.5 °C, 31–33 psig, vacuum: 27 in Hg, sterilization time 18 min, drying time 33 min.

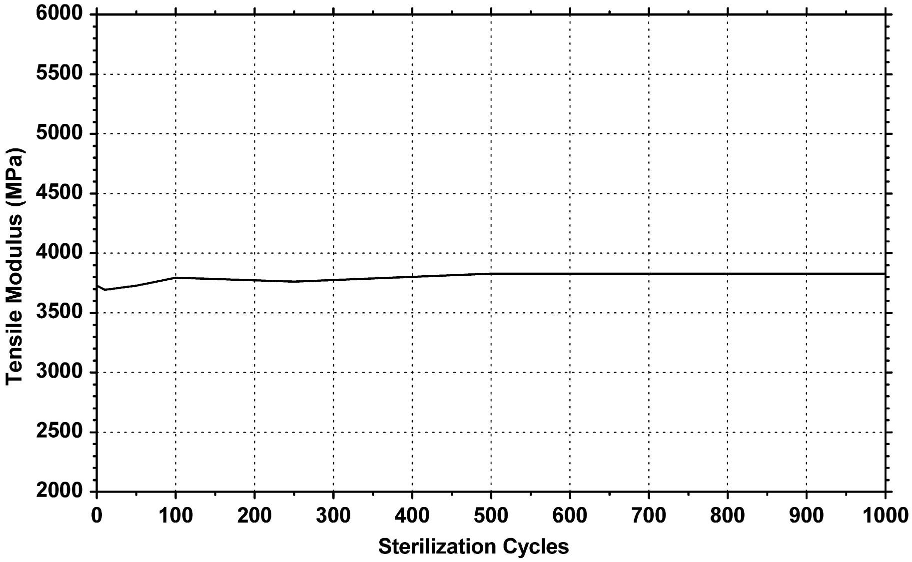
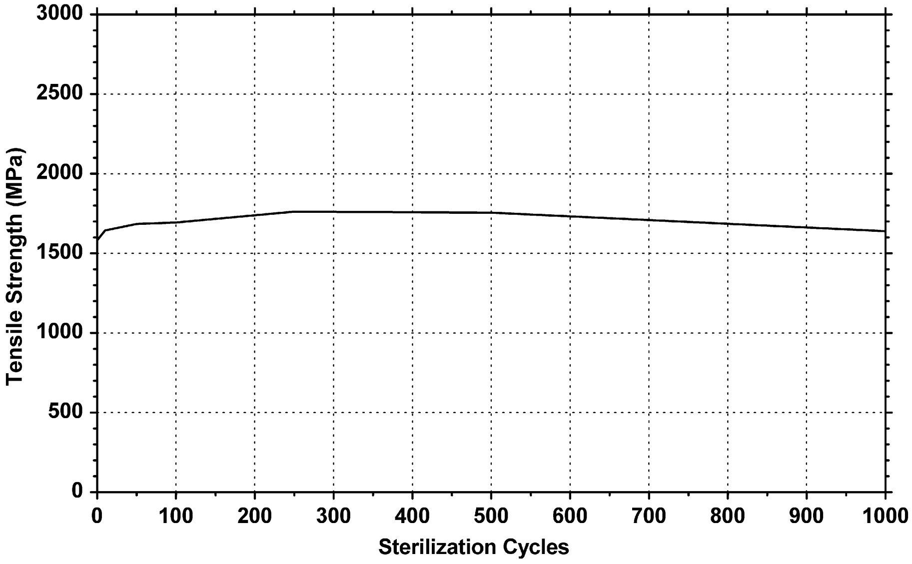


Figure 11.8 Tensile strength versus steam sterilization cycles of Solvay Solexis KetoSpire® PEEK.[2] Note: 135.5 °C, 31–33 psig, vacuum: 27 in Hg, sterilization time 18 min, drying time 33 min.



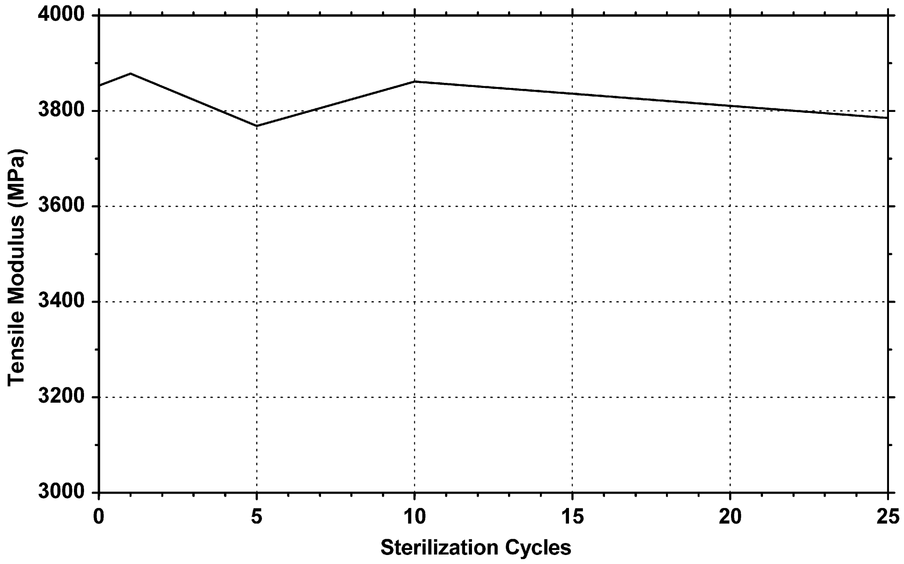


Figure 11.9 Tensile modulus versus vaporized hydrogen peroxide gas plasma sterilization cycles of Solvay Solexis KetoSpire® PEEK.[2] Note: Cycle = 45 °C, 58% H_2O_2, preplasma 10 min, exposure 12 min, diffusion time 4 min.

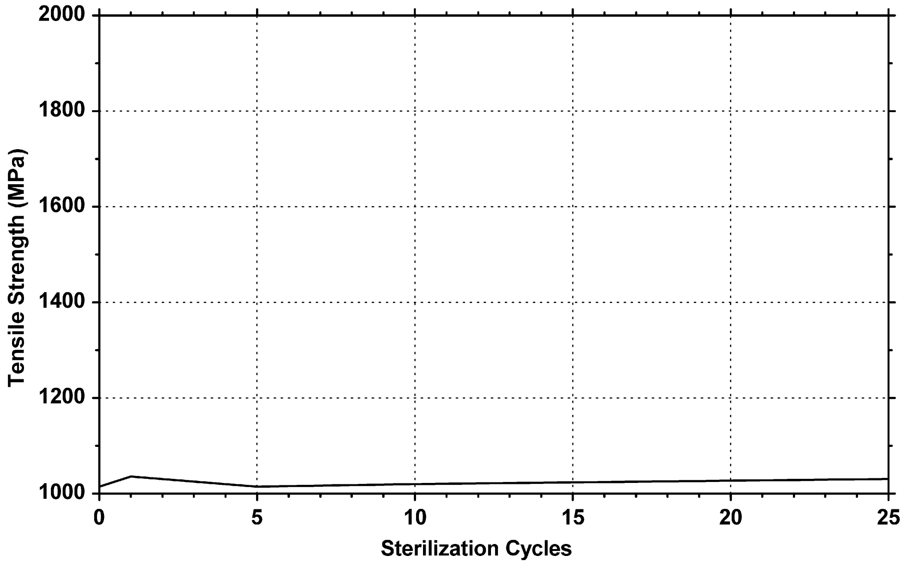


Figure 11.10 Tensile strength versus vaporized hydrogen peroxide gas plasma sterilization cycles of Solvay Solexis KetoSpire® PEEK.[2] Note: Cycle = 45 °C, 58% H_2O_2, preplasma 10 min, exposure 12 min, diffusion time 4 min.

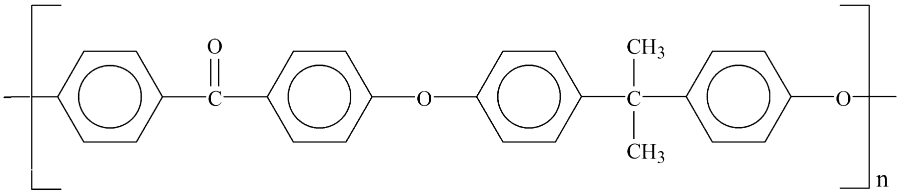


Figure 11.11 Structure of a polyaryletherketone.

- PEK (polyetherketone).
- PEEK (polyetheretherketone, discussed separately)
- PEKK (polyetherketoneketone).
- PEEKK (polyetheretherketoneketone).
- PEKEKK (polyetherketoneetherketoneketone).

Generally PAEK is a lower cost alternative to PEEK.

Manufacturers and trade names: Solvay Advanced Polymers AvaSpire®.

Sterile applications: Dental applications, film, hospital goods, medical appliances, medical/health care applications, and surgical instruments.

Data for PAEK plastics are found in Figs 11.12–11.17.

11.3 Polyphenylene Sulfide

Polyphenylene sulfide (PPS) is a semicrystalline material. It offers an excellent balance of properties, including high temperature resistance, chemical resistance, flowability, dimensional stability, and electrical characteristics. PPS must be filled with fibers and fillers to overcome its inherent brittleness. Because of its low viscosity, PPS can be molded with high loadings of fillers and reinforcements. Because of its outstanding flame resistance, PPS is ideal for high-temperature electrical applications. It is unaffected by all industrial solvents. The structure of PPS is shown in Fig. 11.18. The CAS number is 26125-40-6.

There are several variants to regular PPS that may be talked about by suppliers or may be seen in the literature. There are:

- Regular PPS is of "modest" molecular weight. Materials of this type are often used in coating products.
- Cured PPS is PPS that has been heated to high temperature, above 300 °C, in the presence of air or oxygen. The oxygen causes some cross-linking

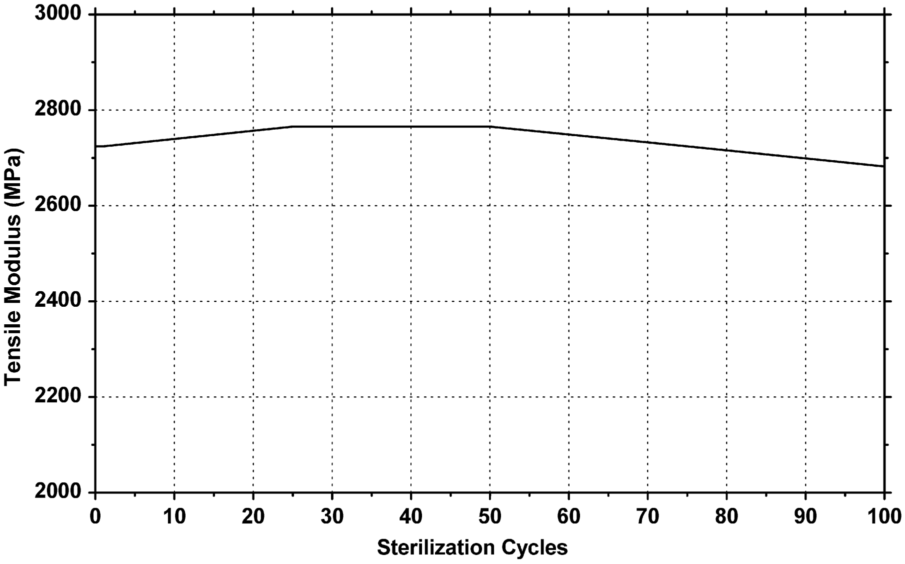


Figure 11.12 Tensile modulus versus EtO sterilization cycles of Solvay Solexis AvaSpire® PAEK.[2] Note: Cycle = 55 °C, 60 min, 70% RH, aeration 60 min.

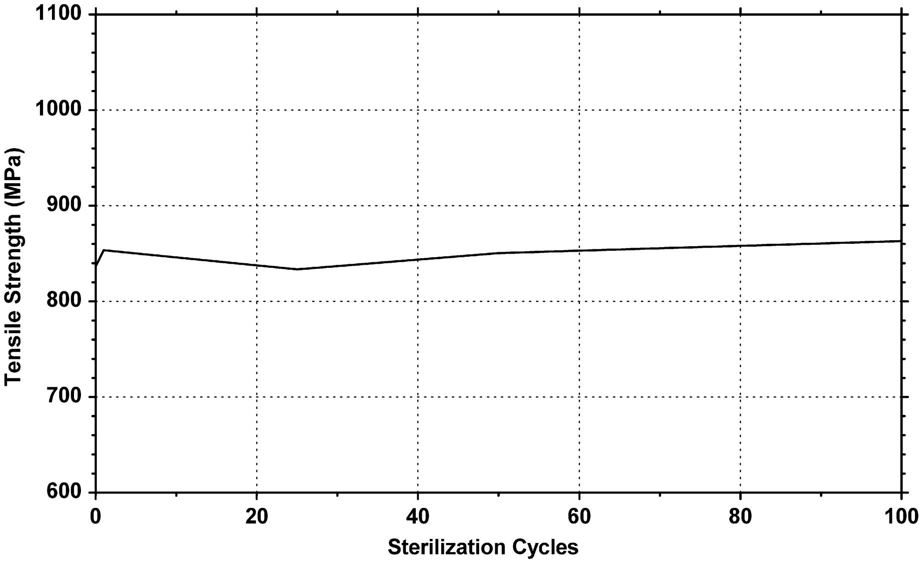


Figure 11.13 Tensile strength versus EtO sterilization cycles of Solvay Solexis AvaSpire® PAEK.[2] Note: Cycle = 55 °C, 60 min, 70% RH, aeration 60 min.

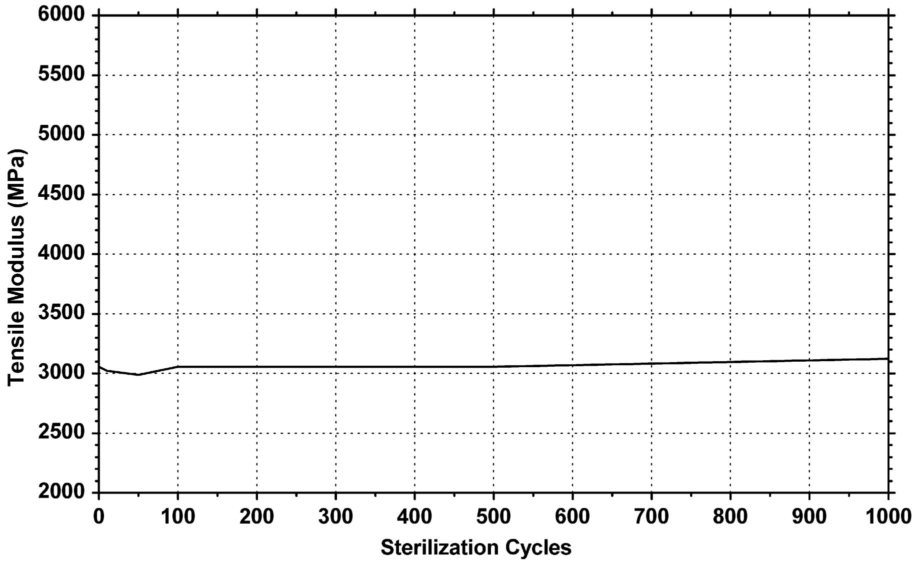


Figure 11.14 Tensile modulus versus steam sterilization cycles of Solvay Solexis AvaSpire® PAEK.[2] Note: 135.5 °C, 31–33 psig, vacuum: 27 in Hg, sterilization time 18 min, drying time 33 min.

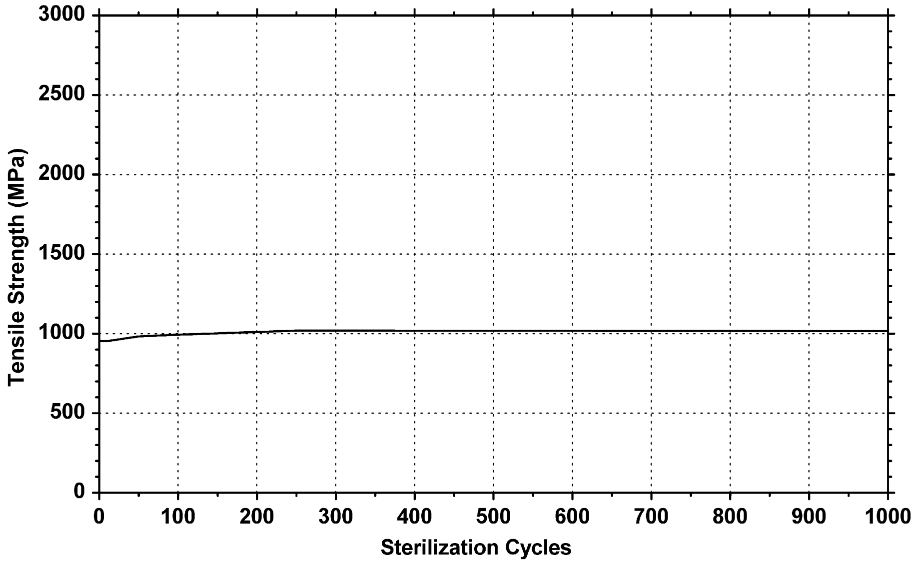


Figure 11.15 Tensile strength versus steam sterilization cycles of Solvay Solexis AvaSpire® PAEK.[2] Note: 135.5 °C, 31–33 psig, vacuum: 27 in Hg, sterilization time 18 min, drying time 33 min.

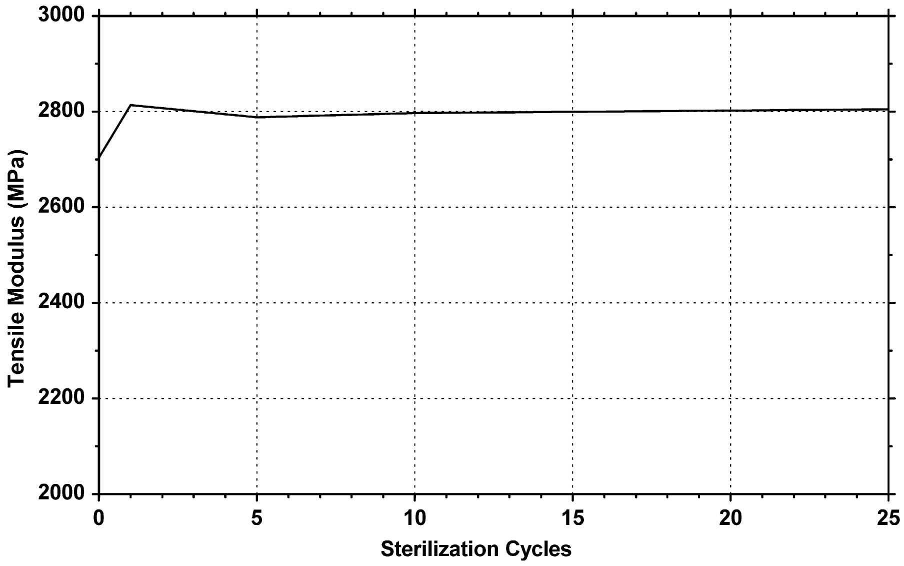


Figure 11.16 Tensile modulus versus vaporized hydrogen peroxide gas plasma sterilization cycles of Solvay Solexis AvaSpire® PAEK.[2] Note: Cycle = 45 °C, 58% H_2O_2, pre-plasma 10 min, exposure 12 min, diffusion time 4 min.

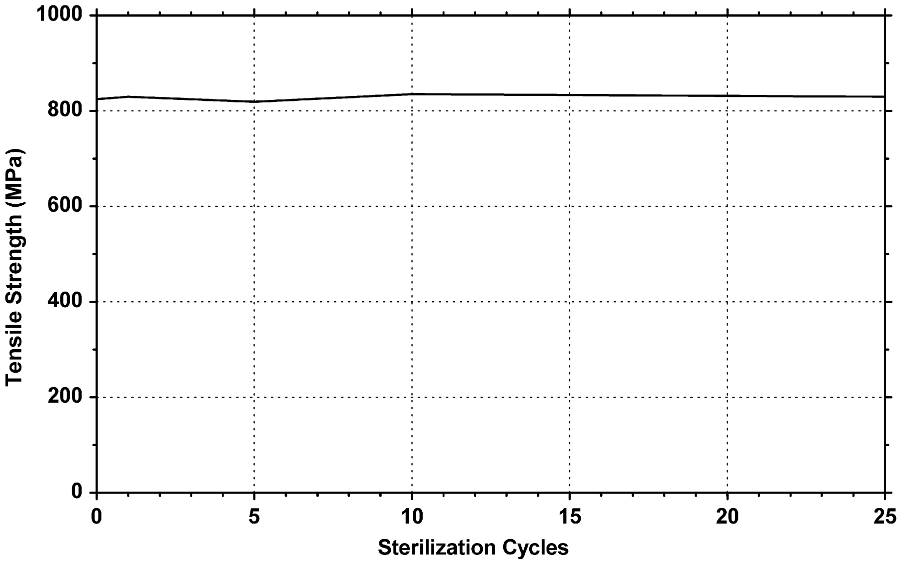


Figure 11.17 Tensile strength versus vaporized hydrogen peroxide gas plasma sterilization cycles of Solvay Solexis AvaSpire® PAEK.[2] Note: Cycle = 45 °C, 58% H_2O_2, pre-plasma 10 min, exposure 12 min, diffusion time 4 min.

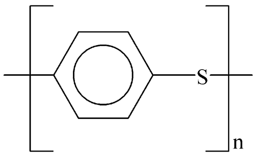


Figure 11.18 Structure of polyphenylene sulfide.

and chain extension called oxidative cross-linking. This results in some thermoset-like properties such as improved thermal stability, dimensional stability, and improved chemical resistance.

- High molecular weight (HMW) linear PPS has a molecular weight about double of that of regular PPS. The higher molecular weight improves elongation and impact strength.
- HMW branched PPS has higher molecular weight than regular PPS, but it also has polymer chain branches along the main molecule backbone. This provides improved mechanical properties.

PPS properties are summarized:

- Continuous use temperature of 220 °C
- Excellent dimensional properties
- Transparent
- Improved impact strength and toughness as compared to polyethersulfone (PES)
- Excellent hydrolytic stability
- High stress-cracking resistance
- Good chemical resistance
- Good surface release properties
- Expected continuous temperature of 180 °C.

Manufacturers and trade names: Dinippon Ink, Chevron Phillips Ryton®, Ticona Fortron®, and Toray Torelina®.

Sterile applications: Medical devices requiring repeated sterilization, i.e. handles for sterile tools.

Gamma radiation resistance: Ryton R-4 exhibits no significant deterioration of mechanical properties with relatively high exposures to gamma radiation. Typical radiation tolerance level (cumulative) is 1000 kGy.

Steam or autoclaving resistance: PPS can be autoclave sterilized, maintaining sufficient dimensional stability during steam sterilization at 134 °C and 2.2 bar with a resulting water absorption of 0.02%. PPS is suitable for repeated sterilization.

Data for PPS plastics are found in Tables 11.3−11.5 and Fig. 11.19−11.20.

11.4 Polysulfone

Polysulfone (PSU) is a rigid, strong, tough, high-temperature amorphous thermoplastic. The structure of PSU is shown in Fig. 11.21. Its CAS number is 25135-51-7.

Its properties summarized:

- High thermal stability
- High toughness and strength

Table 11.3 Effect of Gamma Radiation Sterilization on Polypropylene Sulfide[6]

Radiation dose (Mrad)	300	500	1000	5000
Properties Retained (%)				
Tensile strength	100	—	—	—
Elongation	100.9	—	—	—
Flexural strength	93.3	103.5	105.2	99.3
Modulus	101.7	95.3	96.8	95.8
Notched Izod impact strength	95.9	—	—	—

Table 11.4 Effect of Gamma Radiation on Mechanical Properties of Ryton® PPS R-4[7]

Radiation Dose (Mrad)	Flexural Strength (MPa)	Modulus of Elasticity (MPa)
0	198	13100
500	205	12480
1000	208	12690
5000	197	12550

- Good environmental stress-crack resistance
- Inherent fire resistance
- Transparency.

Manufacturers and trade names: Solvay Advanced Polymers Udel®.

Sterile applications: Membranes and fluid handling applications and medical plastic ultraflow (MPU) quick connect couplings.

General sterilization resistance: Udel PSUs maintains a high enough glass transition temperature to withstand different sterilization techniques including steam, ethylene oxide, and gamma and electron beam (e-beam) radiation.

Gamma and electron beam radiation resistance: Udel PSUs are highly resistant to degradation by gamma or e-beam radiation. There is no evidence of change in mechanical properties after irradiation at 2.5, 4, or 6 Mrad. Tensile strength, elongation, modulus, and notched Izod impact values remain essentially unchanged. There is no significant change in chemical resistance following irradiation. PSU discolors during irradiation; the level of discoloration increases with the radiation dosage.

Ultrason® S offers very high resistance to gamma radiation over the entire range of service temperatures. Gassing is very slight; transmittance of gamma rays is very high. MPU couplings can be gamma and e-beam radiation sterilized with 50 kGy maximum.

Ethylene oxide (EtO) resistance: MPU couplings can be ethylene oxide sterilized up to five cycles.

Autoclave or steam sterilization resistance: Udel® can withstand greater than 1000 autoclave cycles at 140 °C with no significant change in mechanical properties. Transparent PSU will retain its clarity during extended service life.

Ultrason® parts can be repeatedly sterilized in superheated steam. After more than 100 sterilization cycles, samples remain transparent and largely retain their high level of mechanical properties. MPU couplings can be autoclave sterilized at 121 °C (270 °F) for 60 min. The maximum number of cycles recommended is 25.

Dry heat sterilization: Products made from PSU can be dry heat sterilized at 140 °C; recommended exposure is 6 h in dry 125 °C heat.

Chemical sterilants: Udel® PSU performs well, retaining its strength in a wide variety of aqueous disinfectants including buffered glutaraldehyde, phenol, quaternary ammonium, iodophor and formaldehyde types, and detergent germicide.

Data for PSU plastics are found in Table 11.6 and Figs 11.22−11.33.

11.5 Polyphenylsulfone

Polyphenylsulfone (PPSU) is a rigid, strong, tough, high-temperature amorphous thermoplastic. It has a high heat deflection temperature of 405 °F

Table 11.5 Comparison of Radiation Effects on Mechanical Properties of Ryton® PPS Compounds[7]

Conditions		**Gamma**		**Mainly Neutron**	
Temperature		50–55 °C		50–55 °C	
Dosage		300 Mrad		400 Mrad	
Property	**Unexposed**	**Exposed**	**% Change**	**Exposed**	**% Change**
Ryton PPS R-4					
Tensile (MPa)	210	210	0	189	−9.8
Elongation (%)	1.08	1.09	+0.9	0.98	−9.3
Flexural modulus (MPa)	17,652	18,633	+2.0	18,633	+2.0
Flexural strength (MPa)	262	244	−6.7	226	−13.9
Izod impact, ft-lbf/in, notched	1.48	1.42	−4.1	1.30	−12.2
Ryton PPS R-10 5002C					
Tensile (MPa)	108	105	−2.7	9.3	91
Elongation (%)	0.30	0.33	+1.1	0.36	+20.0
Flexural modulus (MPa)	22,555	23,536	+2.7	22,555	+.09
Flexural strength (MPa)	152	150	−1.3	143	−5.8
Izod impact, ft-lbf/in notched	0.74	0.71	−4.1	0.71	−4.1
Ryton PPS R-10 7006A					
Tensile (MPa)	135	138	+2.2	118	−13.0
Elongation (%)	0.37	0.49	+32.4	0.58	+56.7
Flexural modulus (MPa)	21,574	21,574	+1.5	20,594	−3.5
Flexural strength (MPa)	205	202	−1.4	195	−4.8
Izod impact, ft-lbf/in, notched	0.86	0.83	−3.5	0.80	−7.0

(207 °C), it can withstand continuous exposure to heat, and still absorb tremendous impact without cracking or breaking. It is inherently flame retardant and offers exceptional resistance to bases and other chemicals. The structure of PPSU is shown in Fig. 11.34.

Its properties summarized:

- 207 °C Heat Deflection Temperature (HDT)
- Superior toughness
- Exceptional hydrolytic stability
- Good chemical resistance
- Transparent.

Manufacturers and trade names: Solvay Solexis Radel® R.

Sterile applications: Medical trays and cases, medical wands, endoscopic probe positioning ferrule, trial implants – medical instruments, endoscopic equipment. Radiation therapy and brachytherapy components, trays for trauma products, biotechnology and laboratory equipment, and analytical and diagnostic equipment.

General sterilization resistance: Radel® R polyphenylsulfone has been proven to withstand the rigors of all commercially available sterilization technologies. It is an incredibly strong polymer that can withstand continuous exposure to heat and still

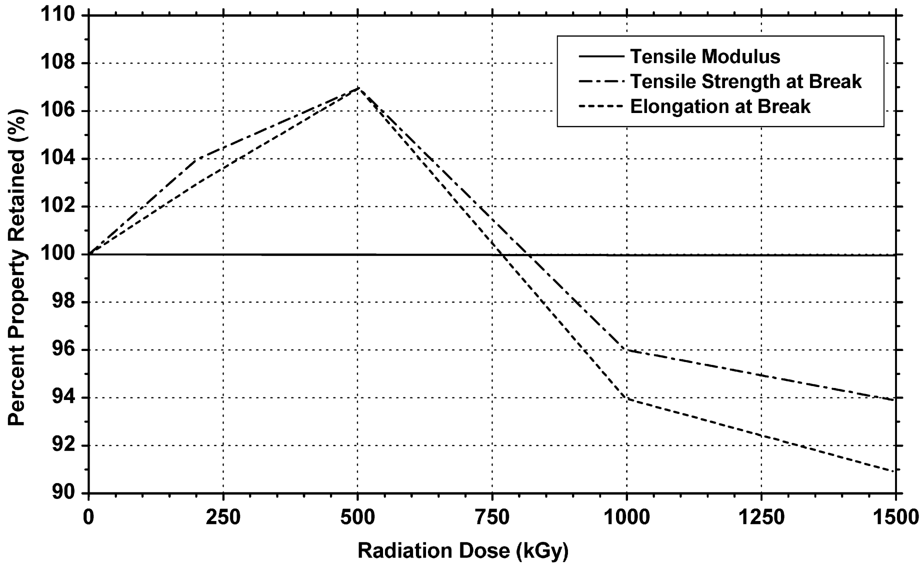


Figure 11.19 Retention of properties versus gamma radiation dose of Ticona Fortron® MT 9205 C4 PPS.[7]

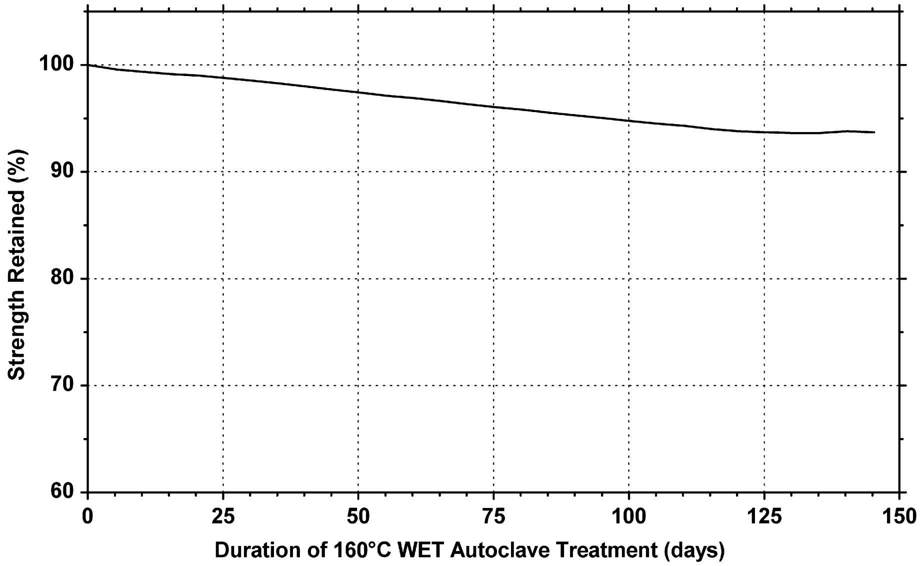


Figure 11.20 Strength retained after steam sterilization of Ticona Fortron® PPS.[7]

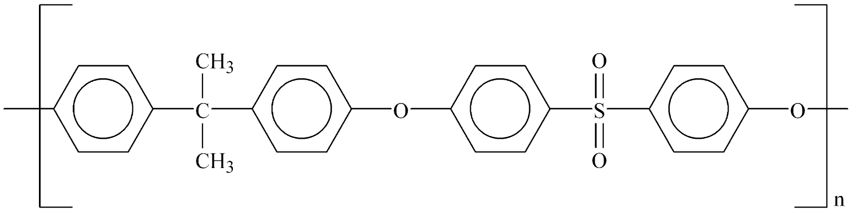


Figure 11.21 Structure of polysulfone.

Table 11.6 Effect of Gamma Radiation Sterilization on Solvay Udel® P1700 PSU[8]

Exposure Conditions			
Radiation dose (Mrad)	2.5	4	6
Properties Retained (%)			
Tensile strength	98.1	98.1	103.9
Elongation	96.1	102.3	86.7
Modulus	102.8	102.8	111.1
Notched Izod impact	100	100	107.7
Melt flow rate	85.2	74.1	6.5

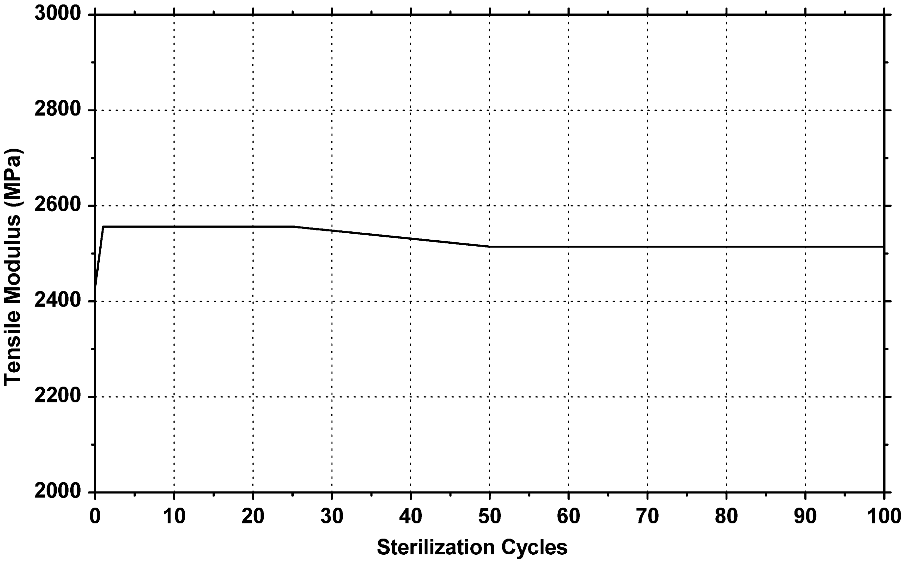


Figure 11.22 Tensile modulus versus EtO sterilization cycles of Solvay Solexis Udel® PSU.[2] Note: Cycle = 55 °C, 60 min, 70% RH, aeration 60 min.

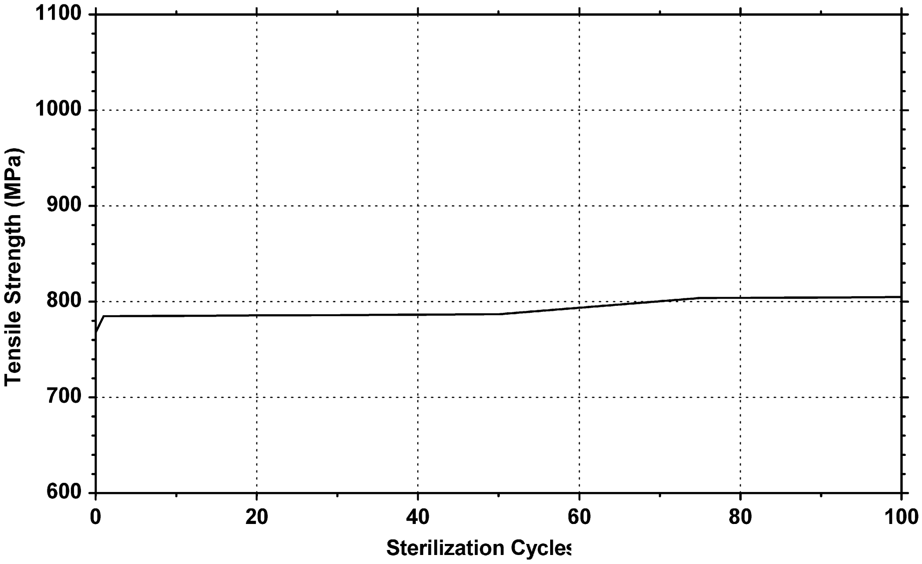


Figure 11.23 Tensile strength versus EtO sterilization cycles of Solvay Solexis Udel® PSU[2]. Note: Cycle = 55 °C, 60 min, 70% RH, aeration 60 min.

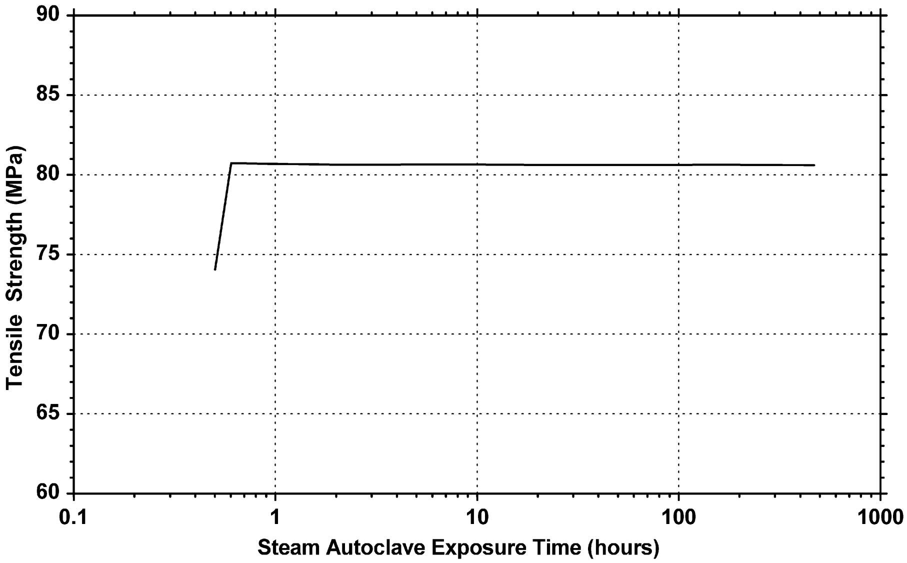


Figure 11.24 Steam autoclave exposure time versus tensile strength of polysulfone.[9]

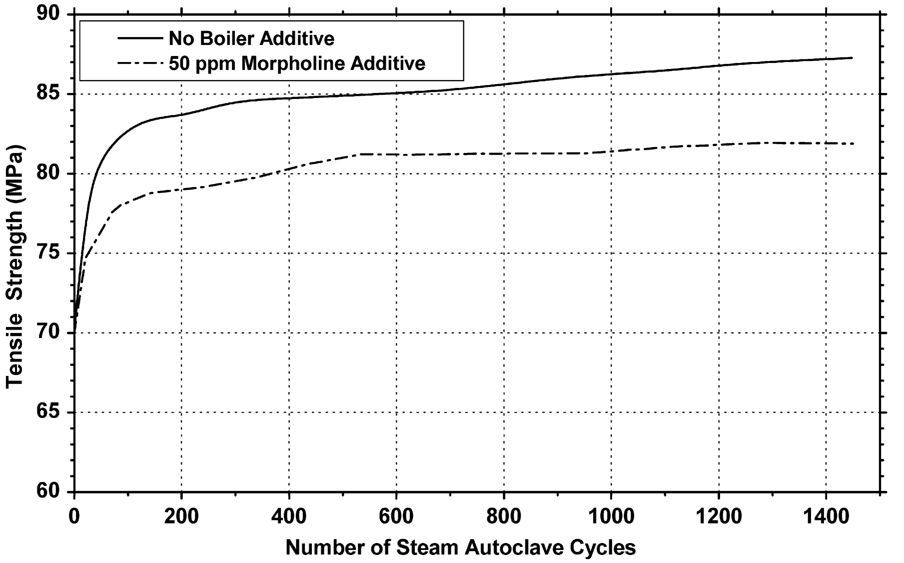


Figure 11.25 Number of steam sterilization cycles versus tensile strength of polysulfone.[10]

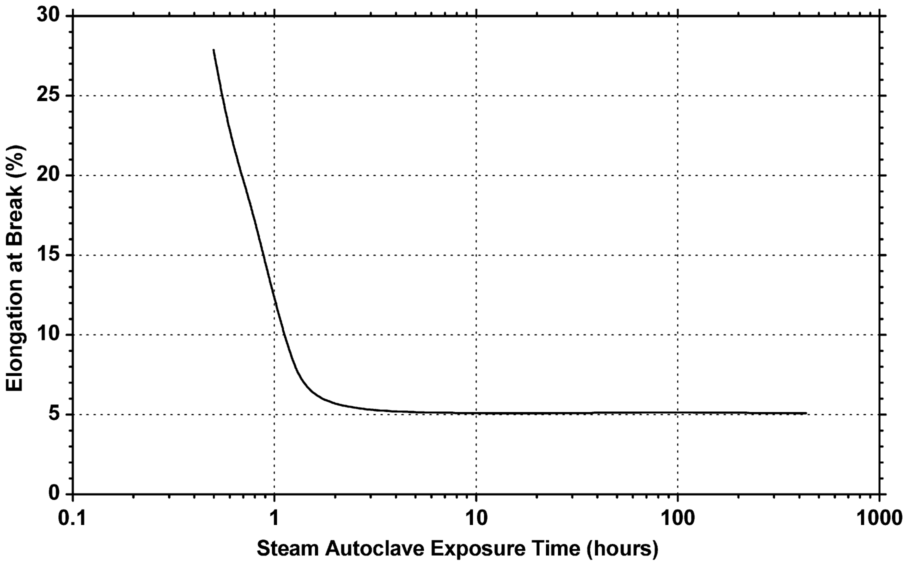


Figure 11.26 Steam autoclave exposure time versus elongation at break of polysulfone.[9]

Figure 11.27 Steam autoclave exposure time versus tensile modulus of polysulfone.[9]

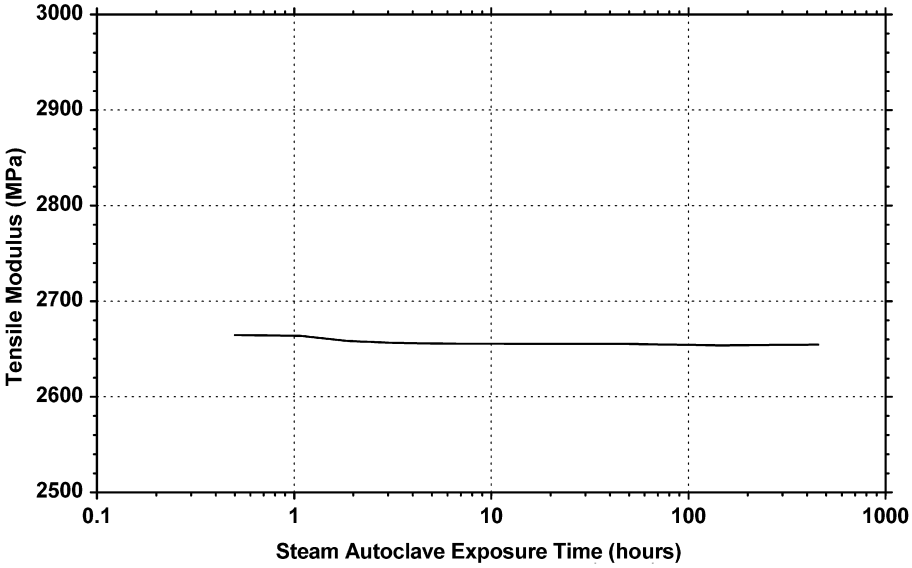


Figure 11.28 Steam autoclave exposure time versus tensile impact strength of polysulfone.[9]

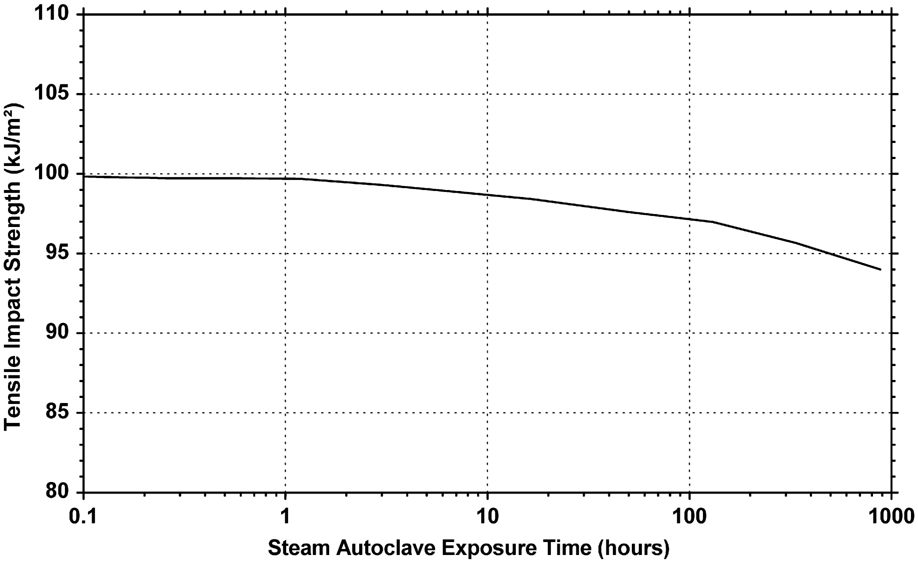
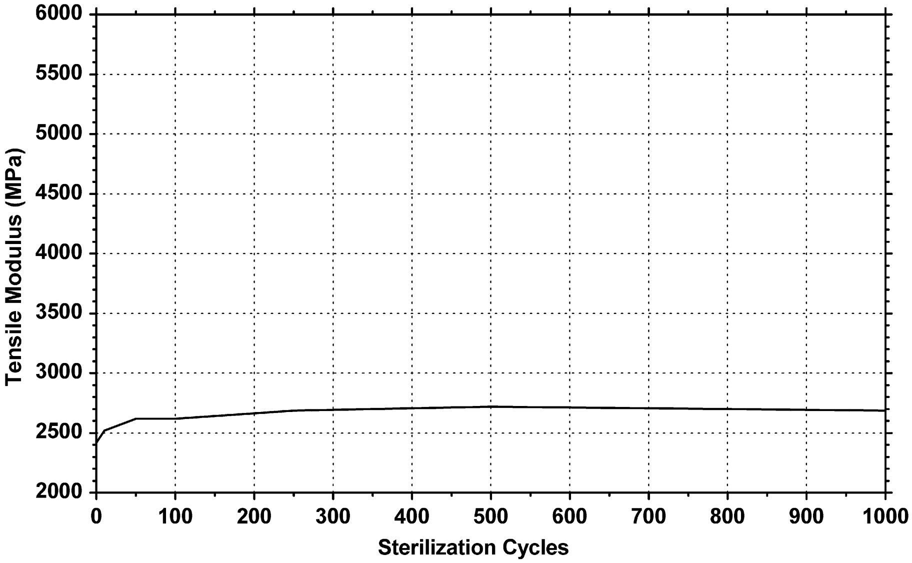


Figure 11.29 Tensile modulus versus steam sterilization cycles of Solvay Solexis Udel® PSU.[2] Note: 135.5 °C, 31–33 psig, vacuum: 27 in Hg, sterilization time 18 min, drying time 33 min.



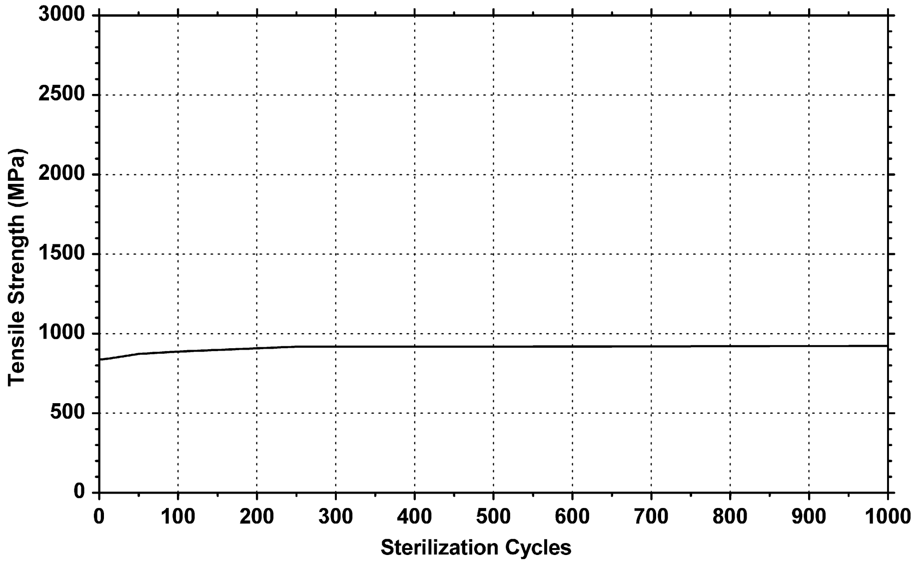


Figure 11.30 Tensile strength versus steam sterilization cycles of Solvay Solexis Udel® PSU.[2] Note: 135.5 °C, 31–33 psig, vacuum: 27 in Hg, sterilization time 18 min, drying time 33 min.

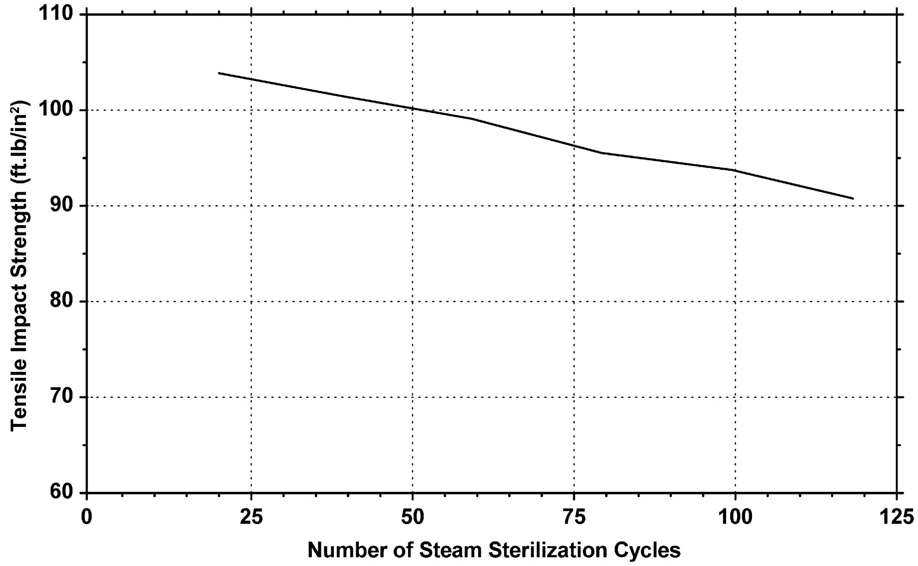


Figure 11.31 Tensile impact after steam sterilization of polysulfone.[11]

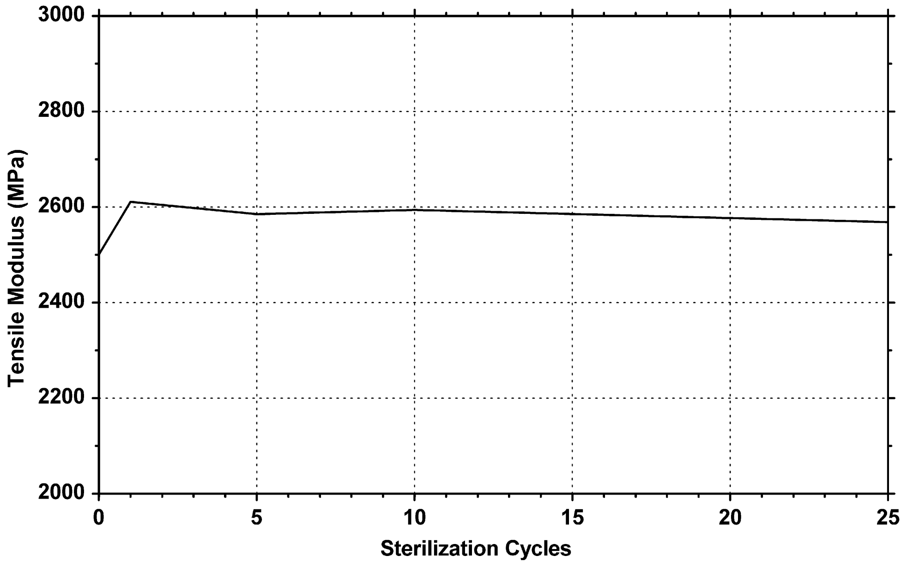


Figure 11.32 Tensile modulus versus vaporized hydrogen peroxide gas plasma sterilization cycles of Solvay Solexis Udel® PSU.[2] Note: Cycle = 45 °C, 58% H_2O_2, pre-plasma 10 min, exposure 12 min, diffusion time 4 min.

Figure 11.33 Tensile strength versus vaporized hydrogen peroxide gas plasma sterilization cycles of Solvay Solexis Udel® PSU.[2] Note: Cycle = 45 °C, 58% H_2O_2, pre-plasma 10 min, exposure 12 min, diffusion time 4 min.

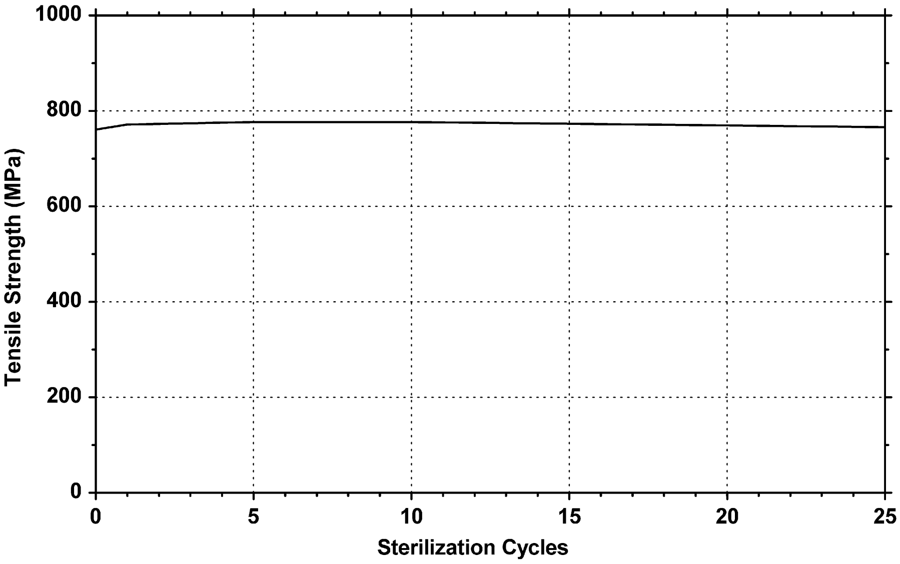
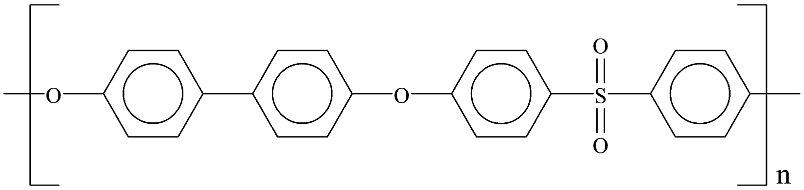


Figure 11.34 The structure of polyphenylsulfone.



absorb tremendous impact without cracking or breaking. It is virtually unaffected by thousands of autoclave cycles and stands up to highly aggressive chemical disinfectants and other commercial sterilization procedures.

Autoclave or steam sterilization resistance: Radel® R-5000, R-5100 NT15, R-5500, and R-5800 resins pass more than 1000 sterilization cycles with morpholine of steam sterilization without cracking, crazing, or rupture.

Data for PPSU plastics are found in Table 11.7 and Fig. 11.35–11.43.

11.6 Polyethersulfone

PES is an amorphous polymer and a high-temperature engineering thermoplastic. Even though PES has high-temperature performance, it can be processed on conventional plastics processing equipment. Its chemical structure is shown in Fig. 11.44. Its CAS number is 25608-63-3. PES has an outstanding ability to withstand exposure to elevated temperatures in air and water for prolonged periods.

Because PES is amorphous, mold shrinkage is low, and is suitable for applications requiring close

Table 11.7 Effect of Low-Temperature Hydrogen Peroxide Gas Plasma (STERRAD® NX) Sterilization on Polyphenylsulfone[12]

Cycles	Tensile Strength (MPa)	Mass (g)	Elongation (%)	Dynatup Impact (J)
0	65	11.49	93	84
130	51	11.23	11	20
300	52	10.6	9	6

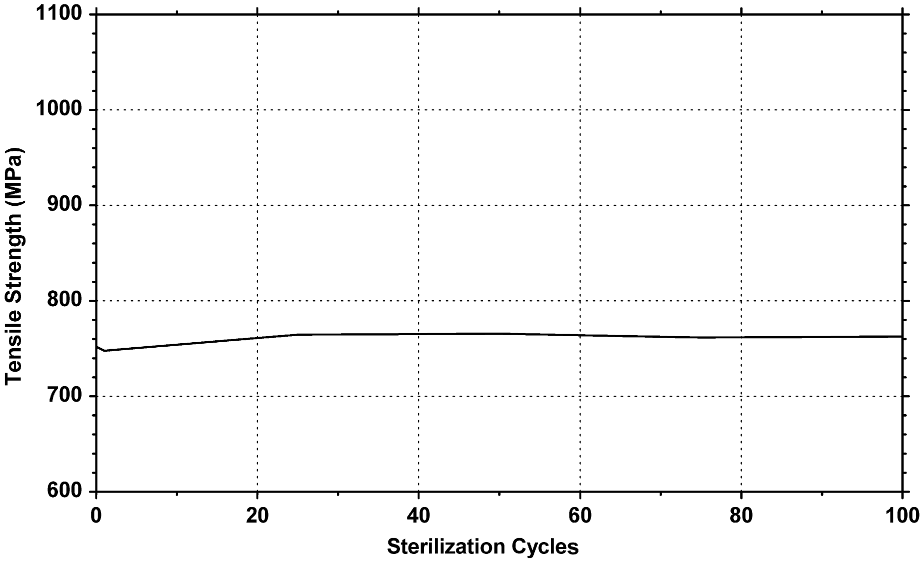


Figure 11.35 Tensile strength after EtO sterilization of Solvay Solexis Radel® R PPSU.[2] Note: Cycle = 55 °C, 60 min, 70% RH, aeration 60 min.

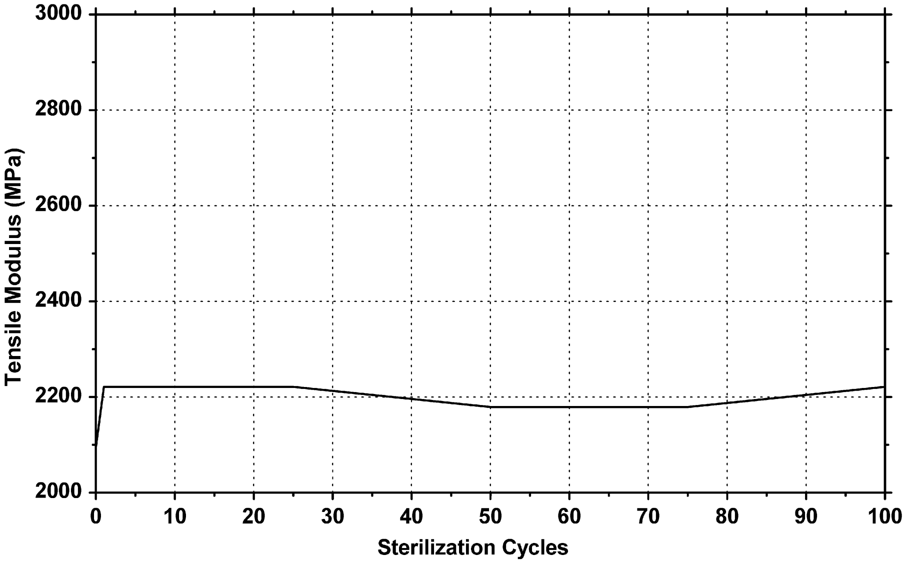


Figure 11.36 Tensile modulus after EtO Sterilization of Solvay Solexis Radel® R PPSU.[2] Note: Cycle = 55 °C, 60 min, 70% RH, aeration 60 min.

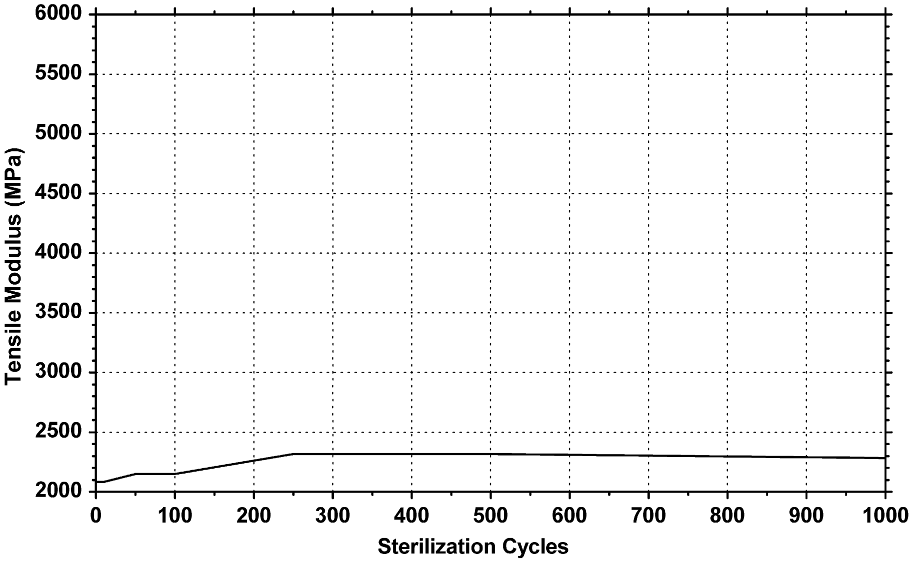


Figure 11.37 Tensile modulus after steam sterilization of Solvay Solexis Radel® R PPSU.[2] Note: 135.5 °C, 31–33 psig, vacuum: 27 in Hg, sterilization time 18 min, drying time 33 min.

Figure 11.38 Tensile strength after steam sterilization of Solvay Solexis Radel® R PPSU.[2] Note: 135.5 °C, 31–33 psig, vacuum: 27 in Hg, sterilization time 18 min, drying time 33 min.

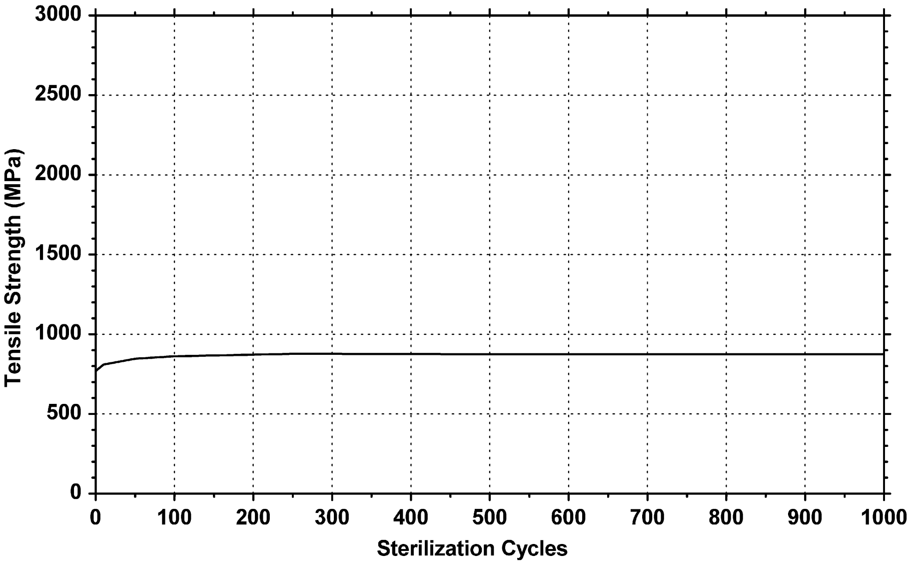


Figure 11.39 Tensile impact after steam sterilization of Solvay Solexis Radel® R PPSU.[11]

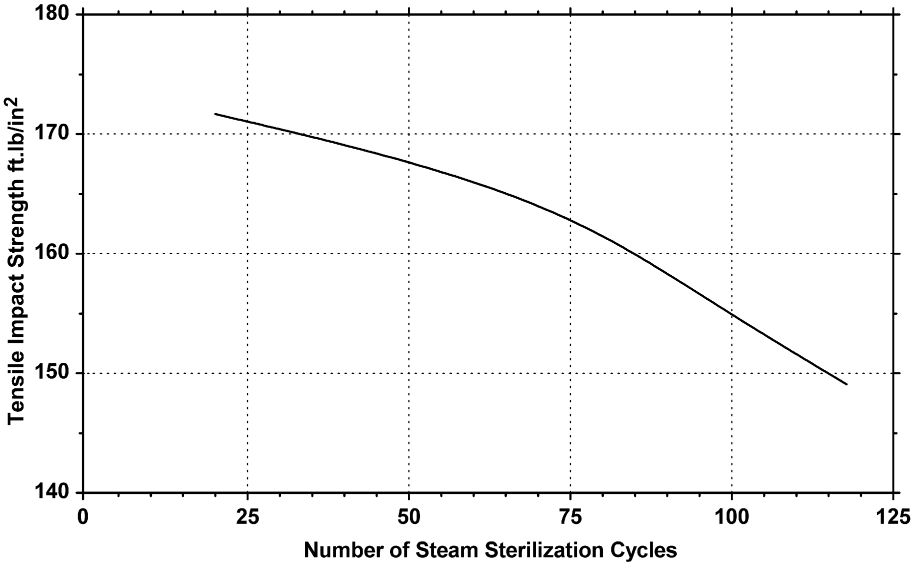
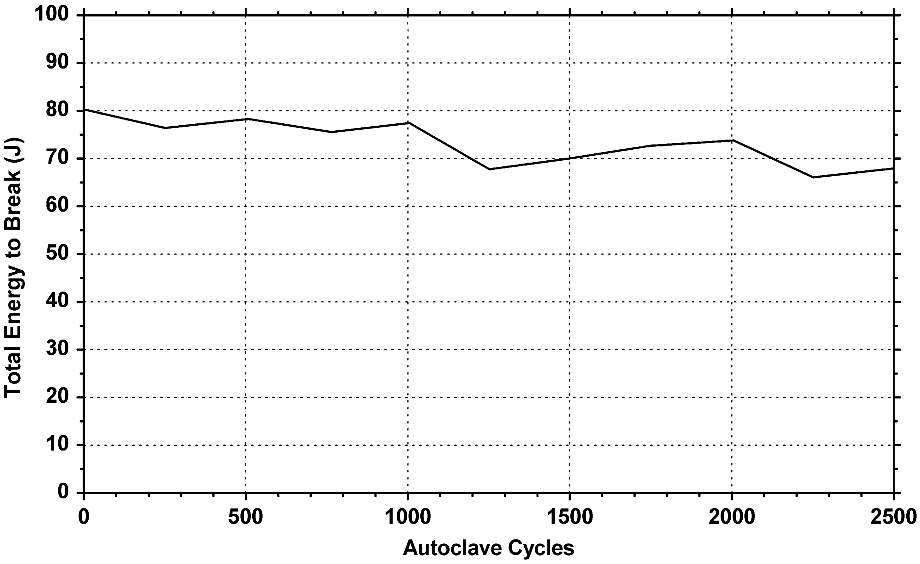


Figure 11.40 High speed impact (Dynatup) after 134 °C steam autoclave with 50 ppm morpholine of polyphenylsulfone.[12]



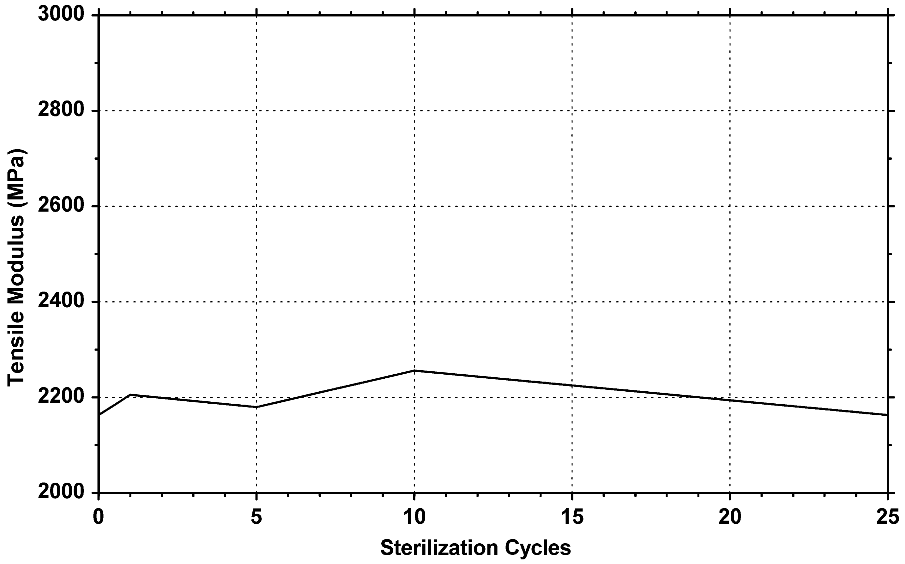


Figure 11.41 Tensile modulus after vaporized hydrogen peroxide gas plasma sterilization of Solvay Solexis Radel® R PPSU.[2] Note: Cycle = 45 °C, 58% H_2O_2, pre-plasma 10 min, exposure 12 min, diffusion time 4 min.

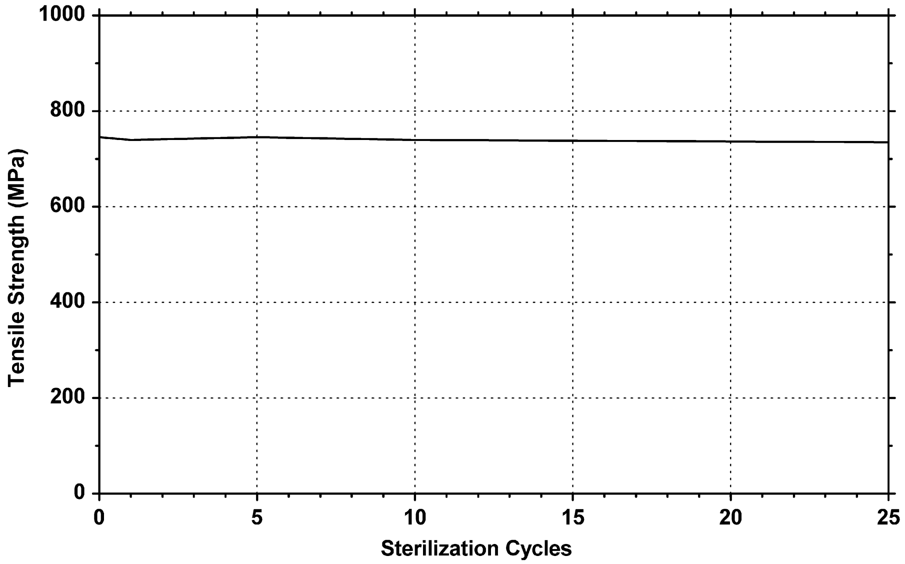


Figure 11.42 Tensile strength after vaporized hydrogen peroxide gas plasma sterilization of Solvay Solexis Radel® R PPSU.[2] Note: Cycle = 45 °C, 58% H_2O_2, pre-plasma 10 min, exposure 12 min, diffusion time 4 min.

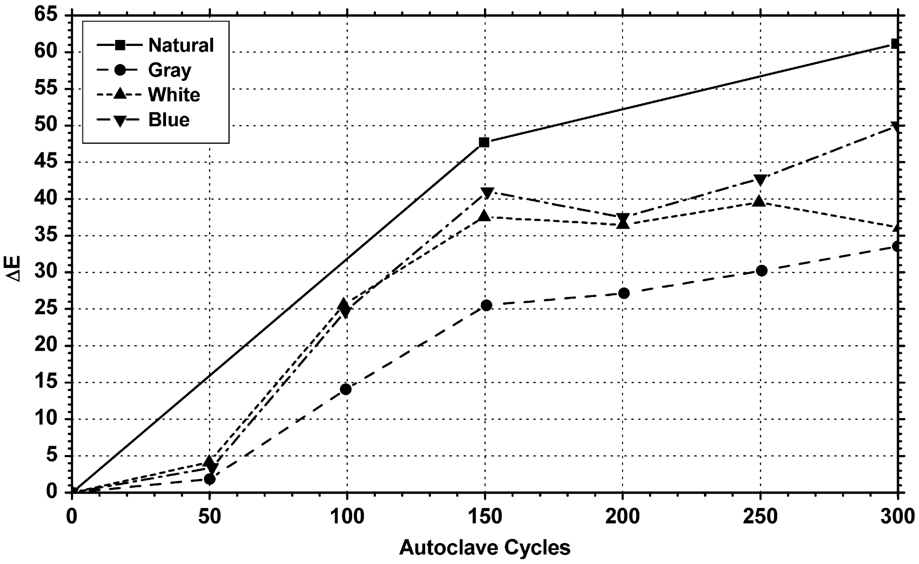


Figure 11.43 Color stability after low-temperature hydrogen peroxide gas plasma (STERRAD® NX) sterilization on different colors of polyphenylsulfone.[12]

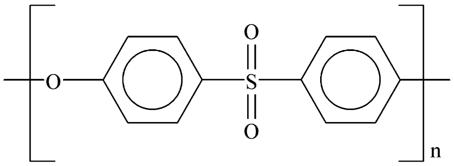


Figure 11.44 Structure of polyethersulfone.

tolerances and little dimensional change over a wide temperature range. Its properties include:

- Excellent thermal resistance – T_g 224 °C
- Outstanding mechanical, electrical, flame, and chemical resistance
- Very good hydrolytic and sterilization resistance
- Good optical clarity.

Manufacturers and trade names: BASF Ultrason® E, Sumitomo Chemical Co., Ltd, SUMIKAEXCEL® PES, and Solvay Advanced Polymers Veradel®.

Sterile applications: Medical equipment that requires repeated sterilization.

General sterilization resistance: Radel A withstands cold sterilants, disinfectants, and germicides.

Gamma and electron beam radiation resistance: Ultrason® E offers very high resistance to gamma radiation over the entire range of service temperatures. Ultrason® E products exposed to high-energy radiation suffer a noticeable decrease in tensile strength at yield and a significant decrease in ultimate elongation. Gassing is very slight; transmittance for gamma rays is very high.

Autoclave or steam sterilization resistance: Ultrason® E parts can be repeatedly sterilized in superheated steam. After more than 100 sterilization cycles, samples remain transparent and largely retain their high level of mechanical properties. Ultrason® E differs from Ultrason® S in that it absorbs more water and is thus suitable only for steam sterilization without a vacuum phase. In order to avoid environmental stress cracking, the level of molded in stress in parts should be as low as possible. Radel® resins have superior resistance to steam and boiling water. Hydrolytic stability of injection molded 1/8-inch-thick test bars was tested by exposure to 132 °C steam containing 50 ppm of morpholine. The molded bars were tested both unstressed and with 500 and 1000 psi constant applied stress. The stress was applied via weights attached to one end while fixing the other end horizontally as a cantilevered beam. Steam exposure was 30 min/cycle returning to room temperature before starting another cycle. Tensile impact (ASTM D1822) after steam exposure shows Radel® A-200 maintaining good tensile impact through 1000+ cycles while polyetherimide deteriorated significantly.

Data for PES plastics are found in Table 11.8 and Fig. 11.45–11.48.

11.7 Parylene (Poly(*p*-Xylylene))

Parylene is the generic name for members of a series of polymers. The basic member of the series, called Parylene N, is poly-para-xylylene, a completely linear, highly crystalline material. The structures of four Parylene types are shown in Fig. 11.49.

Parylene polymers are not manufactured and sold directly. They are deposited from the vapor phase by a process which in some respects resembles vacuum metalizing. The Parylenes are formed at a pressure of about 0.1 torr from a reactive dimmer in the gaseous

Table 11.8 Effect of 140 °C Steam Sterilization on Tensile Strength and Impact Strength of Sumitomo Chemical SUMIKAEXCEL PES 4100 G

Period (Weeks)	Tensile Strength (MPa)	Rate of Change (%)	Charpy Impact Strength (J/m)	Rate of Change (%)
Control	81	100	382	100
2	88	108	176	46
7	93	114	137	35
14	92	113	137	34
29	81	100	137	37
42	84	104	147	39

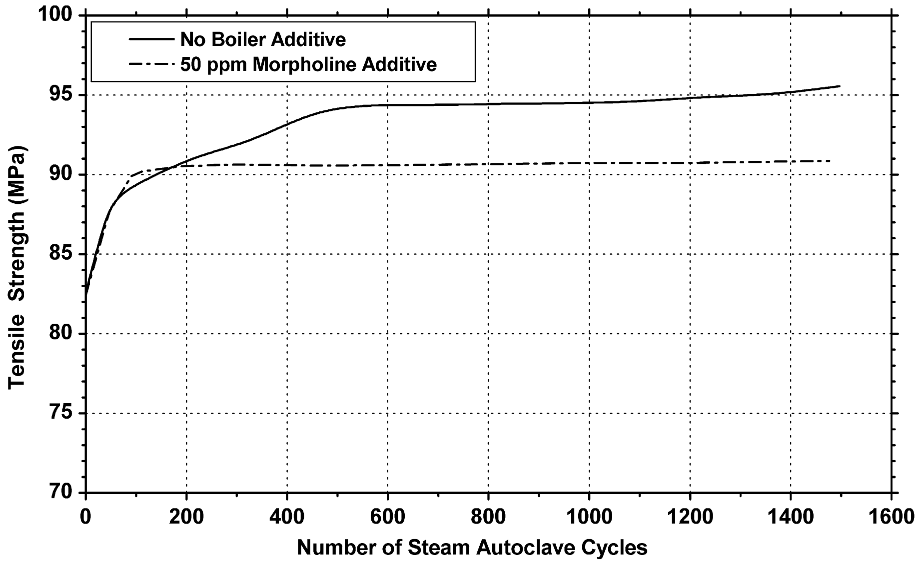


Figure 11.45 Number of steam sterilization cycles versus tensile strength of polyethersulfone.[10]

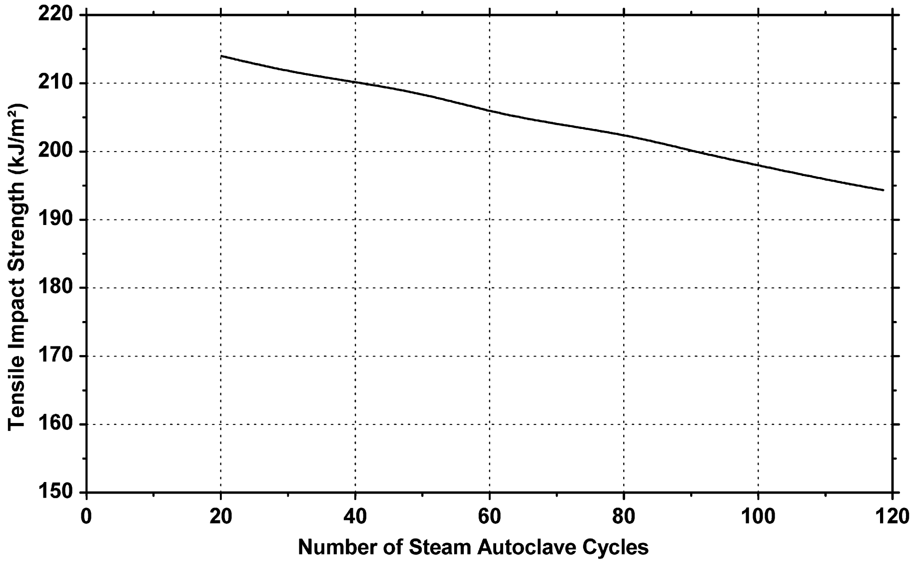


Figure 11.46 Number of steam sterilization cycles (30 min at 132 °C) versus tensile impact strength of polyethersulfone.[11]

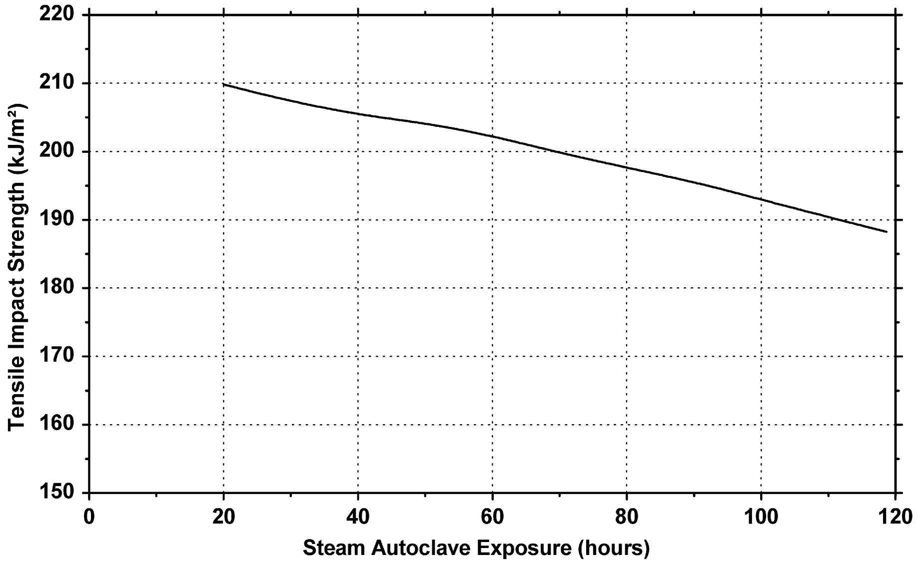
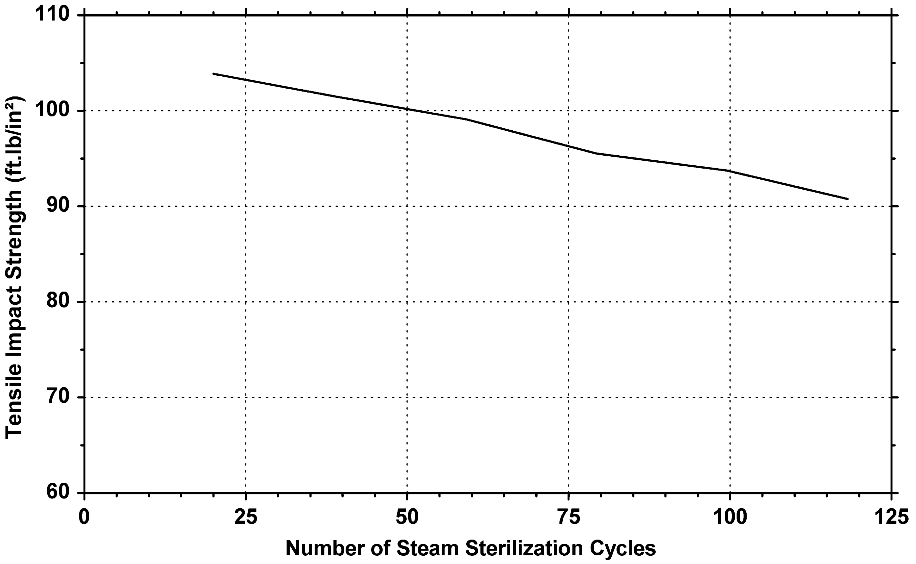


Figure 11.47 Number of steam sterilization cycles versus tensile impact strength of Radel® A200 polyethersulfone.[11]

Figure 11.48 Tensile impact after steam sterilization of Radel® PES.[11]



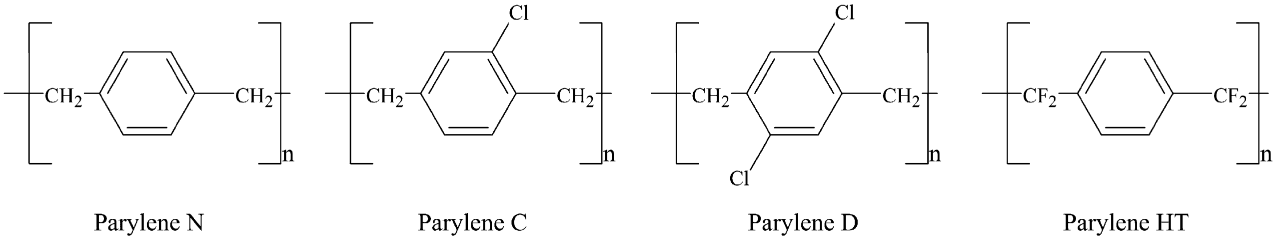


Figure 11.49 Structures of the Parylene polymer molecules.

or vapor state. Unlike vacuum metalizing, the deposition is not line of sight, and all sides of an object to be encapsulated are uniformly impinged by the gaseous monomer. Due to the uniqueness of the vapor phase deposition, the Parylene polymers can be formed as structurally continuous films from as thin as a fraction of a micrometer to as thick as several mils.

The first step is the vaporization of the solid dimer at approximately 150 °C. The second step is the quantitative cleavage (pyrolysis) of the dimer vapor at the two methylene–methylene bonds at about 680 °C to yield the stable monomeric diradical, para-xylylene. Finally, the monomeric vapor enters the room temperature deposition chamber where it spontaneously polymerizes on the substrate. The substrate temperature never rises more than a few degrees above ambient.

Parylene is used as a coating on medical devices ranging from silicone tubes to advanced coronary stents and synthetic rubber products ranging from medical grade silicone rubber to ethylene propylene diene monomer rubber (EPDM).

The manufacturer of coating equipment and starting materials is Para Tech Coating, Inc. They also offer coating services.

Manufacturers and trade names: Para Tech Coating, Inc. Parylene.

Sterile applications and uses: Needles, prosthetic devices, implantable components, catheters, electrodes, stents, epidural probes, and cannulae assemblies.

Parylene coatings respond to these sterilization methods in a variety of ways (see summary of responses in Table 11.9). With regard to tensile properties, Parylene N and C were largely unaffected by any of these sterilization techniques. Only steam appears to have had any effect, causing an annealing impact on samples coated with Parylene C, seen as an increase in film crystallinity with a slight change in the tensile properties. Similarly, the tensile modulus property of Parylene N exhibited a minor change.

H_2O_2 plasma sterilization: Treatment appeared to alter dielectric strength, with a minimal change in Parylene C and no change in Parylene N.

Data for Parylene plastics are found in Table 11.9.

Table 11.9 Effects of Various Sterilization Methods on Parylene[13]

Sterilization Method	Parylene N					Parylene C				
	Dielectric Strength	Moisture Vapor Transmission	Tensile Strength	Tensile Modulus	Coefficient of Friction COF	Dielectric Strength	Moisture Vapor Transmission	Tensile Strength	Tensile Modulus	COF
Steam	None	Δ43%	None	Δ12%	Δ38%	None	Δ5*	Δ17%	Δ9%	None
EtO	None	Δ21%	None	None	Δ33%	None	8%	None	None	None
E-beam	NA	None	None	None	None	NA	None	None	None	None
H_2O_2 plasma	None	None	None	None	Δ48%	Δ9%	None	None	None	Δ188%
Gamma	None	None	None	None	None	None	Δ5%	None	None	None

Note: NA = not applicable.

**5% values are not likely to be statistically significant.*

11.8 Polyoxymethylene (Acetal Homopolymer)/Polyoxymethylene Copolymer (Acetal Copolymer)

Acetal polymers, also known as polyoxymethylene (POM) or polyacetal, are formaldehyde-based thermoplastics that have been commercially available since the 1960s. Polyformaldehyde is thermally unstable. It decomposes on heating to yield formaldehyde gas. Two methods of stabilizing polyformaldehyde for use as an engineering polymer were developed and introduced by DuPont, in 1959, and Celanese in 1962 (now Ticona).

DuPont's method for making polyacetal yields a homopolymer through the condensation reaction of polyformaldehyde and acetic acid (or acetic anhydride). The acetic acid puts acetate groups (CH_3COO-) on the ends of the polymer as shown in Fig. 11.50, which provide thermal protection against decomposition to formaldehyde.

Further stabilization of acetal polymers also includes the addition of antioxidants and acid scavengers. Polyacetals are subject to oxidative and acidic degradation, which leads to molecular weight decline. Once the chain of the homopolymer is ruptured by such an attack, the exposed polyformaldehyde ends may decompose to formaldehyde and acetic acid.

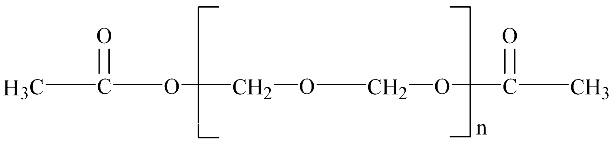
The Celanese route for the production of polyacetal yields a more stable copolymer product via the reaction of trioxane, a cyclic trimer of formaldehyde, and a cyclic ether, such as ethylene oxide or 1,3 dioxolane. The structures of these monomers are shown in Fig.11.51. The polymer structure is given in Fig. 11.52.

The improved thermal and chemical stability of the copolymer versus the homopolymer is a result of randomly distributed oxyethylene groups, which is circled in Fig. 11.52. All polyacetals are subject to oxidative and acidic degradation, which leads to molecular weight reduction. Degradation of the copolymer ceases, however, when one of the randomly distributed oxyethylene linkages is reached. These groups offer stability to oxidative, thermal, acidic, and alkaline attack. The raw copolymer is hydrolyzed to an oxyethylene end cap to provide thermally stable polyacetal copolymer.

The copolymer is also more stable than the homopolymer in an alkaline environment. Its oxyethylene end cap is stable in the presence of strong bases. The acetate end cap of the homopolymer, however, is readily hydrolyzed in the presence of alkalis, causing significant polymer degradation.

The homopolymer is more crystalline than the copolymer. The homopolymer provides better mechanical properties, except for elongation. The oxyethylene groups of the copolymer provide improved long-term chemical and environmental stability. The copolymer's chemical stability results in better retention of mechanical properties over an extended product life.

Acetal polymers have been particularly successful in replacing cast and stamped metal parts due to their toughness, abrasion resistance, and ability to withstand prolonged stresses with minimal creep. Polyacetals are inherently self-lubricating. Their lubricity allows the incorporation of polyacetal in a variety of metal-to-polymer and polymer-to-polymer interface applications such as bearings, gears, and switch plungers. These properties have permitted the material to meet a wide range of market requirements.



$$H_3C-\overset{\overset{O}{\|}}{C}-O-\left[CH_2-O-CH_2-O\right]_n-\overset{\overset{O}{\|}}{C}-CH_3$$

Figure 11.50 Chemical structure of acetal homopolymer.

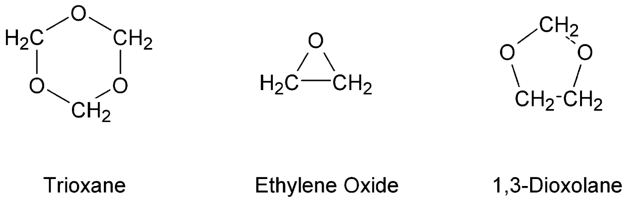
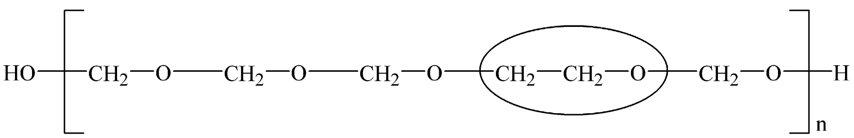


Figure 11.51 Chemical structure polyoxymethylene copolymer monomers.



$$HO-\left[CH_2-O-CH_2-O-CH_2-O-CH_2-CH_2-O-CH_2-O\right]_n-H$$

Figure 11.52 Chemical structure of acetal copolymer.

Table 11.10 Exposure of DuPont Delrin® to 2 meV Electrons[14]

Dose (Mrad)	Tensile Strength (MPa)	Elongation (%)	Izod Impact Strength (J/m)
0	69	15	75
0.6	67	11.5	53
2.3	43	0.9	11

The properties of polyacetals can be summarized as follows:

- Excellent wear resistance
- Very good strength, stiffness
- Good heat resistance
- Excellent chemical resistance
- Opaque
- Moderate to high price
- Somewhat restricted processing.

Ionizing radiation: Great caution is advisable in case of sterilization using ionizing radiation; the total dose should not exceed 20 kGy (2 Mrad).

Ethylene oxide sterilization: Repeated sterilization in ethylene oxide can be carried out at room temperature without problems, employing familiar methods.

Autoclave sterilization: Properly and flawlessly manufactured parts made of Ultraform® POM can be sterilized in hot steam at 121 °C and, with some limitations, even at 134 °C, over the course of many cycles, whereby the high molecular grades perform best. Plasma sterilization is also a good option.

Chemical disinfection is not recommended.

Manufacturers and trade names: DuPont™ Delrin®, BASF Ultraform®, and Ticona Celcon®.

Applications and uses: Metal and glass replacement.

Data for acetal plastics are found in Table 11.10.

11.9 Self-Reinforced Polymers

Self-reinforced polymers (SRPs) are rigid rod polyphenylenes with a structure shown in Fig. 11.53. A choice of side groups permits optimization of the properties. One "R" side group used in a commercial product is shown in Fig. 11.54. Even without fiber reinforcement, PrimoSpire® SRP delivers tensile properties that are comparable to those of many reinforced plastics. Plus, you get the added benefits of lighter weight and no loss of ductility.

These properties combine with high compressive strength — one of the highest among plastics — to make PrimoSpire® SRP an excellent candidate for weight-sensitive applications that have historically relied on composites and specialty metals for superior mechanical performance.

Key features of SRPs include:

- Exceptional strength and stiffness without reinforcements

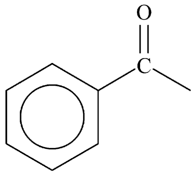


Figure 11.54 The structure of the R-group in a commercial self-reinforced polyphenylene rigid rod polymer.

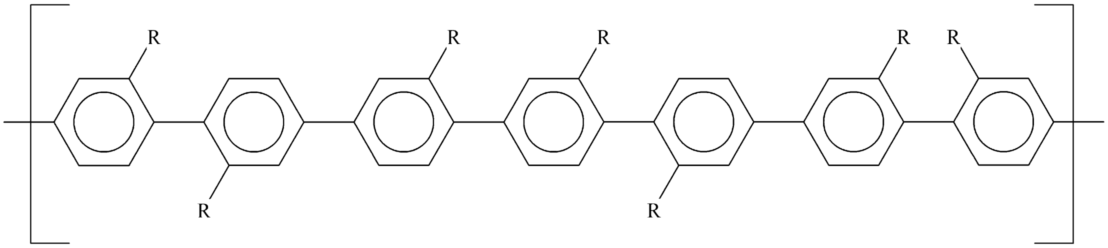


Figure 11.53 The structure of the polyphenylene rigid rod polymer.

Figure 11.55 Tensile modulus versus EtO sterilization cycles of Solvay Solexis PrimoSpire® SRP.[2] Note: Cycle = 55 °C, 60 min, 70% RH, aeration 60 min.

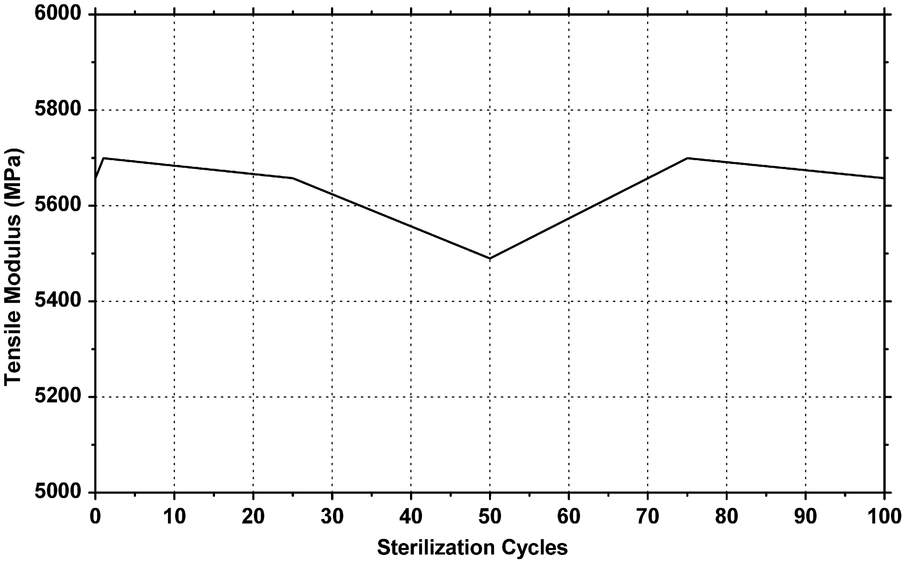


Figure 11.56 Tensile strength versus EtO sterilization cycles of Solvay Solexis PrimoSpire® SRP.[2] Note: Cycle = 55 °C, 60 min, 70% RH, aeration 60 min.

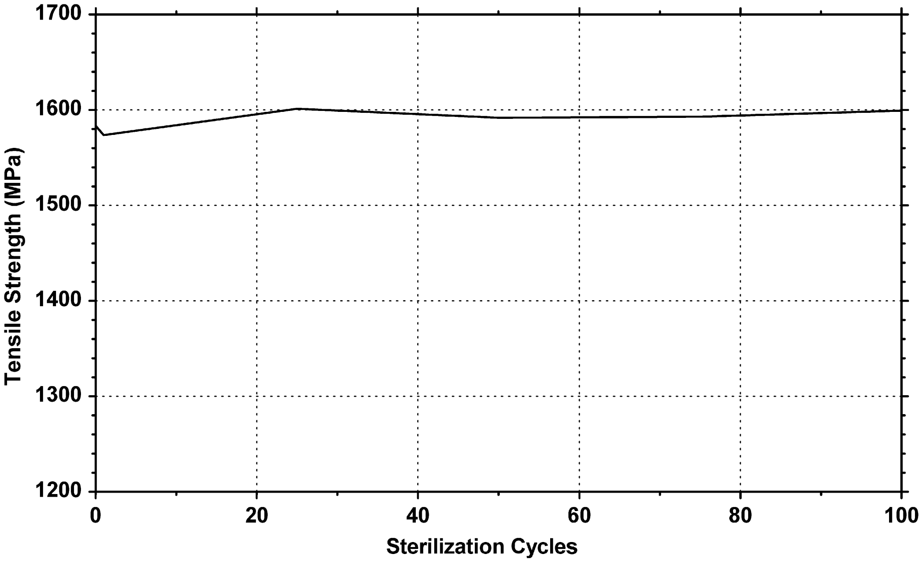
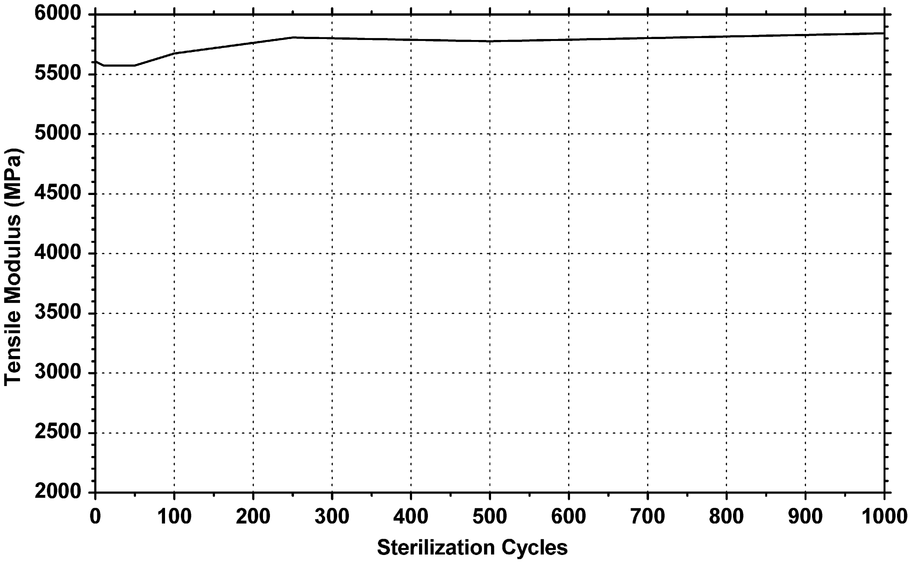


Figure 11.57 Tensile modulus after steam sterilization of Solvay Solexis PrimoSpire® SRP.[2] Note: 135.5 °C, 31–33 psig, vacuum: 27 in Hg, sterilization time 18 min, drying time 33 min.



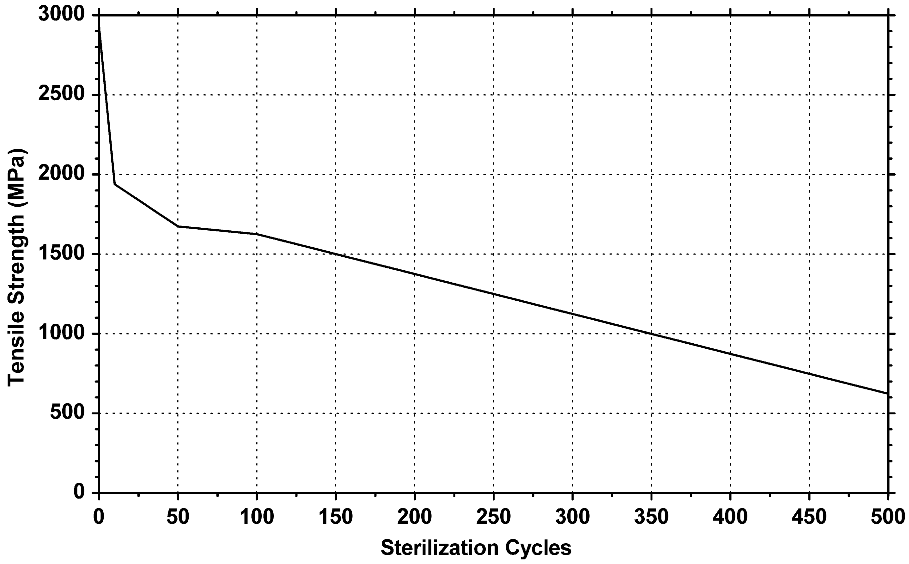


Figure 11.58 Tensile strength after steam sterilization of Solvay Solexis PrimoSpire® SRP.[2] Note: 135.5 °C, 31–33 psig, vacuum: 27 in Hg, sterilization time 18 min, drying time 33 min.

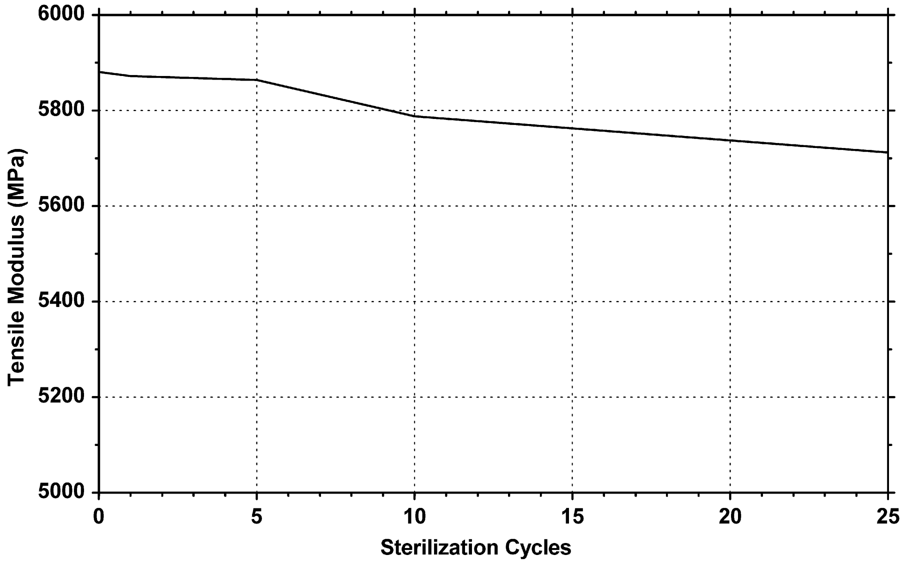


Figure 11.59 Tensile modulus after vaporized hydrogen peroxide gas plasma sterilization of Solvay Solexis PrimoSpire® SRP.[2] Note: Cycle = 45 °C, 58% H_2O_2, pre-plasma 10 min, exposure 12 min, diffusion time 4 min.

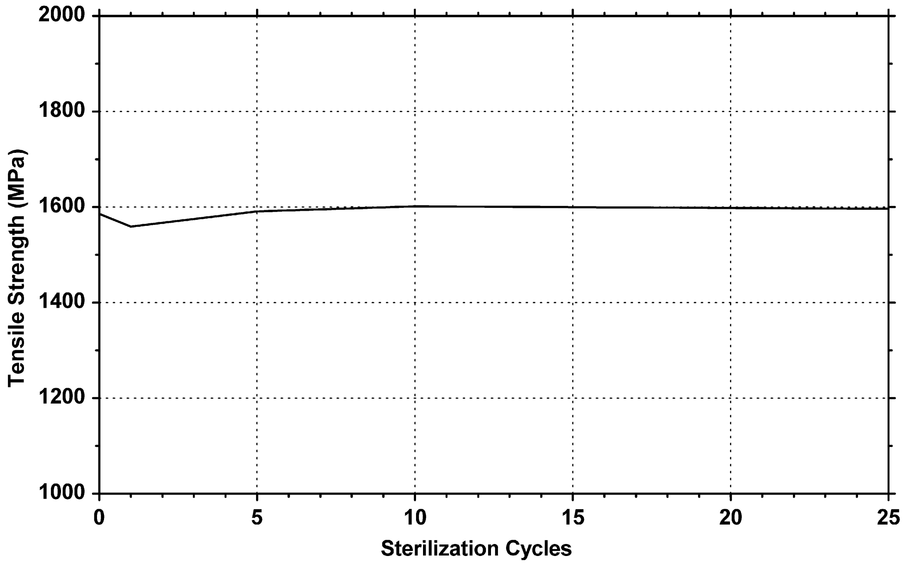


Figure 11.60 Tensile strength after vaporized hydrogen peroxide gas plasma sterilization of Solvay Solexis PrimoSpire® SRP.[2] Note: Cycle = 45 °C, 58% H_2O_2, pre-plasma 10 min, exposure 12 min, diffusion time 4 min.

- Outstanding mechanical performance
- Inherent flame resistance and ablative properties
- Excellent chemical resistance
- Exceptional hardness and surface finish
- Very low coefficient of linear thermal expansion
- Very low moisture absorption.

Manufacturers and trade names: Solvay Solexis PrimoSpire® SRP (formerly Mississippi Polymers Technologies Parmax™).

Applications and uses: Surgical instruments and medical devices.

Data for SRP plastics are found in Fig. 11.55−11.60.

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12 Renewable Resource and Biodegradable Polymers

The polymers covered in this chapter are those that are produced from "renewable resource raw materials" such as corn or that are "biodegradable or compostable." Biopolymers are materials that either occur naturally (i.e. proteins, sugars) or are synthesized from naturally occurring biological materials like sugars, fats, oil, and starch, and these are included in this chapter. This is a developing area in packaging materials and medical products and though there are a relatively limited number of polymers used commercially, they will certainly become more numerous and more common in the future.

Biodegradable plastics are made out of ingredients that can be metabolized by naturally occurring microorganisms in the environment. Some petroleum-based plastics will biodegrade eventually, but that process usually takes a very long time and contributes to global warming through the release of carbon dioxide.

The ASTM D6400-04 Standard Specification for Compostable Plastics has definitions for various types of degradable plastics as follow:

- *Degradable plastics* are designed to undergo a significant change in their chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification.
- *Biodegradable plastics* are plastics in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae.
- *Photodegradable plastics* are plastics in which the degradation results from the action of natural daylight.
- *Oxidatively degradable plastics* are degradable plastics in which the degradation results from oxidation.
- *Hydrolytically degradable plastics* are degradable plastics in which the degradation results from hydrolysis.
- *Compostable plastics* are plastics that undergo degradation by biological processes during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials. They leave no visually distinguishable or toxic residue.

Renewable plastic is derived from natural plant products such as corn, oats, wood, and other plants, which helps ensure the sustainability of the earth. Poly(lactic acid) (PLA) is currently the most widely researched and used 100% biodegradable plastic packaging polymer and is made entirely from corn-based cornstarch. Details on PLA are included in a following section.

Interest in these materials is strong as the number of commercially available materials grows. Table 12.1 lists some of the commercial materials recently available.

Some of the abbreviations: PHBV, polyhydoxybutyrate valerate; PBS-co-PBST, polybutylene succinate copolymer poly(butylene succinate-terephthalate); PBS-co-PBSA, polybutylene succinate copolymer polybutylene succinate adipate; PHV, polyhydroxy valerate; LDPE, low-density polyethylene; PTT, polytrimethylene terephthalate; PBAT, poly(butylene adipate-co-terephthalate); EPS, expanded polystyrene; PDO, poly(dioxanone).

Sterilization studies of biopolymers are relatively scarce when compared to other polymers. Table 12.2 does summarize the compatibility of some of the biopolymers with the various common sterilization methods. The abbreviations are covered with the different polymers in the following sections.

The following sections contain the details of several of the more common green polymers.

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00012-5

Table 12.1 A List of Some Renewable Resource and Biodegradable Polymer-Based Products Including Trade Name and Trademarks[1]

Trade Mark	Owner	Material
Aqua-Novon	Novon International Inc. (USA)	Polycaprolactone
BAK®	Bayer AG Corporation (Germany)	Polyester amide
BioBag International AS	Polargruppen (Norway)	Mater-Bi®
Bioceta, Biocell, Biocelat	Mazucchelli, S.p.A. (Italy)	Cellulose acetate
Biofan	Gunze (Japan)	poly-3-hydroxybutyrate/ poly-3-hydroxy butyrate
Bioflex®	Biotec GmbH (Germany)	Starch
Biogreen	Mitsubishi Gas Chemical Co. (Japan)	poly-3-hydroxy butyrate
Biomax®	DuPont (USA)	poly butylene succinate-co-Polybutylene succinate terephthalate
Biomer	Biomer (Germany)	Polyester, poly-3-hydroxybutyrate
Bionolle 1000	Showa Highpolymer Co. (Japan)	poly butylene succinate
Bionolle 3000	Showa Highpolymer Co. (Japan)	poly butylene succinate-co-polybutylene succinate adipate
Biopac	Biopac Ltd (UK)	Starch
BioPar®	Biop AG Biopolymer GmbH (Germany)	Starch, biodegradable synthetic polymer
Biophan®	Trespaphan GmbH (Germany)	Poly Lactic Acid
Bioplast®	Biotec GmbH (Germany)	Starch, Poly Lactic Acid, co-polyester
Biopol™	Monsanto Co. (Italy)/ Metabolix, Inc. (UK)	poly-3-hydroxybutyrate, polyhydroxy valerate, and Polyhydroxyalkanoates
Biopur®	Biotec GmbH (Germany)	Starch
Bioska	PlastiRoll Oy (Finland)	Starch/Poly vinyl Alcohol
Bio-Solo	Indaco Manufacturing Ltd (Canada)	Starch, patented additives, Polyethylene
Biostarch®	Biostarch (Australia)	Maize starch
Bio-Stoll	Stoll Papierfolien (Germany)	Starch, Low density polyethylene/Ecostar, additive
Biotec®	Bioplast GmbH (Germany)	Thermoplastic starch (TPS®)
BioRez®	Trans Furans Chemicals (Netherlands)	Furan resin
Biothene®	Biothene (UK)	Biofuels from planted soy
CAPA®	Solvay Polymers (Italy)	Polycaprolactone
CelGreen PH/P-CA	Daicel Chemical Industries Ltd (Japan)	Polycaprolactone/cellulose acetate
CelloTherm	UCB Films (UK)	Regular cellulose (for microwave)

Table 12.1 (*Continued*)

Trade Mark	Owner	Material
Chronopol	Chronopol-Boulder, CO (USA)	Poly Lactic Acid
Clean Green	StarchTech Inc, MN (USA)	Starch-based biopolymers
Cohpol™	VTT Chemical Technology (Finland)	Starch ester
Cornpol®	Japan Corn Starch (Japan)	Modified starch
Corterra	Shell Chemicals (USA/NL)	polytrimethylene terephthalate
Degra-Novon®	Novon International Inc. (USA)	Polyolefin + additives
EarthShell®	EarthShell Corp., MD (USA)	Starch composite materials
Eastar Bio	Eastman Chemical Company (USA)	Co-polyester
ECM Masterbatch Pellets	ECM Biofilms (USA)	Additives for polyolefin products
Ecoflex®	BASF Corporation (Germany)	Poly(butyleneadipate)-co-Poly(butylene adipate-co-terphthalate)
Eco-Flow	National Starch & Chemical (USA)	Starch-based biodegradable products
Eco-Foam®	National Starch & Chemical	Foamed starch
Eco-Lam	National Starch & Chemical	Starch, Polyethylene Terephthalate, Polypropylene
EcoPLA®	Cargill Dow Polymers (USA)	Poly Lactic Acid
Ecoplast	Groen Granulaat (Netherlands)	Starch
EnPol	IRe Chemical Co. Ltd (South Korea)	poly butylene succinate-co-polybutylene succinate adipate
Envirofil™	EnPac/DuPont/ConAgra (USA)	Starch/Poly vinyl Alcohol
Enviromold®	Storopack Inc. (USA)	Polystyrene expanded products
EnviroPlastic®	Planet Polymer Technologies Inc. (USA)	Cellulose acetate
EverCorn™	EverCorn Inc. (USA)	Starch
Fasal®	Japan Corn Starch Co., Ltd. (Japan) Department Agrobiotechnology, Tulln, (Austria)	50% Wood wastes
FLO-PAK BIO 8®	FP International (USA)	Starch (corn or wheat)
Gohsenol	Nippon Gohsei (Japan)	Poly vinyl Alcohol
GreenFill	Green Light Products Ltd (UK)	Starch/Poly vinyl Alcohol
Greenpol®	SK Corporation (South Korea)	Starch, aliphatic polyester
Hydrolene®	Idroplax S.r.L. (Italy)	Poly vinyl Alcohol
LACEA®	Mitsui Chemicals Inc. (Japan)	Poly Lactic Acid from fermented glucose
Lacty	Shimadzu Corp. (Japan)	Poly Lactic Acid
Lignopol	Borregaard Deutschland GmbH	Lignin
Loose Fill®	STOROpack (Germany)	expanded polystyrene/starch
Lunare	Nippon Shokubai Co., Ltd	Polyethylenesuccinate/adipate

(*Continued*)

Table 12.1 (*Continued*)

Trade Mark	Owner	Material
Mater-Bi™	Novamont S.p.A. (Italy)	Starch/cellulose derivative
Mazin	Mazin International (USA)	Poly Lactic Acid
Mirel™	Metabolix Inc. (USA)	Corn sugar
NatureFlex™	Innovia Films (UK)	Regenerated cellulose film
NatureWorks®	Cargill Co. (USA)	Poly Lactic Acid
Nodax™	Procter & Gamble Co. (USA)	poly-3-hydroxybutyrate-co-polyhydroxyalkanoate
Novon®	Ecostar GmbH (Germany)	Starch
Paragon	Avebe Bioplastic (Germany)	Starch
Plantic®	Plantic Technologies (Australia)	Cornstarch materials
Poly-NOVON®	Novon International	Starch additives
Polystarch	Willow Ridge Plastics Inc. (USA)	Additives
POLYOX™	Union Carbide Corporation (USA)	Poly(ethylene oxide)
POVAL	Kuraray Povol Co., Ltd (Japan)	Poly vinyl Alcohol
Pullulan	Hayashibara Biochemical (Japan)	Starch
RenaturE®	Storopack Inc. (Germany)	Starch
ReSourceBags™	Ventus Kunststoff GmbH	Mater-Bi®
Sconacell®	Buna SOW Leuna (Germany)	Starch acetate, plasticizer
Sky-green	Sunkyong Ltd (South Korea)	Aliphatic-co-polyester
Solanyl®	Rodenburg Biopolymers (Netherlands)	Starch (from potato waste)
Sorona®	DuPont Tate & Lyle (USA)	polydioxone
SoyOyl™	Urethane Soy Systems Co. Inc. (USA)	Soy-based products
SPI-Tek	Symphony Plastic Technologies Plc (UK)	Additives
Supol®	Supol GmbH (Germany)	Starch plant oil and sugars
TONE®	Union Carbide Corp. (USA)	Polycaprolactone
Trayforma	Stora Enso Oyj (Finland)	Cellulose, food trays
Vegemat®	Vegeplast S A S (France)	Starch

Table 12.2 Sterilization Compatability of Some Biopolymers[6]

Biopolymer	Steam	Dry Heat	Ethylene Oxide	Gamma Radiation	E-Beam
PLLA	Fair	Good	Good	Good	Good
PLA	Poor	Fair	Good	Good	Good
PHB	Poor	Poor	Good	Fair	Fair
PGA	Good	Good	Good	Good	Good
PLGA	Poor	Poor	Good	Fair	Fair
PCL	Fair	Good	Good	Good	Good

12.1 Polyanhydrides

Polyanhydrides currently are used mainly in the medical device and pharmaceutical industry.[2] Figure 12.1 shows the generalized structure of an anhydride polymer and two polyanhydrides that are used to encapsulate certain drugs. The poly(bis carboxyphenoxypropane) (pCCP) is relatively slow to degrade. The poly(sebacic anhydride) (pSA) is fast to degrade. Separately neither of these materials can be used, but if a copolymer is made in which 20% of the structure is pCCP and 80% is pSA, the overall properties meet the needs of the drug. Polyanhydrides are now being offered for general uses.

They can be sterilized by gamma radiation with minimal effect on their properties.[3]

12.2 Cellophane™

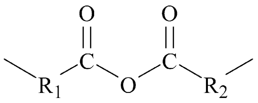
Cellophane™ is a polymeric cellulose film made from the cellulose from wood, cotton, hemp, or other sources. The raw material of choice is called dissolving pulp, which is white like cotton and contains 92–98% cellulose. The cellulose is dissolved in alkali in a process known as mercerization. It is aged several days. The mercerized pulp is treated with carbon disulfide to make an orange solution called viscose or cellulose xanthate. The viscose solution is then extruded through a slit into a bath of dilute sulfuric acid and sodium sulfate to reconvert the viscose into cellulose. The film is then passed through several more baths, one to remove sulfur, one to bleach the film, and one to add glycerin to prevent the film from becoming brittle. Cellophane™ has a CAS number of 9005-81-6. The approximate chemical structures are shown in Fig. 12.2.

The Cellophane™ may be coated with nitrocellulose or wax to make it impermeable to water vapor. It may also be coated with polyethylene or other materials to make it heat sealable for automated wrapping machines.

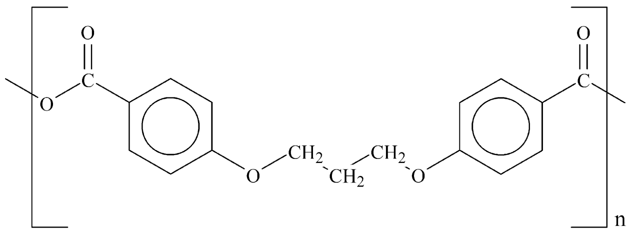
Manufacturers and trademarks: Innovia Cellophane™.

Applications and uses: Cellulosic film applications include tapes and labels, photographic film, coatings for paper, glass, and plastic. Medical applications for cellulosic films include dialysis membranes.

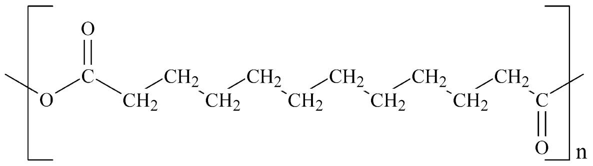
Cuprophan cellulose membranes are widely used for dialysis membranes and are sterilized by high-energy radiation.[4] Regenerated cellulose is used in Cellu·Sep® membranes. The common method of Cellu·Sep® membrane sterilization is exposure to ethylene oxide (EtO) gas. Alternative sterilization



General Anhydride Structure



Poly(bis carboxyphenoxypropane), pCCP



poly(sebacic anhydride) pSA

Figure 12.1 Polyanhydride chemical structures.

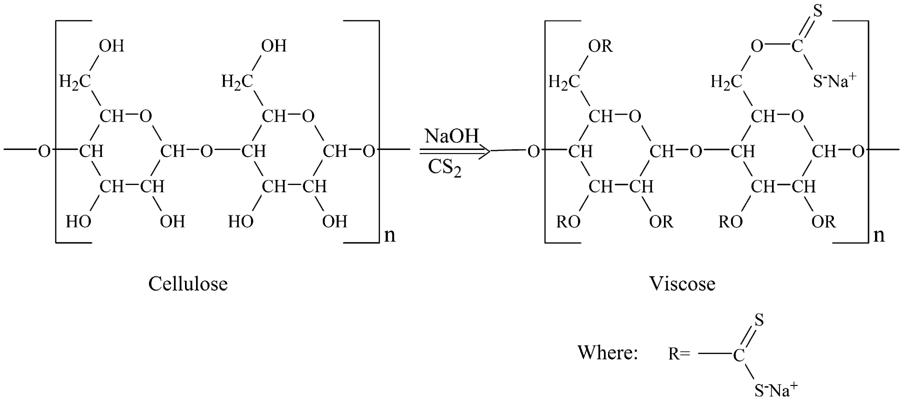


Figure 12.2 Conversion of raw cellulose to viscose.

methods are gamma irradiation and steam autoclaving. The suggested preparation of membranes before sterilization is to soak the membrane for 30 min in distilled water. For chemical sterilization with EtO, the prepared membrane is placed in an open polyethylene bag in a vacuum oven. A gas mixture of 20% EtO/80% CO_2 by a total pressure of 1 atm is used. The membrane is exposed for 5 h at 40 °C. For gamma irradiation, the membrane is sealed in a polyethylene bag and exposed to gamma rays for a total dose of 2.5 Mrad. For autoclaving, the length of the cycle should be kept as short as possible. Membranes may be safely autoclaved at 121 °C at 100 kPa (1 bar) for 10 min. They should not be permitted to dry out afterward. Dry heating over a period of 48 h at 80 °C is also permitted.

12.3 Nitrocellulose

Nitrocellulose is made by treating cellulose with a mixture of sulfuric and nitric acids. This changes the hydroxyl groups (-OH) on the cellulose to nitro groups ($-NO_3$) as shown in Fig. 12.3. Nitrocellulose, also know as gun cotton, is the main ingredient of smokeless gunpowder and it decomposes explosively. In the early twentieth century, it was found to make an excellent film and paint. Nitrocellulose lacquer was used as a finish on guitars and saxophones for most of the twentieth century and is still used in some current applications. Manufactured by (among others) DuPont, the paint was also used on automobiles sharing the same color codes as many guitars including Fender and Gibson brands. Nitrocellulose lacquer is also used as an aircraft dope, painted onto fabric-covered aircraft to tauten and provide protection to the material. Its CAS number is 9004-70-0.

Nitrocellulose is not usually used by itself for film applications but more commonly is part of multilayered films structures, especially those based on Cellophane™.

Manufacturers and trade names: Innovia Films Cellophane™.

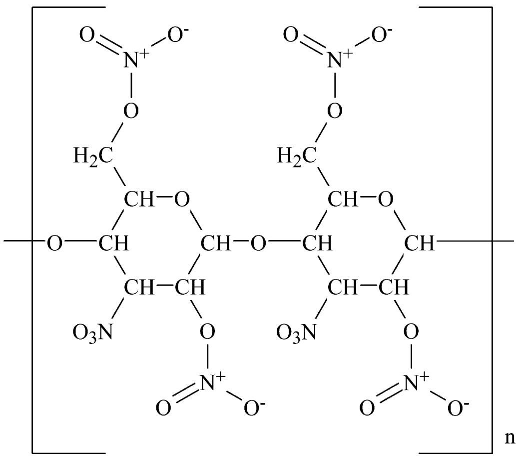


Figure 12.3 Structure of nitrocellulose.

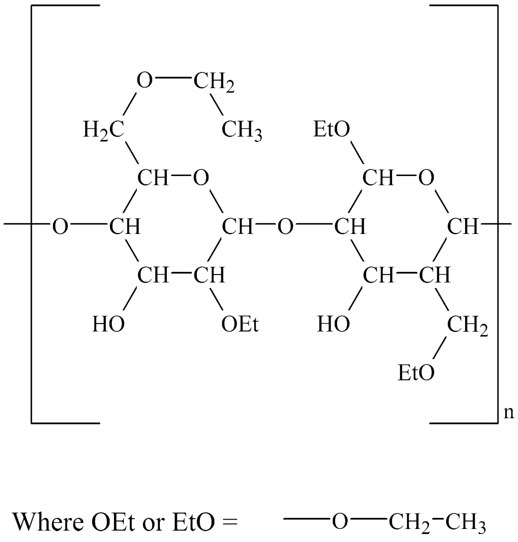


Figure 12.4 Structure of ethyl cellulose.

Applications and uses: Food wrap; nitrocellulose membrane filters are commonly used to filter-sterilize solutions.

Nitrocellulose membranes can be autoclaved (liquid cool cycle) or gamma irradiated.

12.4 Ethyl Cellulose (Hydroxyethylcellulose)

Ethyl cellulose is similar in structure to cellulose and cellulose acetate but some of the hydroxyl (-OH) functional groups are replaced on the cellulose by the ethoxy group (-O-CH_2-CH_3). Ethyl cellulose has a CAS number of 9004-57-3 and its structure is shown in Fig. 12.4.

Manufacturers and trade names: Dow Ethocel™ and Ashland Aqualon®.

Applications and uses: Pharmaceutical applications, cosmetics, nail polish, vitamin coatings, printing inks, specialty coatings, and food packaging.

12.5 Polycaprolactone

Polycaprolactone (PCL) is biodegradable polyester with a low melting point of around 60 °C and a glass transition temperature of about −60 °C. PCL is prepared by ring-opening polymerization of ε-caprolactone using a catalyst such as stannous octanoate. The structure of PCL is shown in Fig. 12.5.

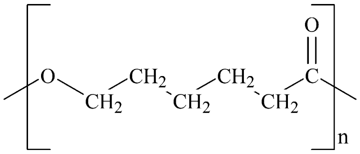


Figure 12.5 Structure of polycaprolactone.

PCL is degraded by hydrolysis of its ester linkages in physiological conditions (such as in the human body) and has therefore received a great deal of attention for use as an implantable biomaterial. In particular, it is especially interesting for the preparation of long-term implantable devices. A variety of drugs have been encapsulated within PCL beads for controlled release and targeted drug delivery. PCL is often mixed with starch to obtain a good biodegradable material at a low price.

Manufacturers and trade names: Perstorp CAPA® (previously Solvay) and Dow Chemical Tone (discontinued).

Applications and uses: The mix of PCL and starch has been successfully used for making trash bags in Korea (Yukong Company).

Data for PCL plastics are found in Fig. 12.6.

12.6 Poly Lactic Acid (PLA) and Poly L-Lactic Acid (PLLA)

PLA is derived from renewable resources, such as cornstarch or sugarcanes. PLA polymers are considered biodegradable and compostable. PLA is a thermoplastic, high-strength, high-modulus polymer that can be made from annually renewable sources to yield articles for use in either the industrial packaging field or the biocompatible/bioabsorbable medical device market. Bacterial fermentation is used to make lactic acid, which is then converted to the lactide dimer to

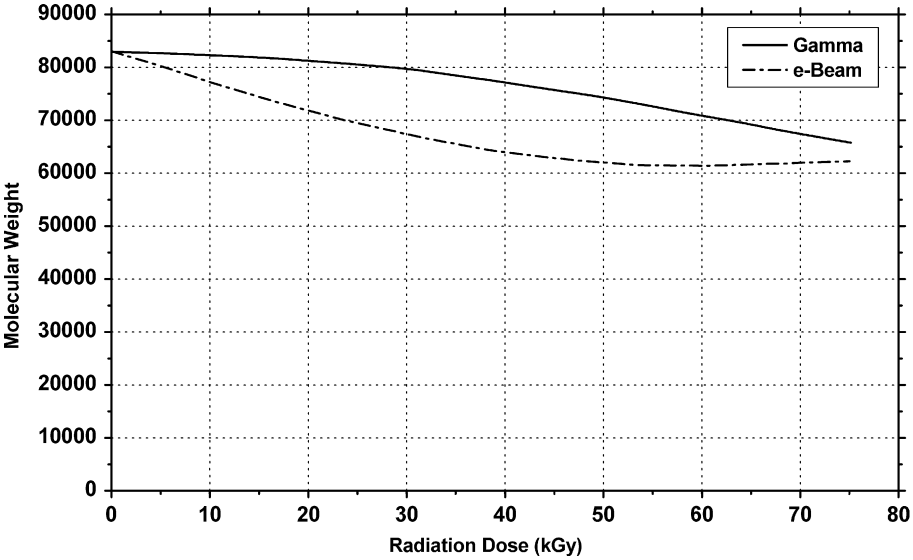


Figure 12.6 The effect of ionizing irradiation on the molecular weight of polycaprolactone.[6]

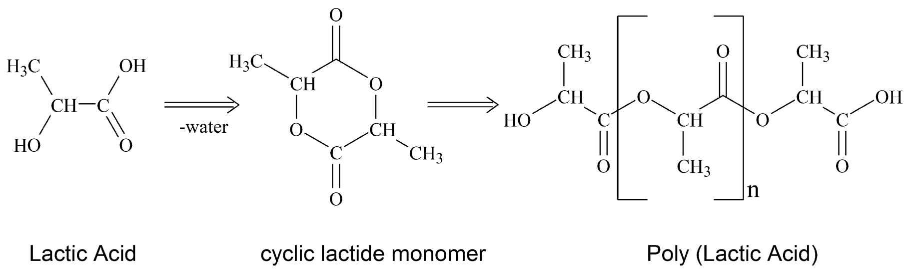


Figure 12.7 Conversion of lactic acid to polylactic acid.

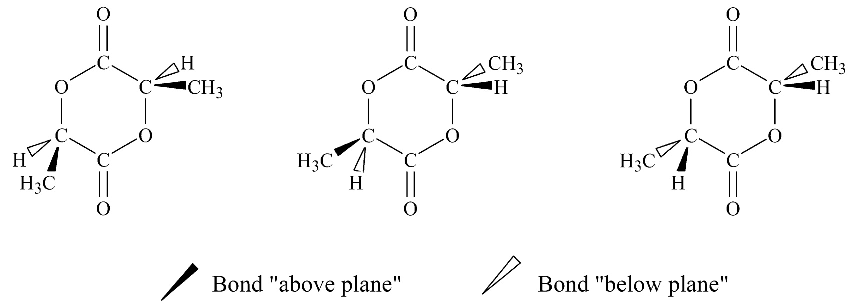


Figure 12.8 Stereoisomeric structures of the lactide dimer.

remove the water molecule that would otherwise limit the ability to make high molecular weight polymer. The lactide dimer, after the water is removed, can be polymerized without the production of the water. This process is shown in Fig. 12.7. The PLA CAS number is 9002-97-5.

The dimer can be isolated into three forms: the optically active L-lactide, the optically active D-lactide, and the optically inactive DL mixture DL-lactide. These stereoisomer structures are shown in Fig. 12.8. The enantiomeric ratio of the dimer can be controlled. Fermentation-derived lactic acid is 95% L-isomer.

Manufacturers and trade names: FKur Bio-Flex®, Cereplast Inc. Compostables®, Mitsubishi Chemical Fozeas®, Natureworks LLC Ingeo™, Alcan Packaging Ceramis®-PLA, Pro-Tech Biologische und Technische Produkte GmbH BioMat, and Melitta Haushaltsprodukte GmbH & Co KG SWIRL.

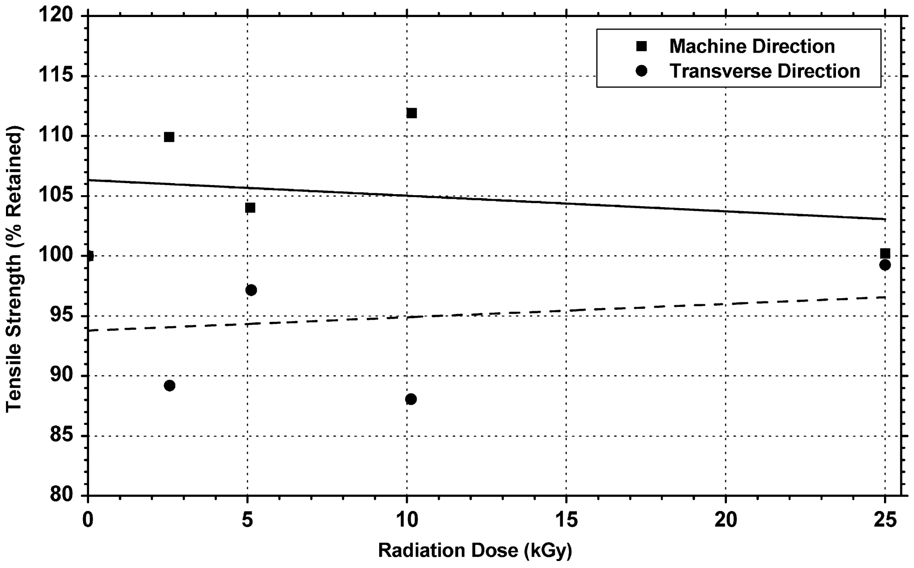


Figure 12.9 The effect of gamma irradiation dose on the tensile strength of Pro-Tech Biologische und Technische Produkte GmbH BioMat PLA film.[5]

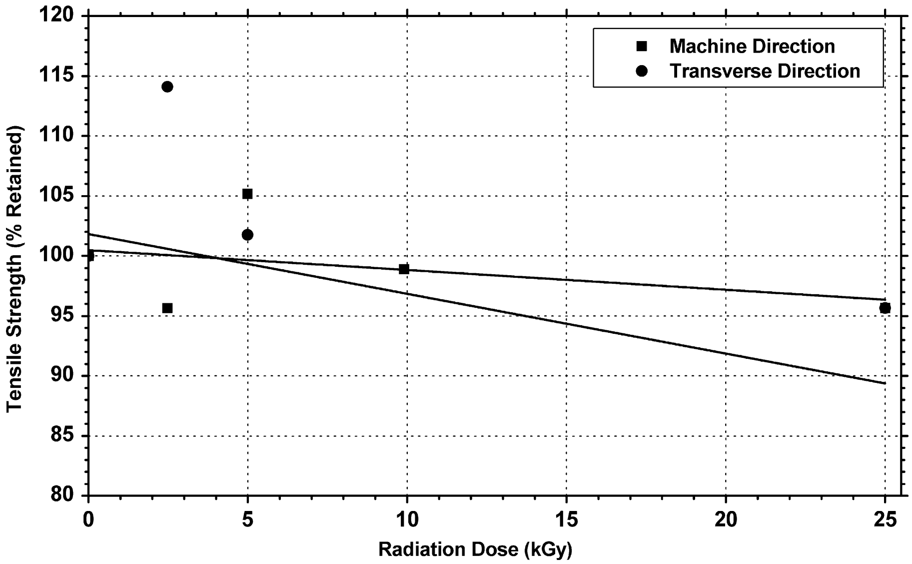


Figure 12.10 The effect of gamma irradiation dose on the retention of tensile strength of Melitta Haushaltsprodukte GmbH & Co KG SWIRL PLA film.[5]

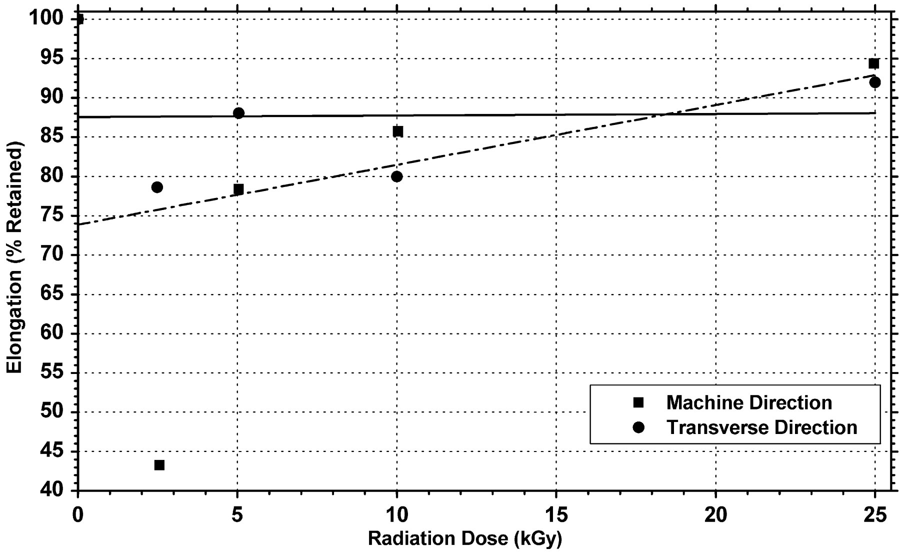


Figure 12.11 The effect of gamma irradiation dose on the retention of elongation of Pro-Tech Biologische und Technische Produkte GmbH BioMat PLA film.[5]

Applications and uses: Biomedical applications, such as sutures, stents, dialysis media, and drug delivery devices. It is also being evaluated as a material for tissue engineering, loose-fill packaging, compost bags, food packaging, and disposable tableware. PLA can be in the form of fibers and nonwoven textiles; potential uses: upholstery, disposable garments, awnings, and feminine hygiene products.

Data for PLA plastics are found in Figs 12.9—12.16.

12.7 Poly-3-Hydroxybutyrate

Polyhydroxyalkanoates (PHAs) are naturally produced and include poly-3-hydroxybutyrate (PHB or PH3B), PHV, and polyhydroxyhexanoate; a PHA copolymer called PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) is less stiff and tougher, and it may be used as packaging material. Chemical structures of some of these polymers are shown in Fig. 12.17.

Articles made of PHB thermoplasts retain their original shape at 121 °C or 132 °C. Because of this, perishable goods can be canned into packages produced of Biomer resins and preserved by steam sterilization.

Manufacturers and trade names: FKur Bio-Flex®, Cereplast Inc. Compostables®, Mitsubishi Chemical Fozeas®, NatureWorks LLC Ingeo™, Alcan Packaging Ceramis®-PLA, Metabolix/ADM

Figure 12.12 The effect of gamma irradiation dose on the retention of elongation of Melitta Haushaltsprodukte GmbH & Co KG SWIRL PLA film.[5]

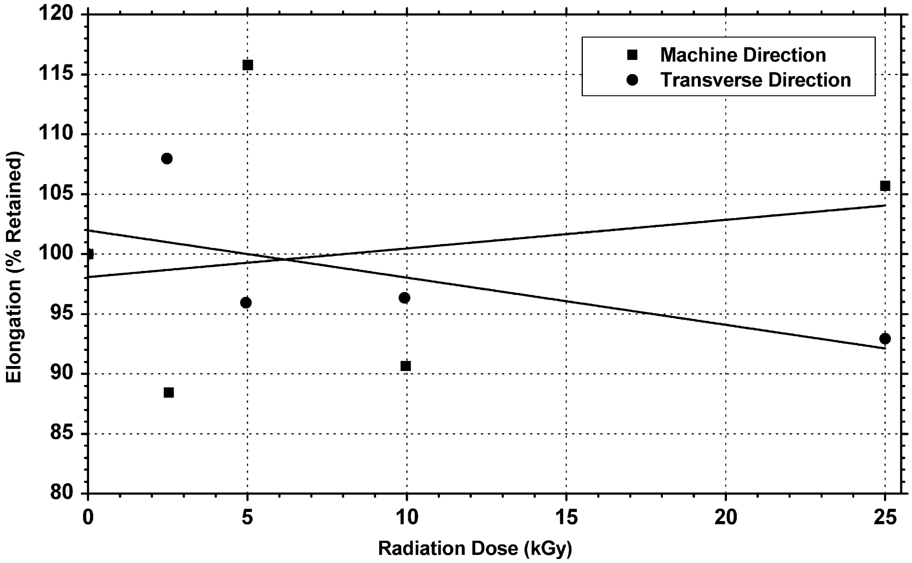


Figure 12.13 The effect of electron beam sterilization on the molecular weight of polylactic acid.[6]

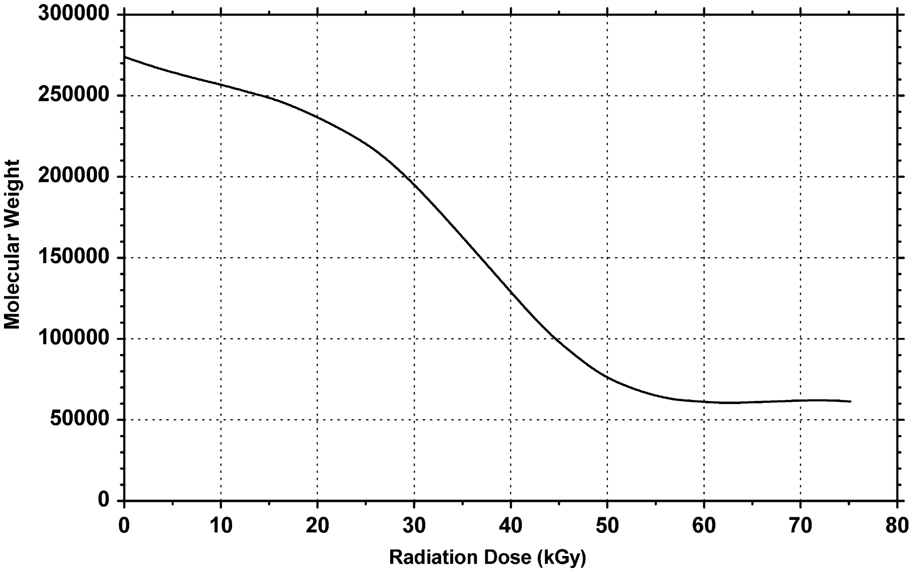
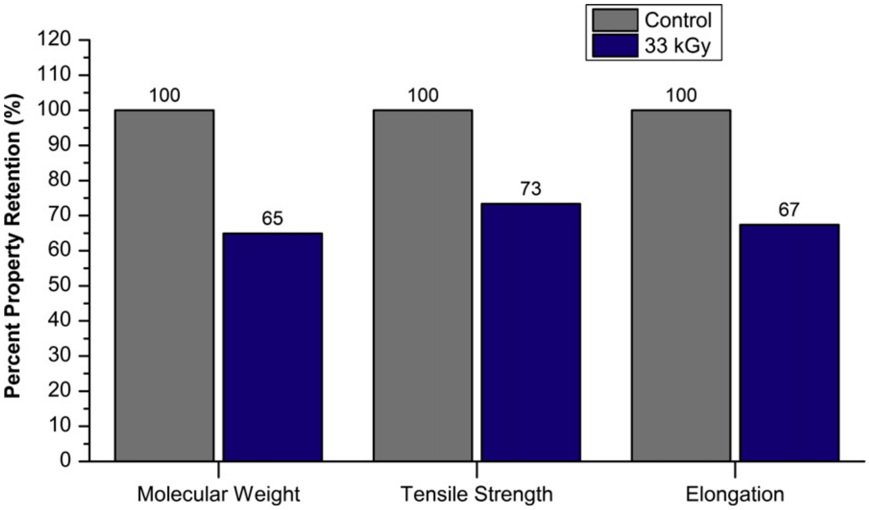


Figure 12.14 The effect of electron beam sterilization on the retention of several properties of polylactic acid.[6]



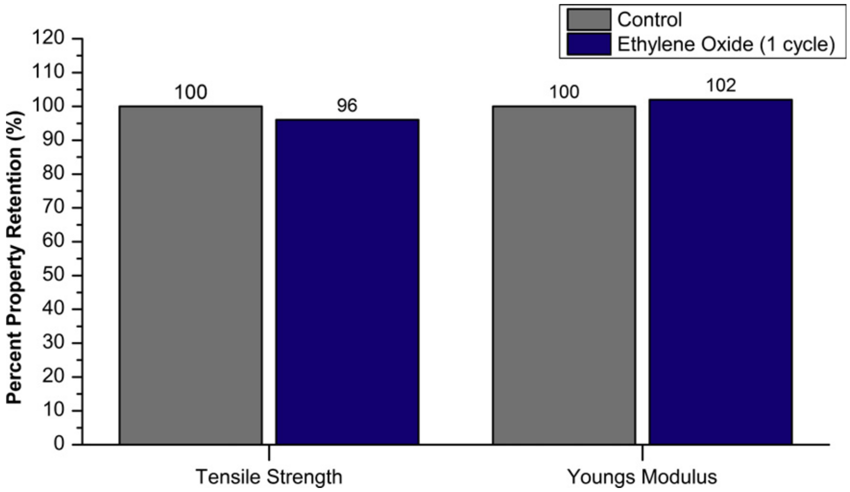


Figure 12.15 The effect of EtO sterilization on retention of several properties of poly L-lactic acid.

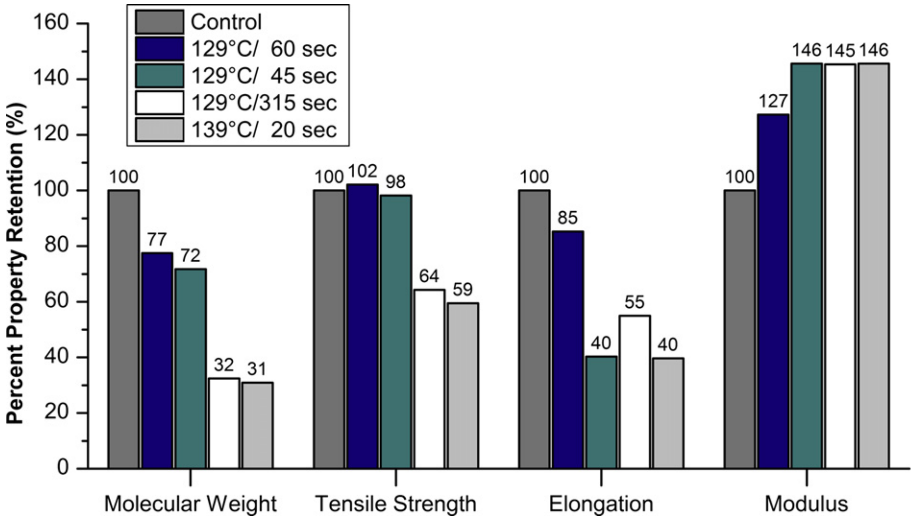


Figure 12.16 The effect of steam autoclave sterilization under various conditions on the retention of several properties of poly L-lactic acid.

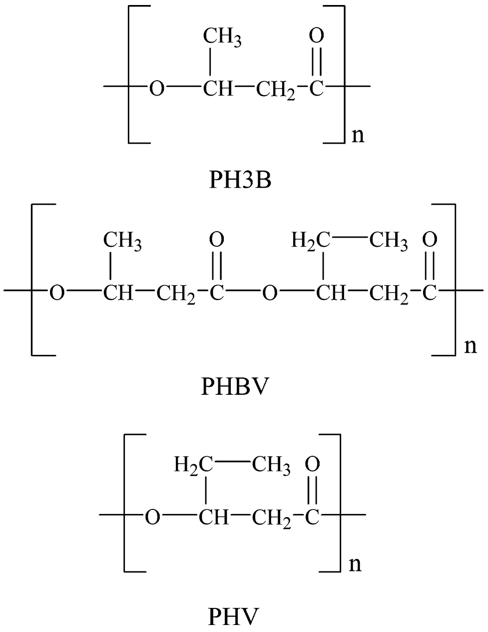


Figure 12.17 Structures of several polyhydroxyalkanoates.

Tirel, Tianan Enmat, Copersucar Biocycle, Biomer Biomer L, and Procter & Gamble Nodax.

Applications and uses: Biomedical applications, such as sutures, stents, dialysis media, and drug delivery devices. It is also being evaluated as a material for tissue engineering, loose-fill packaging, compost bags, food packaging, and disposable tableware. PLA can be in the form of fibers and nonwoven textiles; potential uses: upholstery, disposable garments, awnings, and feminine hygiene products.

Data for PHB plastics are found in Figs 12.18−12.20.

12.8 Polyglycolic Acid

Polyglycolic acid (PGA) and its copolymers have found limited use as absorbable sutures and are being evaluated in the biomedical field, where its rapid degradation is useful. That rapid degradation has

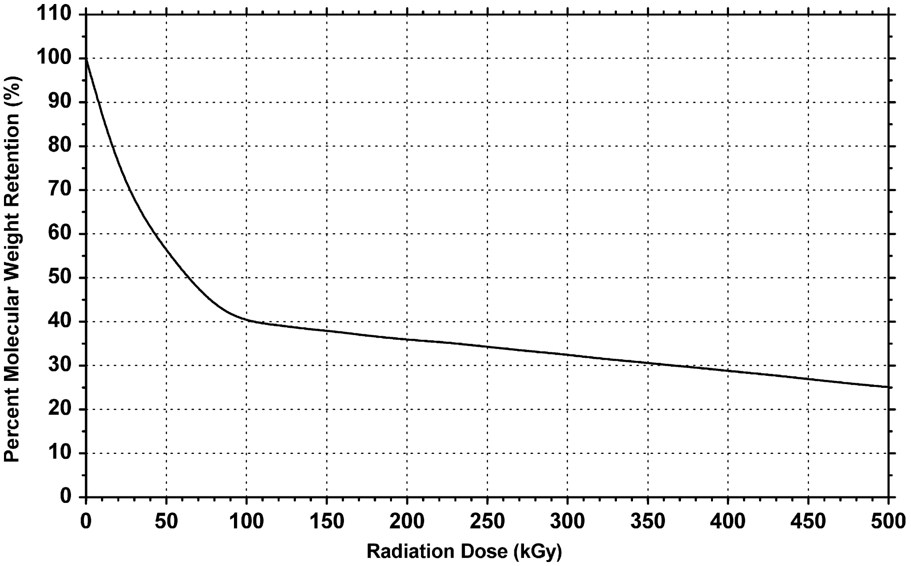


Figure 12.18 The effect of gamma irradiation on the retention of molecular weight of poly-3-hydroxybutyrate.

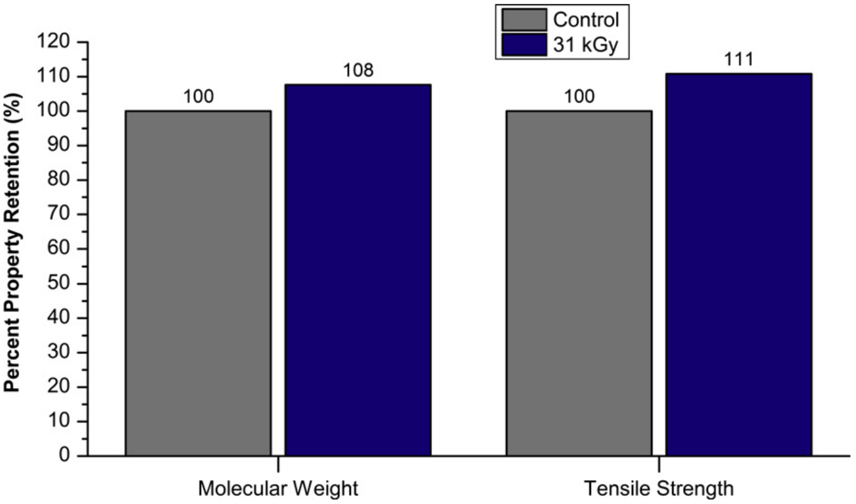


Figure 12.19 The effect of 31 kGy of gamma irradiation on the retention of molecular weight and tensile strength of poly-3-hydroxybutyrate.

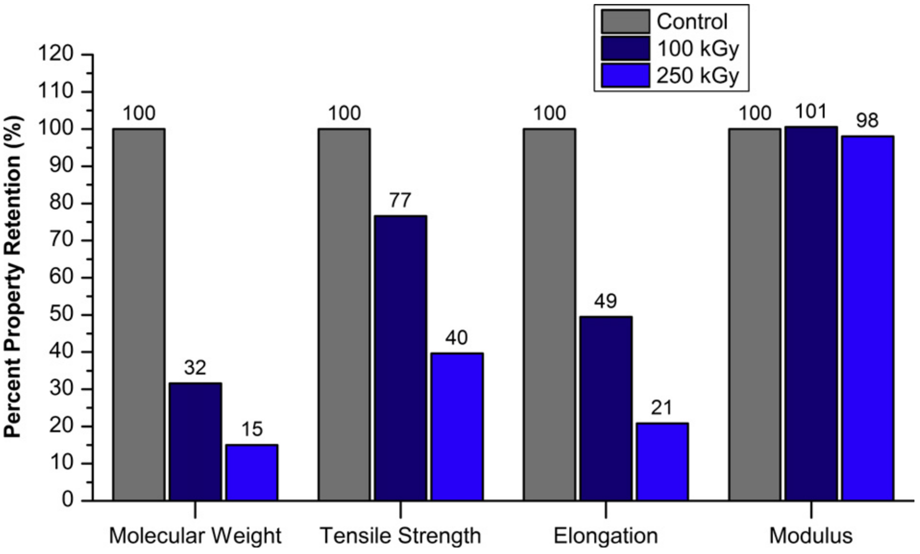


Figure 12.20 The effect of gamma irradiation on the retention of several properties of polyhydroxy butyrateehydroxy valerate.

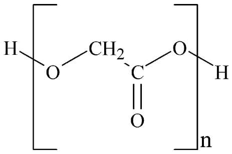


Figure 12.21 Polyglycolic acid chemical structures.

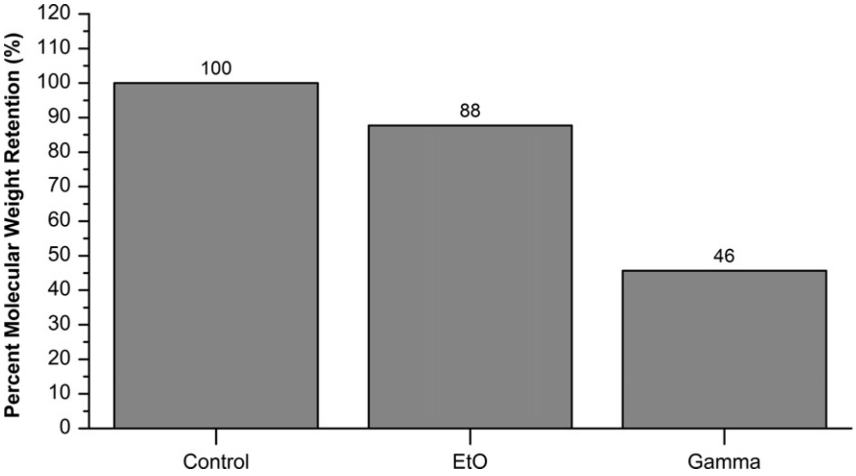


Figure 12.22 Effect of sterilization methods on the retention of molecular weight of Polyglycolic acid.

limited it use in other applications. The structure of polyglycolic acid is shown in Fig. 12.21

Data for PGA plastics are found in Fig. 12.22.

References

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13 Elastomers

An elastomer is a polymer with the property of "elasticity," generally having notably low Young's modulus and high yield strain compared with other materials.[1] The term is often used interchangeably with the term "rubber". Elastomers are amorphous polymers existing above their glass transition temperature, so that considerable segmental motion of the polymer chain is possible and therefore; it is expected that they would also be very permeable. At ambient temperatures, rubbers are thus relatively soft and deformable. Their primary uses are for seals, adhesives, and molded flexible parts. Elastomers may be thermosets (requiring vulcanization, a form of cross-linking) or thermoplastic, called thermoplastic elastomers (TPEs).

TPEs have two big advantages over the conventional thermoset (vulcanized) elastomers. Those are ease and speed of processing. Other advantages of TPEs are the ability to recycle scrap, lower energy costs for processing, and the availability of standard, uniform grades (not generally available in thermosets).

TPEs are molded or extruded on standard plastics-processing equipment in considerably shorter cycle times than those required for compression or transfer molding of conventional rubbers. They are made by copolymerizing two or more monomers, using either the block or graft polymerization techniques discussed in Chapter 2. One of the monomers provides the hard, or crystalline, polymer segment that functions as a thermally stable component; the other monomer develops the soft or amorphous segment, which contributes the elastomeric or rubbery characteristic. This is shown in Fig. 13.1 in which the hard crystalline parts of the molecule are the thick lined segments of the polymer chain. As shown, the hard segments can align together forming crystalline regions.

Physical and chemical properties can be controlled by varying the ratio of the monomers and the length of the hard and soft segments. Block techniques create long-chain molecules that have various or alternating hard and soft segments. Graft polymerization methods involve attaching one polymer chain to another as a branch. The properties that are affected by each phase can be generalized:

"Hard phase" – plastic properties:

1. Processing temperatures
2. Continuous use temperature
3. Tensile strength
4. Tear strength
5. Chemical and fluid resistance
6. Adhesion to inks, adhesives, and over-molding substrates.

"Soft phase" – elastomeric properties:

1. Lower service temperature limits
2. Hardness
3. Flexibility
4. Compression set and tensile set.

ISO 18064[2] sets a standard nomenclature system for TPEs. All have a prefix "TP" followed by a letter representing each category of TPEs.

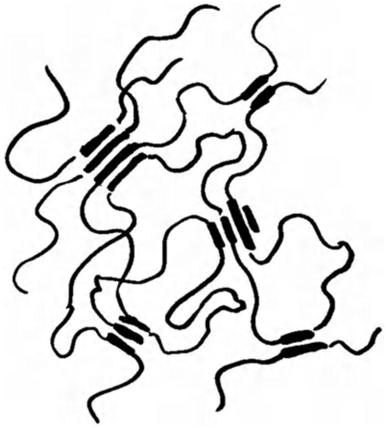


Figure 13.1 Schematic of the structure of a thermoplastic elastomer.

The Effect of Sterilization on Plastics and Elastomers. http://dx.doi.org/10.1016/B978-1-4557-2598-4.00013-7

The categories are outlined below:

1. TPA – Polyamide thermoplastic elastomer, comprising a block copolymer of alternating hard and soft segments with amide chemical linkages in the hard blocks and ether and/or ester linkages in the soft blocks.
2. TPC – Copolyester thermoplastic elastomer, consisting of a block copolymer of alternating hard segments and soft segments, the chemical linkages in the main chain being ester and/or ether.
3. TPO – Olefinic thermoplastic elastomer, consisting of a blend of a polyolefin and a conventional rubber, the rubber phase in the blend having little or no cross-linking.
4. TPS – Styrenic thermoplastic elastomer, consisting of at least a triblock copolymer of styrene and a specific diene, where the two end blocks (hard blocks) are polystyrene and the internal block (soft block or blocks) is a polydiene or hydrogenated polydiene.
5. TPU – Urethane thermoplastic elastomer, consisting of a block copolymer of alternating hard and soft segments with urethane chemical linkages in the hard blocks and ether, ester or carbonate linkages, or mixtures of them in the soft blocks.
6. TPV – Thermoplastic rubber vulcanizate, consisting of a blend of a thermoplastic material and a conventional rubber in which the rubber has been cross-linked by the process of dynamic vulcanization during the blending and mixing step.
7. TPZ – Unclassified thermoplastic elastomer, comprising any composition or structure other than those grouped in TPA, TPC, TPO, TPS, TPU, and TPV.

Not all these categories are discussed in this chapter.

Each of the general types can be further classified into sub types. The abbreviated term of each category of TPEs is followed, after a hyphen, by a combination of symbols to describe a specific member of each category. Some of these details are mentioned in the sections on the appropriate materials.

Cross-linked silicones, which are thermosets, are also discussed in this chapter.

13.1 Thermoplastic Polyether Block Polyamide Elastomers (TPA-ET or PEBA)

One type of polyamide thermoplastic elastomer (TPA) is a block copolymer with polyether soft segments and the hard segment is the polyamide (Nylon). This is called TPA-ET by ISO 18064. These TPAs are typically plasticizer-free TPEs.[3] For example, Arkema PEBAX® 33 series products are based on Nylon 12 (see Section 7.3) and polytetramethylene glycol segments. They are easy to process by injection molding and profile or film extrusion. Often they can be easily melt blended with other polymers, and many compounders will provide custom products by doing this. Their chemistry allows them to achieve a wide range of physical and mechanical properties by varying the monomeric block types and ratios. Their characteristics include:

- Light weight
- Great flexibility (extensive range)
- Resiliency
- Very good dynamic properties
- High strength
- Outstanding impact resistance properties at low temperature
- Easy processing
- Good resistance to most chemicals.

Manufacturers and trade names: Arkema PEBAX® and EMS-Grivory Grilflex®.

Sterile applications and uses: Medical/surgical garments and sheeting.

PEBAX® can be sterilized by ethylene oxide process, steam, and gamma radiation (up to 10 Mrad).[4]

13.2 Thermoplastic Copolyester Elastomers (TPC-E or COPE)

Thermoplastic copolyester elastomers (TPC) are block copolymers.[5] When the soft segment is a polyether block, this is TPC-ET. The chemical structure of one such elastomer is shown in Fig. 13.2. The soft

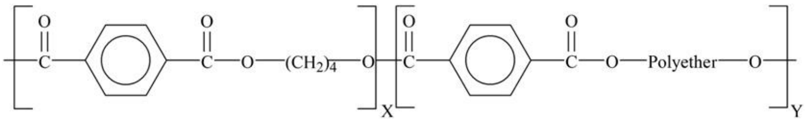


Figure 13.2 Molecular structure of Ticona Riteflex® thermoplastic copolyester elastomers.

blocks may also be polyester (TPC-ES) or mixed polyester and ether (TPC-EE).

These TPEs are generally tougher over a broader temperature range than the urethanes described in Section 13.5. Also, they are easier and more forgiving in processing. They have the following properties:

- Excellent abrasion resistance
- High tensile, compressive, and tear strength
- Good flexibility over a wide range of temperatures
- Good hydrolytic stability
- Resistance to solvents and fungus attack
- Selection of a wide range of hardness.

In these polyester TPCs, the hard polyester segments can crystallize, giving the polymer some of the attributes of semicrystalline thermoplastics, most particularly better solvent resistance than ordinary rubbers, but also better heat resistance. Above the melting temperature of the crystalline regions, these TPCs can have low viscosity and can be molded easily in thin sections and complex structures. Properties of thermoplastic polyester elastomers can be fine-tuned over a range by altering the ratio of hard to soft segments.

In DuPont Hytrel® polyester TPEs, the resin is a block copolymer. The hard phase is polybutylene terephthalate. The soft segments are long-chain polyether glycols.

Manufacturers and trade names: Ticona Riteflex®, DuPont™ Hytrel®, Eastman Ecdel®, and DSM Engineering Plastics Arnitel®.

Sterile applications: Tubing, and flexible medical and pharmaceutical packaging.

Sterilization resistance: Ecdel® elastomers may be autoclave, gamma irradiation, ethylene oxide (EtO), or electron beam (e-beam) sterilized.[6]

Gamma radiation resistance: Injection molded slabs of Hytrel® 4056, Hytrel® 5556, and Hytrel® 7246, 2 mm (0.079 in) thick, were exposed to a 1.5 MeV e-beam in air at 23 °C. The slabs were tested by *ASTM* International, known until 2001 as the *American Society for Testing and Materials (ASTM)*, methods. Exposure to 150 kJ/kg (15 Mrad) produces very little change in the properties of Hytrel®.[7]

Ecdel® elastomer film, when exposed to increasing levels of gamma radiation, experiences a decrease in inherent viscosity and a substantial reduction in tear strength.[6]

Ethylene oxide (EtO) resistance: Ethylene oxide sterilization methods have no significant effect on the properties of Ecdel elastomer films.[6]

Autoclave resistance (steam): Autoclave sterilization methods have no significant effect on the properties of Ecdel elastomer films.[6]

Data for TPCs are found in Tables 13.1–13.4.

Tables 13.1 Effect of Gamma Radiation on Eastman Ecdel® Elastomer 9966[8]

Exposure Conditions				
Gamma dose (Mrad)	1.5	3.0	4.5	
Properties	**% Change**			**Test Method**
Film Inherent Viscosity	−5	−18	−20	
Total extractables	45	215	515	
Tensile stress at yield	4	12	20	ASTM D882
Tensile stress at break	11	3	−2	ASTM D882
Tensile modulus (MPa)	−51	−43	−40	ASTM D882
Tear Strength	−2	−26	−61	ASTM D1004

Table 13.2 Effect of Gamma Radiation on Eastman Ecdel® Elastomer 9966[9]

Exposure Conditions				
Radiation dose (Mrad)	1.5	3	4.5	
Properties	**% Change**			**Test Method**
Tensile strength	84.7	82.3	80.1	ASTM D882
Tensile strength at yield	105.1	112.4	124.8	ASTM D882
Elongation	111.5	102.9	97.6	ASTM D882
Modulus	94.4	111.1	116.7	ASTM D882
Tear resistance	98.6	74.5	39	ASTM D1822

13.3 Olefinic Thermoplastic Elastomers (TPO)

Polyolefin thermoplastic elastomer (TPO) materials are defined as compounds (mixtures) of various polyolefin polymers, semicrystalline thermoplastics, and amorphous elastomers. Most TPOs are composed of polypropylene (PP) and a copolymer of ethylene and propylene called ethylene−propylene rubber.[10] A common rubber of this type is called ethylene propylene diene monomer rubber (EPDM), which has a small amount of a third monomer, a diene (two carbon−carbon double bonds in it). The diene monomer leaves a small amount of unsaturation in the polymer chain that can be used for sulfur cross-linking. The ISO 18064 nomenclature of TPOs is identified by a bracketed term comprising the standard abbreviation for the rubber type (see ISO 1629), a "+" sign, and the standard abbreviation for the thermoplastic type (per ISO 1043-1). The thermoplastic and the rubber type are listed in decreasing order of abundance in the TPO. In the TPO example described above, TPO-(EPDM+PP) could be the name for a blend of ethylene−propylene−diene terpolymer with PP, with no or little cross-linking of the EPDM phase, the amount of EPDM present being greater than that of PP.

Like most TPEs, TPO products are composed of hard and soft segments. TPO compounds include fillers, reinforcements, lubricants, heat stabilizers, antioxidants, ultraviolet (UV) stabilizers, colorants, and processing aids. They are characterized by high impact strength, low density, and good chemical resistance; they are used when durability and reliability are primary concerns.

Manufacturers and trade names: ExxonMobil Chemical (formerly Advanced Elastomer Systems) Santoprene®, LyondellBasell Advanced Polyolefins Dexflex®, RTP 2800 Series.

Applications and uses: Capping distilled water, dairy products, fruit juices, sports drinks, beer, wine, and food, cosmetics, toiletries, and pharmaceutical packaging, sterilized closures, seals, and liners, syringe plungers, gaskets, and grips and bumpers.

Sterilization resistance: TPOs, in general, are resistant to radiation at normal sterilizing doses (may cross-link with commensurate reduction in elongation), autoclaving (121 °C, 15 psi for 20 min), and ethylene oxide gas sterilization. Dry heat is not recommended.[11,12]

Devices and products made from medical grades of Santoprene® rubber can be sterilized effectively using steam autoclaving, gamma radiation, and ethylene oxide with no loss of performance. Repeated sterilizations neither lead to any significant changes in hardness and tensile stress−strain properties nor to toxicity development during subsequent storage.[13]

Gamma radiation resistance: Radiation resistance, optical properties, hardness, and compression set varies with chemistries.[12] Medical grades of Santoprene® can be exposed to up to 4 Mrad of Cobalt-60 gamma radiation with only minimal change in physical properties and no development of toxicity during subsequent storage of the irradiated rubber. The irradiation appears to cause significant, but tolerable, losses of tensile strength and ultimate elongation. The aging after irradiation results in no further loss up to a period of 1 year.[14]

Table 13.3 Effect of Electron Beam Radiation Sterilization on DuPont Hytrel® Elastomers[7]

Material Supplier/ Name	**Hytrel® 4056**			**Hytrel® 5556**			**Hytrel® 7246**			
Shore D hardness	40			55			72			
Exposure Conditions										
Radiation dose (Mrad)	5	10	15	5	10	15	5	10	15	
Properties Retained (%)										**Test Method**
Tensile strength	94.6	94.6	91.7	104	106.3	111.4	102.5	104.8	108.1	ASTM D638
Elongation	92.7	90.9	89.1	120.5	120.5	125.6	95.3	86	90.7	ASTM D638
Modulus	107.4	91.2	89.7	100.7	100.7	98.6	107.3	108.6	111.8	ASTM D638
Surface and Appearance										
Hardness units change	D0	D0	D0	D0	D0	D0	D0	D0	D0	ASTM D638

Note: Note 1.5 MeV electron beam; RH: 70%; 23 °C.

Table 13.4 Effect of Thermal Sterilization on Eastman Ecdel® Elastomer 9966 Film[6]

Exposure Conditions				
Temperature (°C)	125	160	121	
MPa	–	–	0.10	
Time	15 min	15 min	1 h	
Properties % Change				**Test Method**
Tensile strength at break, MD	10	3	13	ASTM D882
Tensile strength at break, TD	4	4	14	ASTM D882
Tensile modulus (MPa), MD	−23	−33	−20	ASTM D882
Tensile modulus (MPa), TD	−23	−24	−10	ASTM D882
Elongation at break, MD	0	−20	6	ASTM D882
Elongation at break, TD	0	8	5	ASTM D882
Tear strength, MD	15	40	13	ASTM D1004
Tear strength, TD	0	−30	10	ASTM D1004

Note: MD-Machine direction; TD-transverse direction

The agarose overlay method was used to determine the cytotoxicity of the irradiated and subsequently stored specimens. No significant toxicity developed at exposures of 4.2 Mrad and lower, and only slight toxicity developed at 5.3 Mrad.[14]

Ethylene oxide (EtO) resistance: Five standard hospital EtO sterilization cycles give no significant loss in hardness or tensile stress–strain properties for both 73 Shore A and 40 Shore D grades. Immediately after sterilization, samples sterilized with EtO had residual amounts of 0.03–0.06% and samples sterilized with ethylene chlorohydrin and ethylene glycol had residual amounts of 0.02–0.03%. The residual amounts virtually disappeared after 31 days.[14]

Steam resistance: Test specimens were evaluated for changes in hardness, tensile stress–strain properties, and swell after exposures of 10, 25, 50, 75, and 100 cycles. The changes in tensile properties are quite minor, insignificant, and well within accepted ASTM D2000 limits. The hardness changes are only

Table 13.5 Properties after Gamma Sterilization of RTP 2800 Series TPOs[15]

Material	Sterilization Level kGy	Tensile Strength (MPa)	Tensile Modulus at 100% (MPa)	Tear (pli)	Shore A Hardness	Yellowness Index
RTP 2800 B-85A	Control	9.4	6.0	263	88	14.03
	25.0–26.1	8.4	5.8	239	86	19.13
	50.8–54.4	7.7	5.7	233	84	19.54
	75.1–76.8	6.9	5.5	218	87	20.42
RTP 2800 B-45A	Control	4.1	1.70	97	54	18.48
	25.0–26.1	3.6	1.59	95	52	21.32
	50.8–54.4	3.2	1.53	84	52	20.61
	75.1–76.8	2.9	1.34	79	51	21.78

marginally significant, but within accepted ASTM limits. The weight change does not significantly change properties.[14]

Regulatory status: Santoprene® medical grades have USP Class VI Certificate of Compliance for biocompatibility. Santoprene®281 grades are certified nontoxic by minimum essential medium (MEM) elution test.

Data for olefinic thermoplastic elastomers are found in Tables 13.5−13.8 and Figs 13.3−13.16.

13.4 Styrenic Block Copolymer Thermoplastic Elastomers (TPS)

Styrenic block copolymer thermoplastic elastomers are multiphase compositions in which the phases are chemically bonded by block copolymerization (see Section 2.2). There are at least three blocks of which two of the phases are hard styrenic polymer segments. The styrenic phases may become fluid when the composition is heated. Another phase is a softer elastomeric material that is rubber like at room temperature. The polystyrene blocks act as cross-links, tying the elastomeric chains together in a three-dimensional network. Styrenic block copolymer TPEs have no commercial applications when the product is just a pure polymer. They must be compounded with other polymers, oils, fillers, and additives to have any commercial value.

According to ISO 18064, the following additional symbols are used for the TPS group:

1. TPS-SBS: Block copolymer of styrene and butadiene
2. TPS-SEBS: Polystyrene-poly(ethylene−butylene)-polystyrene

Table 13.6 Residuals after Ethylene Oxide Sterilization and Aging in ExxonMobil Chemical Santoprene® Olefinic Thermoplastic Elastomers[16]

	EtO (mg/day)		ECH (mg/day)	
Material	**1 Day**	**4 Days**	**1 Day**	**4 Days**
Allowable limit per ISO 10993-7	20	20	12	12
Santoprene™ TPV 181-57W180	<0.18	<0.18	1.554	1.26
Santoprene TPV 281-45MED	0.32	<0.18	3.91	1.48
Santoprene TPV 281-64MED	0.40	<0.18	4.17	1.78
Santoprene TPV 281-87MED	0.35	<0.18	4.13	0.96

Note: ECH, ethylene chlorohydrin; <0.18 means actual values are below detectable levels.

Table 13.7 Effect of Steam Sterilization on Santoprene® 281-45 and 281-55 Olefinic Thermoplastic Elastomers[14]

Material Supplier/ Name	**Santoprene® 281-45**					**Santoprene® 281-55**				
Exposure Conditions										
Number of cycles	10	25	50	75	100	10	25	50	75	100
Properties Retained (%)										
Ultimate Tensile Strength	91	68	93	95	91	86	85	84	92	91
Ultimate Elongation	103	77	103	101	96	86	81	81	78	80
100% Modulus	88	86	89	95	94	92	95	93	104	99
Surface and Appearance										
Hardness units change	A1	A1	A1	A2	A2	A2	A1	A4	A4	A4

Note: Live steam cycle, 5-min rise, 5 min at 134 °C, 5-min cool.

Table 13.8 Effect of Steam Sterilization on ExxonMobil Chemical Santoprene® 283-40 Olefinic Thermoplastic Elastomer[14]

Exposure Conditions					
Number of cycles	10	25	50	75	100
Properties Retained (%)					
Ultimate tensile strength	96	96	95	98	95
Ultimate elongation	98	96	94	86	82
100% Modulus	105	106	106	116	120
Surface and Appearance					
Hardness units change	D2	D1	D0	D2	D1

Note: Live steam cycle, 5-min rise, 5 min at 134 °C, 5-min cool.

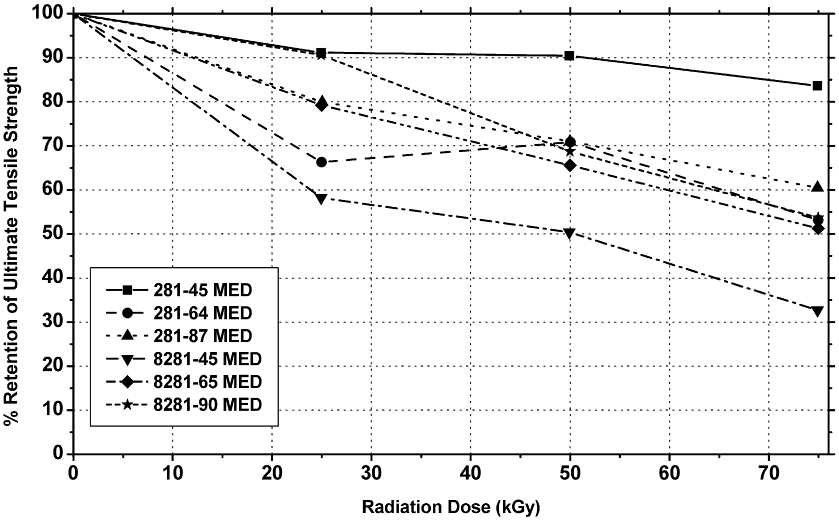


Figure 13.3 Retention of ultimate tensile strength versus gamma exposure of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers.[16]

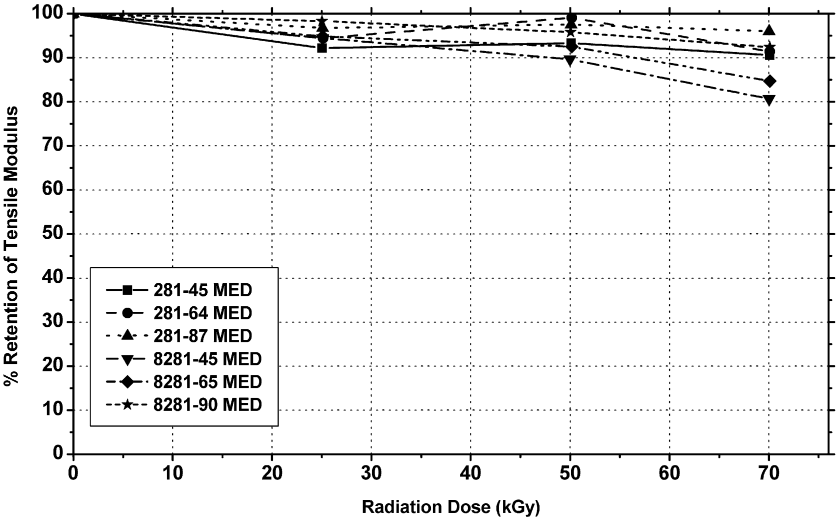


Figure 13.4 Retention of tensile modulus versus gamma exposure of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers.[16]

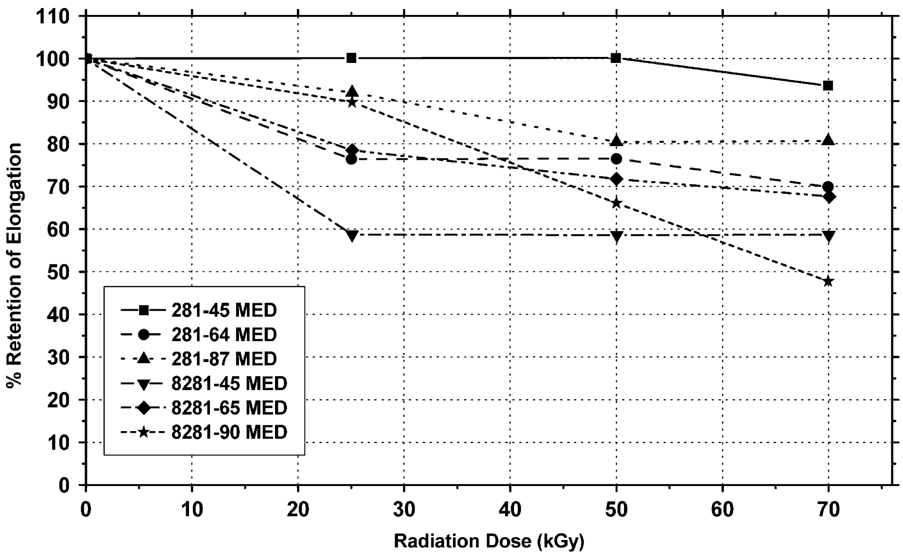


Figure 13.5 Retention of elongation versus gamma exposure of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers.[16]

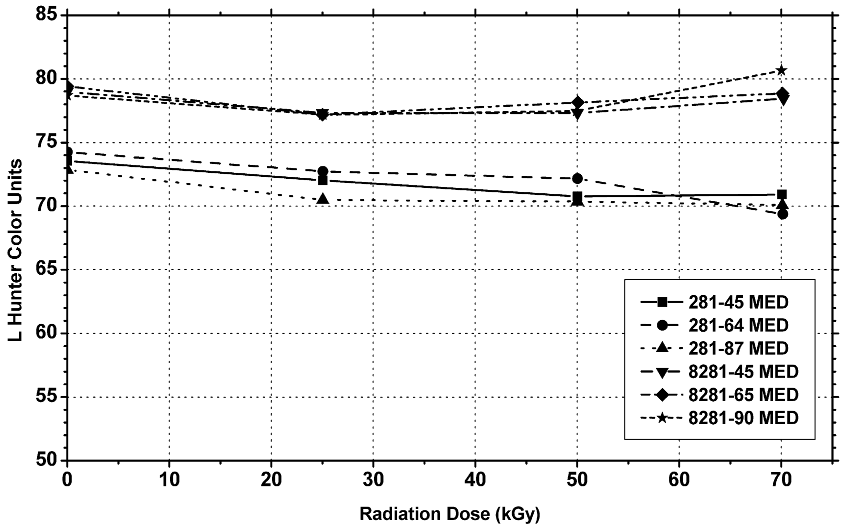


Figure 13.6 Color *L* versus gamma exposure of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers.[16]

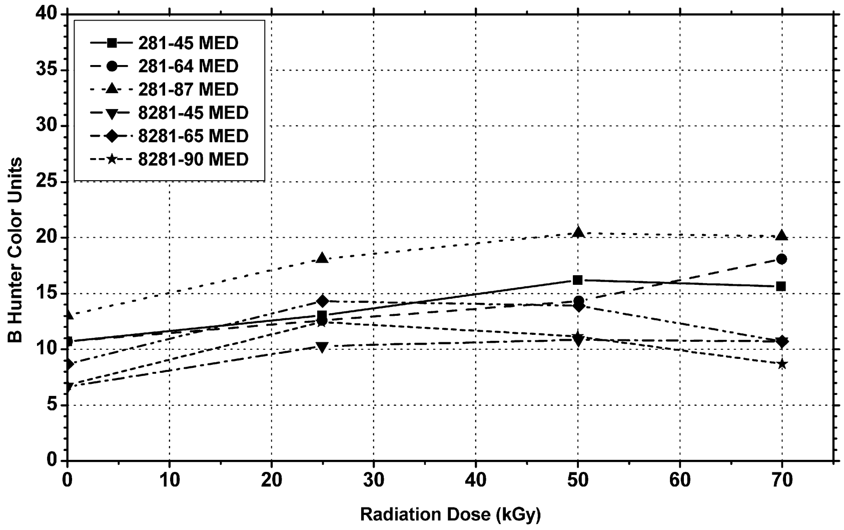


Figure 13.7 Color *B* versus gamma exposure of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers.[16]

Figure 13.8 Percent compression set after 168 h at 100 °C versus gamma exposure of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers.[16]

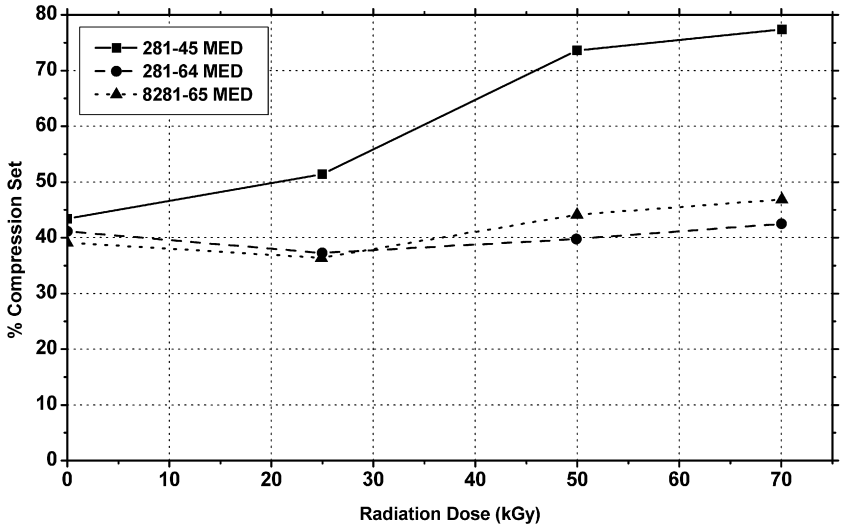


Figure 13.9 Retention of ultimate tensile strength of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers after five autoclave cycles.[16]

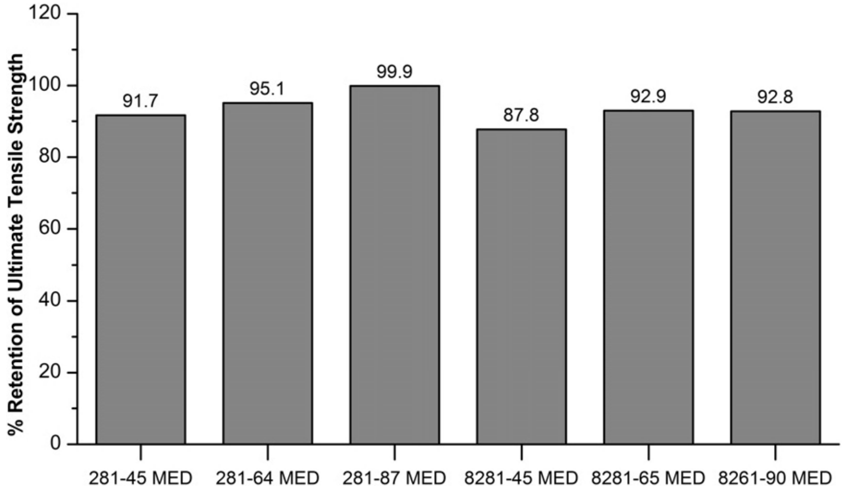
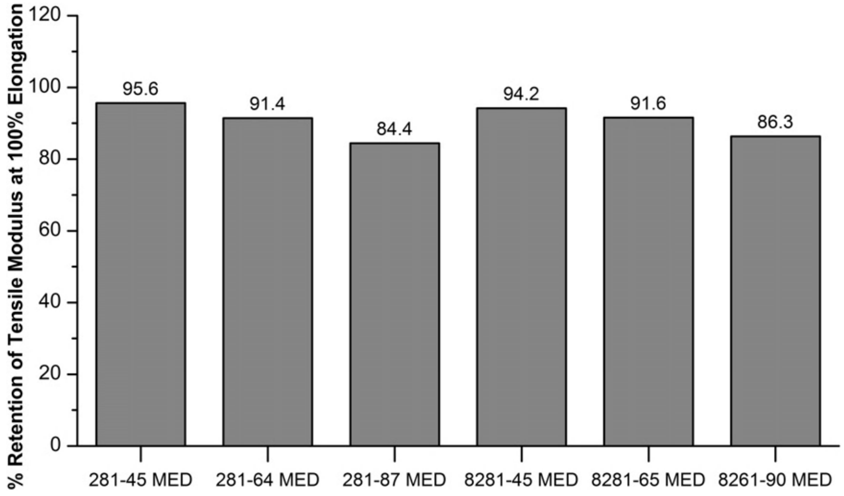


Figure 13.10 Retention of tensile modulus of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers after five autoclave cycles.[16]



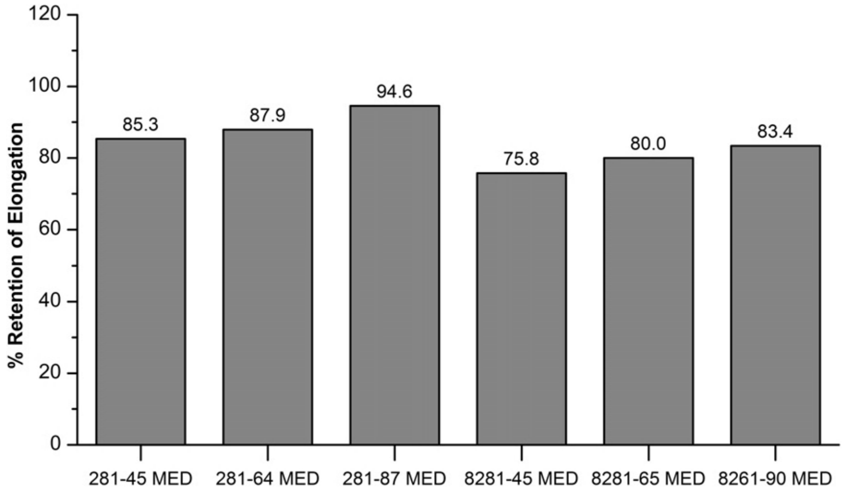


Figure 13.11 Retention of elongation of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers after five autoclave cycles.[16]

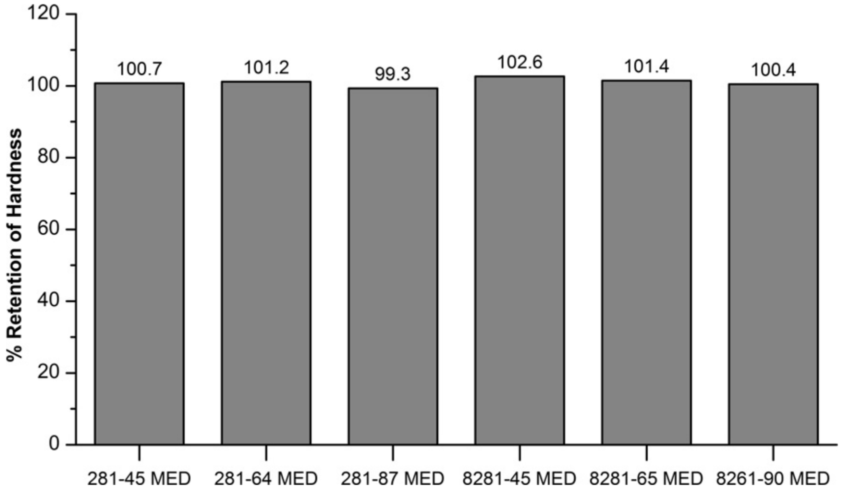


Figure 13.12 Retention of hardness of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers after five autoclave cycles.[16]

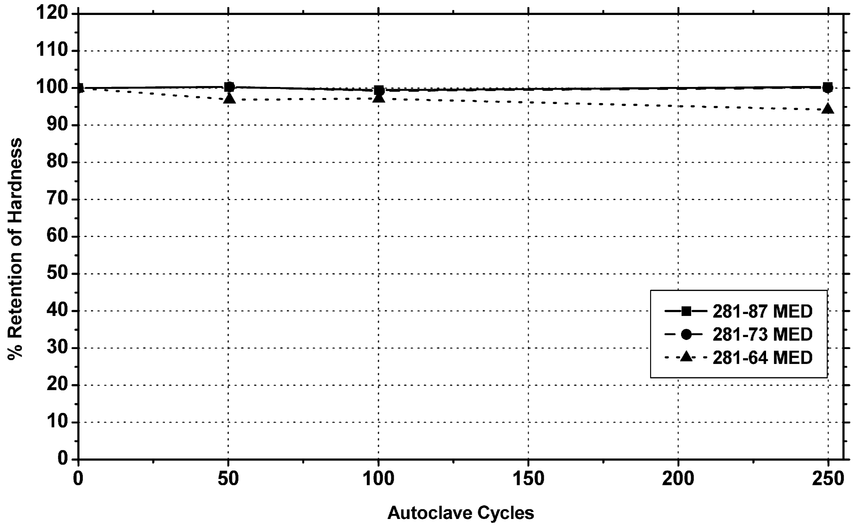


Figure 13.13 Retention of hardness versus autoclave cycles of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers.[16]

Figure 13.14 Retention of ultimate tensile strength versus autoclave cycles of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers.[16]

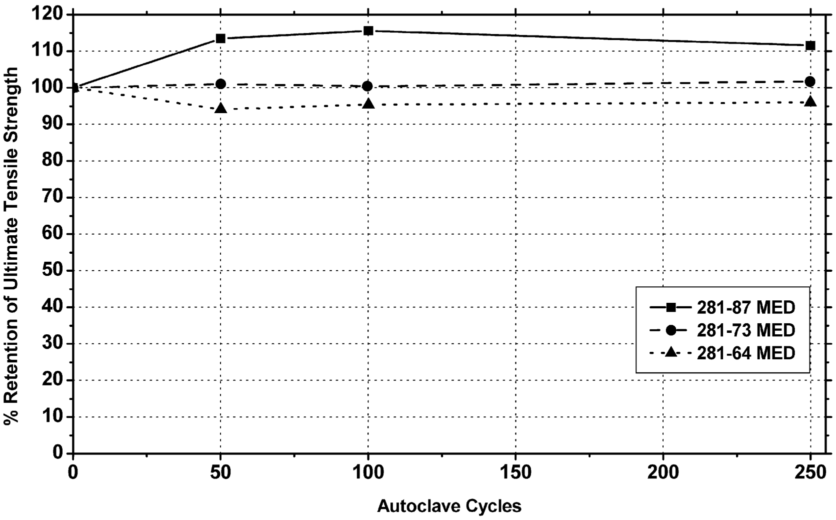


Figure 13.15 Retention of tensile modulus versus autoclave cycles of ExxonMobil Chemical Santoprene® 281-87MED Olefinic Thermoplastic Elastomer.[16] Note: 281-64 MED and 281-73 MED failed 100% elongation after 50 cycles.

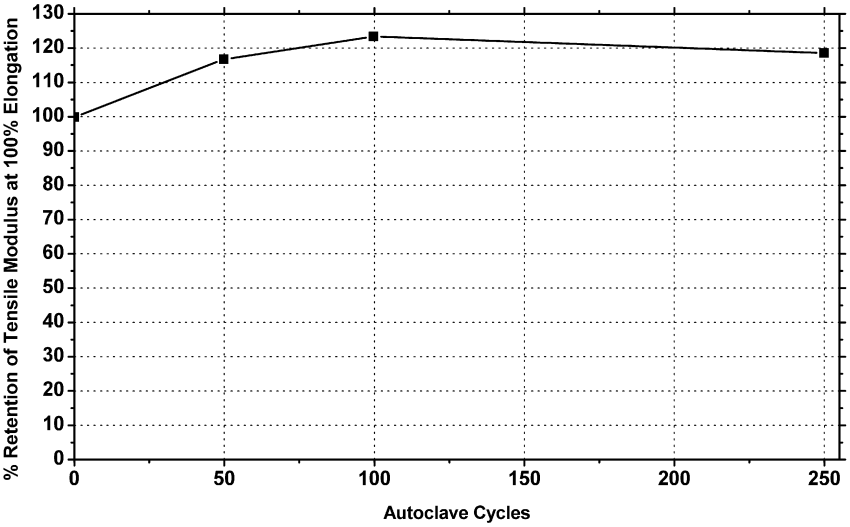
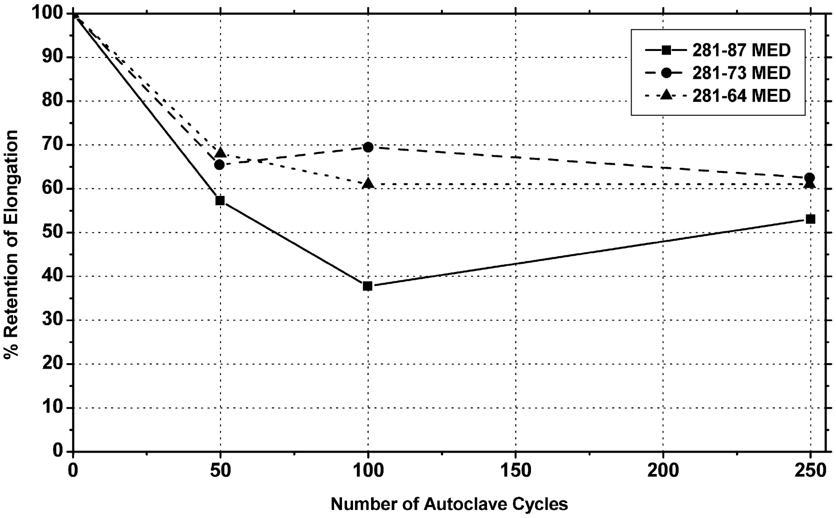


Figure 13.16 Retention of elongation versus autoclave cycles of ExxonMobil Chemical Santoprene® olefinic thermoplastic elastomers.[16]



3. TPS-SEPS: Polystyrene-poly(ethylene−propylene)-polystyrene
4. TPS-SIS: Block copolymer of styrene and isoprene.

Manufacturers and trade names: BASF Styrolux®, RTP 2700 Series.

Sterile applications and uses: Primarily food packaging, packed fruit and vegetables, fresh pasta and cheese, as thermoformed cups and lids, and also in applications including shrink film, must stay fresh as long as possible. Styrolux® co-extruded with other thermoplastics provides transparent barrier-layer composites.

Sterilizability: Styrolux® can be sterilized either with high-energy radiation (gamma or beta radiation) or with ethylene oxide (EtO). Styrolux® retains most of its mechanical properties during this process.[17]

Data for styrenic block copolymer thermoplastic elastomers are found in Tables 13.9−13.15.

13.5 Thermoplastic Polyurethane Elastomers (TPU)

Urethanes are a reaction product of a diisocyanate and long- and short-chain polyether, polyester, or caprolactone glycols.[19] The polyols and the short-chain diols react with the diisocyanates to form linear polyurethane molecules. This combination of diisocyanate and short-chain diol produces the rigid or hard segment. The polyols form the flexible or soft

Table 13.9 Properties after Gamma Sterilization of RTP 2700 Series TPS-SBS[15]

Material	Sterilization Level (kGy)	Tensile Strength (MPa)	Tensile Modulus at 100% (MPa)	Tear (pli)	Shore A Hardness	Yellowness Index
RTP 2700 S-70A	Control	9.6	2.62	223	71	6.84
	25.0−26.1	9.8	2.57	218	71	10.66
	50.8−54.4	8.5	2.56	213	68	12.35
	75.1−76.8	8.4	2.45	208	69	11.86
RTP 2700 S-30A	Control	5.3	0.68	114	34	7.44
	25.0−26.1	6.3	0.66	103	31	10.40
	50.8−54.4	6.3	0.65	113	28	10.83
	75.1−76.8	6.4	0.59	120	28	11.63

Note: Mediprene® 500200 M = Shore Hardness 20 A; Mediprene® 500600 M = Shore Hardness 60 A; Mediprene® 500900 M = Shore Hardness 90 A.

Table 13.10 The Effect of Gamma Sterilization at 25 kGy Radiation Dose on Elasto Mediprene® SBS[18]

Mediprene® Grade	Hardness Change Shore A	Tensile Strength Change %	Elongation at Break Change %	Modulus 100% Change %	Modulus 300% Change %	Yellowness Index Change
Test method	ASTM D2240 (4 mm)	ASTM D638	ASTM D638	ASTM D638	ASTM D638	ASTM D1925
500200 M	−1.5	+29	+56	−17	−15	+5.5
500600 M	0	+10	+24	−10	−9	+6.5
500900 M	0	−11	−2	−5	−5	+10

Note: Mediprene® 500200 M = Shore Hardness 20 A; Mediprene® 500600 M = Shore Hardness 60 A; Mediprene® 500900 M = Shore Hardness 90 A.

Table 13.11 The Effect of Gamma Sterilization at 50 kGy Radiation Dose on Elasto Mediprene® SBS[18]

Mediprene® Grade	Hardness Change Shore A	Tensile Strength Change %	Elongation at Break Change %	Modulus 100% Change %	Modulus 300% Change %	Yellowness Index Change
Test method	ASTM D2240 (4 mm)	ASTM D638	ASTM D638	ASTM D638	ASTM D638	ASTM D1925
500200 M	−3	+58	+98	−25	−25	+9
500600 M	−1.5	+10	+30	−14	−12	+10
500900 M	+0.5	−17	−5	−7	−8	+13

Note: Mediprene® 500200 M = Shore Hardness 20 A; Mediprene® 500600 M = Shore Hardness 60 A; Mediprene® 500900 M = Shore Hardness 90 A.

Table 13.12 The Effect of Ethylene Oxide Sterilization on Elasto Mediprene® SBS[18]

Mediprene® Grade	Hardness Change Shore A	Tensile Strength Change %	Elongation at Break Change %	Modulus 100% Change %	Modulus 300% Change %	Yellowness Index Change
Test method	ASTM D2240 (4 mm)	ASTM D638	ASTM D638	ASTM D638	ASTM D638	ASTM D1925
500200 M	0	+2	+1	+3	+2	+1.5
500600 M	+1	−4	−9	+7	+4	+1.5
500900 M	+0.5	−3	−8	+7	+4	+2

Note: Mediprene® 500200 M = Shore Hardness 20 A; Mediprene® 500600 M = Shore Hardness 60 A; Mediprene® 500900 M = Shore Hardness 90 A.

Table 13.13 The Effect of Steam (autoclave) Sterilization on Elasto Mediprene® 500200 M (Shore Hardness 20 A)[18]

Cycles	Hardness Change Shore A	Tensile Strength Change %	Elongation at Break Change %	Modulus 100% Change %	Modulus 300% Change %
Test method	ASTM D2240 (4 mm)	ASTM D638	ASTM D638	ASTM D638	ASTM D638
1	−0.5	−10	+13	−18	−19
10	−1.5	−2	+31	−20	−23
25	−1.5	−7	+29	−23	−27
50	−2	−1	+40	−22	−27

segment of the final molecule. Figure 13.17 shows the molecular structure in schematic form.

According to ISO 18064, the following more specific symbols may be used:

1. TPU-ARES: Aromatic hard segment, polyester soft segment
2. TPU-ARET: Aromatic hard segment, polyether soft segment
3. TPU-AREE: Aromatic hard segment, soft segment with ester and ether linkages
4. TPU-ARCE: Aromatic hard segment, polycarbonate soft segment

Table 13.14 The Effect of Steam (autoclave) Sterilization on Elasto Mediprene® 500600 M (Shore Hardness 60 A)[18]

Cycles	Hardness Change Shore A	Tensile Strength Change %	Elongation at Break Change %	Modulus 100% Change %	Modulus 300% Change %
Test method	ASTM D2240 (4 mm)	ASTM D638	ASTM D638	ASTM D638	ASTM D638
1	+2	−1	−19	+11	+13
10	+1	+1	−18	+11	+14
25	+1	+3	−15	+11	+14
50	+1	+5	−15	+14	+17

Table 13.15 The Effect of Steam (Autoclave) Sterilization on Elasto Mediprene® 500900 M (Shore Hardness 90 A)[18]

Cycles	Hardness Change Shore A	Tensile Strength Change %	Elongation at Break Change %	Modulus 100% Change %	Modulus 300% Change %
Test method	ASTM D2240 (4 mm)	ASTM D638	ASTM D638	ASTM D638	ASTM D638
1	+1.5	+5	–20	+28	+29
10	0	+6	–26	+30	+34
25	+1.5	+6	–29	+33	+36
50	+1.5	+7	–27	+33	+37

5. TPU-ARCL: Aromatic hard segment, polycaprolactone soft segment
6. TPU-ALES: Aliphatic hard segment, polyester soft segment
7. TPU-ALET: Aliphatic hard segment, polyether soft segment.

The properties of the resin depend on the nature of the raw materials, the reaction conditions, and the ratio of the starting raw materials. The polyols used have a significant influence on certain properties of the thermoplastic polyurethane. Polyether and polyester polyols are both used to produce many products.

The polyester-based TPUs have the following characteristic features:

- Good oil/solvent resistance
- Good UV resistance
- Abrasion resistance
- Good heat resistance
- Mechanical properties.

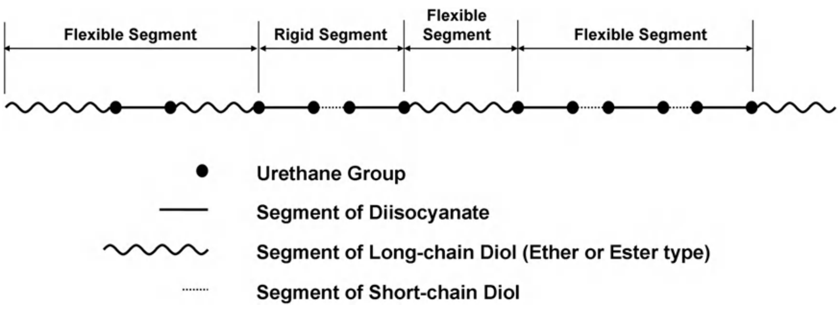


Figure 13.17 Molecular structure of a thermoplastic polyurethane elastomer.

The polyether-based TPUs have the following characteristic features:

- Fungus resistance
- Low temperature flexibility
- Excellent hydrolytic stability
- Acid/base resistance.

In addition to the basic components described above, most resin formulations contain additives to facilitate production and processability. Other additives can also be included such as:

- Demolding agents
- Flame retardants
- Heat/UV stabilizers
- Plasticizers.

The polyether types are slightly more expensive and have better hydrolytic stability and low-temperature flexibility than the polyester types.

Manufacturers and trade names: Lubrizol Isoplast®, Carbothane®, Tecoflex®, Tecoplast®, Tecothane®, Tecophilic®, Estane® TPU, Pellethane®, Bayer MaterialScience Texin® and Desmopan®, and BASF Elastollan®.

Sterile applications: Catheters, valves, needleless syringes, surgical instruments, wound dressings and tape, medical bags, and tubing.

Gamma radiation resistance: The physical properties of transparent rigid thermoplastic polyurethanes (TPUR) including Isoplast® 301, 2530, and 2531, as well as opaque thermoplastic polyurethanes including Isoplast® 101, are not significantly affected by exposure to a maximum of 10 Mrad of gamma radiation. Discoloration is dramatic upon exposure to gamma radiation. Yellowness index increases from 6.3 before exposure to 77.6 after exposure. The discoloration is permanent with minimal bleach back.

Ethylene oxide (EtO) resistance: Transparent and opaque rigid thermoplastic polyurethanes are compatible with multiple cycles of ethylene oxide sterilization. Isoplast® 301 and Isoplast® 101 retain tensile strength and Izod impact properties after exposure to five cycles of ethylene oxide gas. Less than 300 ppm residual EtO was present on the first day following exposure with continued degassing over time.

Regulatory status: Isoplast® 2530 and Isoplast® 2531 have USP Class VI listing.

Data for thermoplastic polyurethane elastomers are found in Tables 13.16–13.33 and Figs 13.18–13.22.

Table 13.16 Effect of Gamma Radiation Sterilization on Lubrizol Opaque Rigid Thermoplastic Urethane[20]

Radiation dose (Mrad)	2.5			10			
Postexposure Conditioning							
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	116.1	112.6	109		107.6	112.6	ASTM D638
Tensile strength at yield	93.4	94.7	92.3		94.7	96.5	ASTM D638
Elongation at break	113.9	109.2	101.2		106.4	112.7	ASTM D638
Dart impact (total energy)	101.6	106.3	101.9	98.2	93.7	100.2	ASTM D3763
Notched Izod impact	102.4	98.8	97.6	100.8	100.4	95.9	ASTM D256

Note: (1) Postexposure conditioning: storage in dark, 21 °C.

Table 13.17 Effect of Gamma Radiation Sterilization on Lubrizol Transparent Rigid Thermoplastic Urethane[20]

Radiation dose (Mrad)	2.5			10			
Postexposure Conditioning							
Time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	109.5	108.9	102.6	106	99.2	89.8	ASTM D638
Tensile strength at yield	94.3	93.3	92.4	94.4	94.1	95.4	ASTM D638
Elongation at break	109.5	116.8	104.4	112.4	91.2	92.7	ASTM D638
Dart Impact (total energy)	93.8	93.8	89.9	90.2	87	87.3	ASTM D3763
Notched Izod impact	85	105	75	80	95	90	ASTM D256

Note: (1) Postexposure conditioning: storage in dark, 21 °C.

Table 13.18 Effect of Gamma Radiation Sterilization on Lubrizol Isoplast® 301 and 101 Rigid Thermoplastic Urethane[21]

Radiation dose (Mrad)	2.5	10	2.5	10	2.5	10	2.5	10	
Postexposure Conditioning									
Type	Storage under fluorescent light				Storage in dark				
Properties Retained (%)									**Test Method**
Tensile strength at break	94.4	96.3	94.8	96.1	94.4	94.4	94.8		ASTM D638
Notched Izod impact	100	84.2	101.2	98.4	100	84.2	101.2	98.4	ASTM D256

Note: (1) Postexposure conditioning: 21 °C, 336 h.

Table 13.19 Effect of Gamma Radiation Sterilization on Lubrizol Isoplast® 2510 Rigid Thermoplastic Urethane[22]

Radiation dose (Mrad)	2.5		10		
Postexposure Conditioning					
Aging time (h)	168	1344	168	1344	
Properties Retained (%)					**Test Method**
Tensile strength at yield	102	118	100	116	ASTM D638
Elongation	103.1	96.4	96.9	100.5	ASTM D638
Flexural strength	100	98.6	98.6	97.2	ASTM D790
Modulus	93	94.1	92.4	90.8	ASTM D638
Flexural modulus	100	102.6	105.3	98.9	ASTM D790
Dart impact (total energy)	82.5	100	98.4	92.1	ASTM D3763
Dart impact (peak energy)	66.7	102	86.3	82.4	ASTM D3763
Notched Izod impact	94.2	98.3	83.8	102.2	ASTM D256
Heat deflection temperature	98.5	98.5	100	100	ASTM D648
Vicat softening point	100	97.8	98.9	97.8	ASTM D1525
Surface and Appearance					
ΔL Color	-13.2	-8	-20.4	-12.9	ASTM D2244
Δa Color	8.8	5.2	12.8	7.2	ASTM D2244
Δb Color	8.2	5.3	8.7	9.4	ASTM D2244

Table 13.20 Effect of Gamma Radiation Sterilization on Lubrizol Isoplast® 2531 Rigid Thermoplastic Urethane[22]

Radiation dose (Mrad)	2.5		10		
Postexposure Conditioning					
Time (h)	168	1344	168	1344	
Properties Retained (%)					**Test Method**
Tensile strength at yield	125	107.8	125	125	ASTM D638
Elongation	87.9	160.6	160.6	139.4	ASTM D638
Flexural strength	103	99	100	102	ASTM D790
Modulus	111.7	100	100.4	102.2	ASTM D638
Flexural modulus	103.8	101.7	100.4	107.2	ASTM D790
Dart impact (total energy)	98.7	97.3	89.3	33.3	ASTM D3763
Dart impact (peak energy)	92.7	105.5	85.5	34.5	ASTM D3763
Notched Izod impact	125	107.8	125	125	ASTM D256
Heat deflection temperature	102.6	100	97.4	100	ASTM D648
Vicat softening point	100	100	99.1	97.2	ASTM D1525
Surface and Appearance					
Δ Yellowness index	64.5	48.3	114.8	85.8	ASTM D1925
Haze (%)	2.23	0.89	1.35	3.89	
Transparency retained (%)	67	85.7	41.8	58.2	

Table 13.21 Effect of Gamma Radiation Sterilization on Lubrizol Pellethane® Thermoplastic Polyurethane Elastomer[23]

Material Supplier/ Name	**Dow Pellethane® 2363-80A**				**Dow Pellethane® 2363-55D**			
Exposure Conditions								
Radiation dose (Mrad)	2.75	2.75	9.6	9.6	2.75	2.75	9.6	9.6
Postexposure Conditioning								
Note	–	Storage in dark	–	Storage in dark	–	Storage in dark	–	Storage in dark
Temperature (°C)	–	23	–	23	–	23	–	23
Time (h)	0	24,090	0	24,090	0	24,090	0	24,090
Properties Retained (%)								
Tensile strength	101.6	106.7	104.1	109.7	93.3	103.4	94.5	106.4
Elongation	102.3	100	111.6	109.3	83.7	86.1	83.7	90.7
Modulus	103.4	123.9	102.3	118.2	99.6	110.8	98.4	112.4
300% Modulus	99	125	87	101.4	105.6	110.3	103.4	109.7

Table 13.22 Effect of Gamma Radiation Sterilization on Lubrizol Pellethane® Thermoplastic Polyurethane Elastomer[22]

Radiation dose (Mrad)	2.5		10		2.5		10		
Postexposure Conditioning									
Aging time (h)	168	1344	168	1344	168	1344	168	1344	
Properties Retained (%)									**Test Method**
Tensile strength at yield	98.2	96.4	94.5	98.2	–	–	–	–	ASTM D638
Elongation	72.5	67.7	91.8	74.4	–	–	–	–	ASTM D638
Flexural strength	98.5	91	106	92.5	–	–	–	–	ASTM D790
Modulus	85.1	87.3	76.9	83.3	–	–	–	–	ASTM D638
Flexural modulus	93.4	82.3	90.9	88.9	–	–	–	–	ASTM D790
Dart impact (total energy)	101.4	104.3	100	102.9	–	–	–	–	ASTM D3763
Dart impact (peak energy)	104.5	106.8	106.8	115.9	–	–	–	–	ASTM D3763
Notched Izod impact	75	125	100	207.8	–	–	–	–	ASTM D256
Heat deflection temperature	100	100	100	100	100	100	100	100	ASTM D648
Vicat softening point	101.8	103.6	101.8	101.8	104.8	100	96.4	97.6	ASTM D1325
Surface and Appearance									
Δ Yellowness index	64.5	20	42.1	28	5.9	3.57	21.91	20.75	ASTM D1925
Haze (%)	2.97	4.24	1.85	−0.71	4.57	4	5.63	3.39	
Transparency retained (%)	76.5	114.8	87.7	58	101.3	124.4	107.7	120.5	

Table 13.23 Effect of Gamma Sterilization on Lubrizol Tecoflex® EG80A Aliphatic Polyurethanes

Exposure Conditions							
Radiation dose (Mrad)	2.5	5	2.5	5	2.5	5	
Postexposure Conditioning							
Time	2 Weeks	2 Weeks	7 Weeks	7 Weeks	15 Months	15 Months	
Properties % Change							**Test Method**
Tensile strength	−2	−11	−7	−8	0	−1	ASTM D638

Table 13.24 Effect of Gamma Sterilization on Lubrizol Tecoflex® EG60D Aliphatic Polyurethanes

Exposure Conditions							
Radiation dose (Mrad)	2.5	5	2.5	5	2.5	5	
Postexposure Conditioning							
Time	2 Weeks	2 Weeks	7 Weeks	7 Weeks	15 Months	15 Months	
Properties % Change							**Test Method**
Tensile strength	−3	−15	−8	−21	−2	−25	ASTM D638

13.6 Polysiloxane/Silicone Rubber

Silicones are also known as siloxanes, polyorganosiloxanes, or polysiloxanes. Silicone rubber is a semi-organic synthetic. Its polymer backbone structure consists of a chain of silicon and oxygen atoms rather than carbon and hydrogen atoms, as in the case with other types of rubber. The molecular structure of silicone rubber results in a very flexible — but weak — chain. Silicones are very stable at low and high temperatures. Although fillers may improve properties somewhat, tear and tensile strengths remain relatively low. Figure 13.23 shows four of the primary groups that make up a typical polysiloxane. To simplify the discussion of polysiloxane composition, the monomers are identified by letters:

Table 13.25 Effect of Electron Beam Radiation Sterilization on Lubrizol Isoplast® 2531 Transparent Rigid Thermoplastic Urethane[22]

Radiation dose (Mrad)	2.5		10		
Postexposure Conditioning					
Aging time (h)	168	1344	168	1344	
Properties Retained (%)					**Test Method**
Tensile strength at yield	107.8	107.8	125	117.2	ASTM D638
Elongation	160.6	163.6	140.4	141.4	ASTM D638
Flexural strength	103	101	103	100	ASTM D790
Modulus	98.7	97.4	89.6	94.4	ASTM D638
Flexural modulus	102.1	113.2	97.4	100	ASTM D790
Dart impact (total energy)	100	94.7	84	73.3	ASTM D3763
Dart impact (peak energy)	94.5	92.7	83.6	72.7	ASTM D3763
Notched Izod impact	107.8	107.8	125	117.2	ASTM D256
Heat deflection temperature	98.7	100	105.3	107.9	ASTM D648
Vicat softening point	99.1	99.1	99.1	97.2	ASTM D1525
Surface and Appearance					
Δ Yellowness index	64	53.1	136.2	124	ASTM D1925
Haze (%)	2.24	2.73	2.07	−1.02	
Transparency retained (%)	68.1	81.3	37.4	51.6	

Some common abbreviations for the polymers include: MQ, VMQ, PMQ, PVMQ, PDMS, and poly(1-trimethylsilyl-1-propyne) or PTMSP.

Manufacturers and trade names: Bayer Corporation Baysilone®; Shincor Silicones KE®; Dow Corning Corp. Silastic®; General Electric Silplus®, Tufel®, SE; and Rhone-Poulenc Inc. Rhodorsil; Wacker Chemie AG Elastosil.

Medical/sterile applications and uses: Prostheses, artificial organs, facial reconstruction, catheters, artificial skin, contact lenses, and drug delivery systems.

Because silicones, in general, are temperature and moisture resistant, they are typically not affected by most sterilization methods. The most common sterilization methods used for medical devices that contain silicone include: dry heat, steam autoclaving, ethylene oxide (EtO), gamma radiation, and e-beam radiation.

Dry heat or steam autoclaving: Will most likely have little effect on silicone's physical properties because of its moisture and heat resistance. The drawback to heat sterilization of silicone materials is that the high heat may cause the silicone to expand, which must be taken into consideration in how the device is configured and packaged.

EtO sterilization: Silicones generally have a high permeability to EtO molecules allowing the EtO to diffuse through the polymer network, inducing sterilization throughout the polymer matrix. The only precaution is to ensure that all the EtO has been removed from the silicone device before it is used, which usually takes 24 h.

Gamma and electron beam sterilization: Radiation is known to induce changes in the molecular architecture of silicone rubber, increasing its molecular weight and decreasing elasticity. The

Table 13.26 Effect of Electron Beam Radiation Sterilization on Lubrizol Isoplast® 2510 Rigid Thermoplastic Urethane[22]

Radiation dose (Mrad)	2.5		10		
Postexposure Conditioning					
Aging time (h)	168	1344	168	1344	
Properties Retained (%)					**Test Method**
Tensile strength at yield	100	118	102	112	ASTM D638
Elongation	122.8	88.6	96.9	91.7	ASTM D638
Flexural strength	104.2	97.2	111.3	95.8	ASTM D790
Modulus	100.5	90.8	89.2	91.9	ASTM D638
Flexural modulus	101.1	97.9	101.6	101.1	ASTM D790
Dart impact (total energy)	100	93.7	95.2	93.7	ASTM D3763
Dart impact (peak energy)	92.2	82.4	84.3	82.4	ASTM D3763
Notched Izod impact	103.5	99.1	99.1	98.7	ASTM D256
Heat deflection temperature	98.5	98.5	107.6	100	ASTM D648
Vicat softening point	100	97.8	97.8	97.8	ASTM D1525
Surface and Appearance					
ΔL Color	−13.1	−7.7	−21.1	−7.9	ASTM D2244
Δa Color	8.7	4.6	15.2	4.6	ASTM D2244
Δb Color	10.2	5.4	16.7	5.6	ASTM D2244

Table 13.27 Effect of Electron Beam Radiation Sterilization on Lubrizol Pellethane® Thermoplastic Polyurethane Elastomer[22]

Radiation dose (Mrad)	2.5		10		2.5		10		
Postexposure Conditioning									
Aging time (h)	168	1344	168	1344	168	1344	168	1344	
Properties Retained (%)									**Test Method**
Tensile strength at yield	92.7	92.7	61.8	87.3	–	–	–	–	ASTM D638
Elongation	90.5	69.3	95.6	69	–	–	–	–	ASTM D638
Flexural strength	101.5	97	68.7	58.2	–	–	–	–	ASTM D790
Modulus	88.2	79.2	53.8	49.3	–	–	–	–	ASTM D638
Flexural modulus	88.9	91.4	55.6	53	–	–	–	–	ASTM D790
Dart impact (total energy)	105.7	107.1	101.4	97.1	–	–	–	–	ASTM D3763
Dart impact (peak energy)	122.7	134.1	88.6	86.4	–	–	–	–	ASTM D3763
Notched Izod impact	82.8	150	142.2	125	–	–	–	–	ASTM D256
Heat deflection temperature	100	100	100	100	100	100	100	100	ASTM D648
Vicat softening point	101.8	107.3	96.4	94.5	104.8	104.8	102.4	104.8	ASTM D1325
Surface and Appearance									
ΔYellowness index	46	21.9	18.7	8.6	−1.52	−1.09	7.37	9.04	ASTM D1925
Haze (%)	4.48	0.64	2.99	3.21	3.75	4.02	5.83	2.75	
Transparency retained (%)	93.8	102.5	102.5	119.8	114.1	125.6	111.5	124.4	

Table 13.28 Effect of Ethylene Oxide (EtO) Sterilization on Lubrizol Opaque Rigid Thermoplastic Urethane[20]

Number of cycles	1			5			
Postexposure Conditioning III							
Aging time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	106.1	93.2	91.4	101.6	104.4	87.6	ASTM D638
Tensile strength at yield	98.6	95.9	93.3	101.2	99.3	101.5	ASTM D638
Elongation at break	79.8	96.5	97.1	104.6	101.7	96.5	ASTM D638
Dart impact (total energy)	104.6	96	104.6	105.8	95.6	97	ASTM D3763
Notched Izod impact	96.3	103.3	96.7	96.3	99.2	89.8	ASTM D256

Note: (1) Preexposure conditioning: time: 8 h; 37.8 °C; RH: 60%. (2) Exposure conditions: 12% EtO and 88% Freon, 49 °C, $\geq$6 h. (3) Postexposure conditioning I: evacuation, 127 mmHg. (4) Postexposure conditioning II: aeration, 32.2 °C, $\geq$16 h. (5) Postexposure conditioning III: storage in dark, hours listed in table.

Table 13.29 Effect of Ethylene Oxide (EtO) Sterilization on Lubrizol Transparent Rigid Thermoplastic Urethane[20]

Number of cycles	1			5			
Postexposure Conditioning III							
Aging time (h)	336	4368	8760	336	4368	8760	
Properties Retained (%)							**Test Method**
Tensile strength at break	104.6	102.5	97.5	100.9	93.7	101.1	ASTM D638
Tensile strength at yield	96.6	92.7	92.4	97.7	92.5	96.1	ASTM D638
Elongation at break	104.4	102.2	105.1	121.2	100.7	113.9	ASTM D638
Dart impact (total energy)	91.6	83.2	84.5	91.5	83.9	81.2	ASTM D3763
Notched Izod impact	90	95	95	100	90	95	ASTM D256

Note: (1) Preexposure conditioning: time: 8 h; 37.8 °C; RH: 60%. (2) Exposure conditions: 12% EtO and 88% Freon, 49 °C, $\geq$6 h. (3) Postexposure conditioning I: evacuation, 127 mmHg. (4) Postexposure conditioning II: aeration, 32.2 °C, $\geq$16 h. (5) Postexposure conditioning III: storage in dark, hours listed in table.

Table 13.30 Effect of Ethylene Oxide (EtO) Sterilization on Lubrizol Isoplast® 101 Rigid Thermoplastic Urethane[21]

Number of cycles	1	5	1	5	
Properties Retained (%)					**Test Method**
Tensile strength at yield	96.3	97.2	98.7	102.6	ASTM D638
Notched Izod impact	94.7	100	96.3	96.3	ASTM D256

Note: (1) Preexposure conditioning: time: 8 h; 37.8 °C; RH: 60%. (2) Exposure conditions: 12% EtO and 88% Freon, 49 °C, ≥6 h. (3) Postexposure conditioning I: evacuation, 127 mmHg. (4) Postexposure conditioning II: aeration, 32 °C, ≥16 h. (5) Postexposure conditioning III: storage in dark, RH: 60%, 336 h.

Table 13.31 Effect of Ethylene Oxide (EtO) Sterilization Residuals Over Time for Lubrizol Isoplast® 101 Rigid Thermoplastic Urethane[21]

Residuals (ppm)	**Ethylene Oxide**
24-h Aeration	160
72-h Aeration	118
168-h Aeration	86
744-h Aeration	70
816-h Aeration	36
864-h Aeration	23

Note: (1) Preexposure conditioning: time: 8 h; 37.8 °C; RH: 60%. (2) Exposure conditions: one cycle, 12% EtO and 88% Freon, 49 °C, ≥6 h, RH: 60%. (3) Postexposure conditioning I: evacuation, 127 mmHg. (4) Postexposure conditioning II: aeration, 32 °C, hours in table.

Table 13.32 Ethylene Oxide (EtO) Sterilization Effects Using Pure EtO Carrier Gas on Lubrizol Isoplast® TPU[24]

Exposure Conditions						
Type	Unexposed	EtO sterilization		EtO sterilization		
Cycles	–	1	3	1	3	
Properties Retained						**Test Method**
Tensile yield (MPa)	69	70	72	71	71	ASTM D638
Elongation (%)	165	173	171	175	173	ASTM D638
Izod impact (J/m)	80	80	85	91	64	ASTM D256
Peak energy (J)	45	56	58	58	55	ASTM D3763

Table 13.33 Ethylene Oxide (EtO) Sterilization Effects Using HCFC-124 Carrier Gas on Isoplast® 2530 TPU[24]

Exposure Conditions						
Type	Unexposed	EtO sterilization		EtO sterilization		
Cycles	–	1	3	1	3	
Properties Retained						**Test Method**
Tensile yield (MPa)	69	69	67	73	71	ASTM D638
Elongation (%)	165	173	171	175	173	ASTM D638
Izod impact (J/m)	80	80	85	91	64	ASTM D256
Peak energy (J)	45	56	58	58	55	ASTM D3763

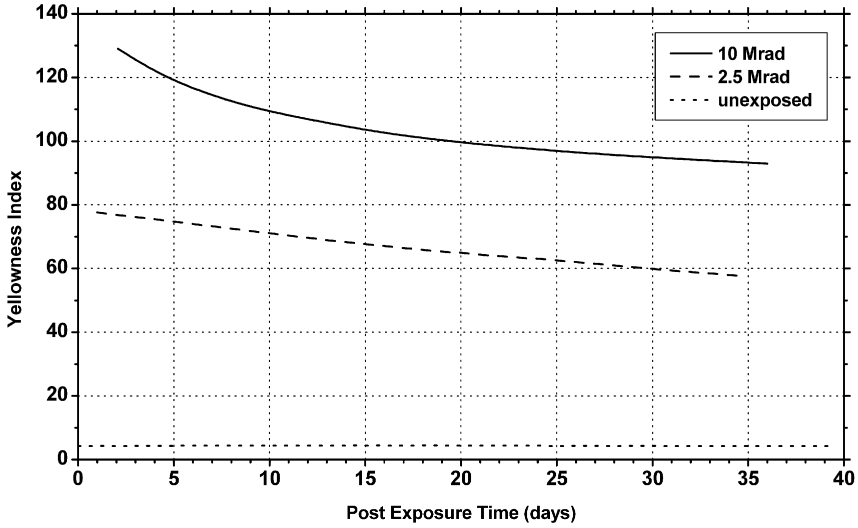


Figure 13.18 Post-gamma radiation exposure time versus yellowness index of Lubrizol Isoplast® 301 rigid thermoplastic urethane.[21]

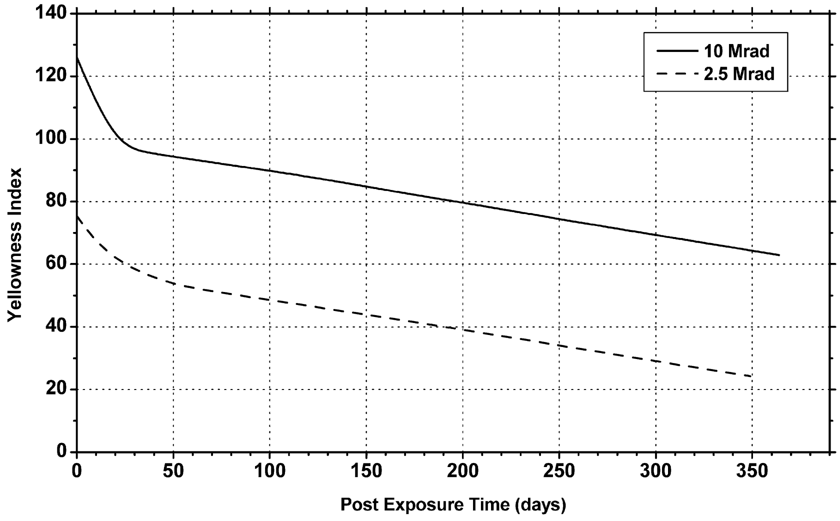


Figure 13.19 Post-gamma radiation exposure time versus yellowness index of Lubrizol rigid thermoplastic urethane.[20]

Figure 13.20 Post 2.5 Mrad gamma radiation exposure time versus ΔE color change of Lubrizol Isoplast® 101 rigid thermoplastic urethane after light and dark storage.[21]

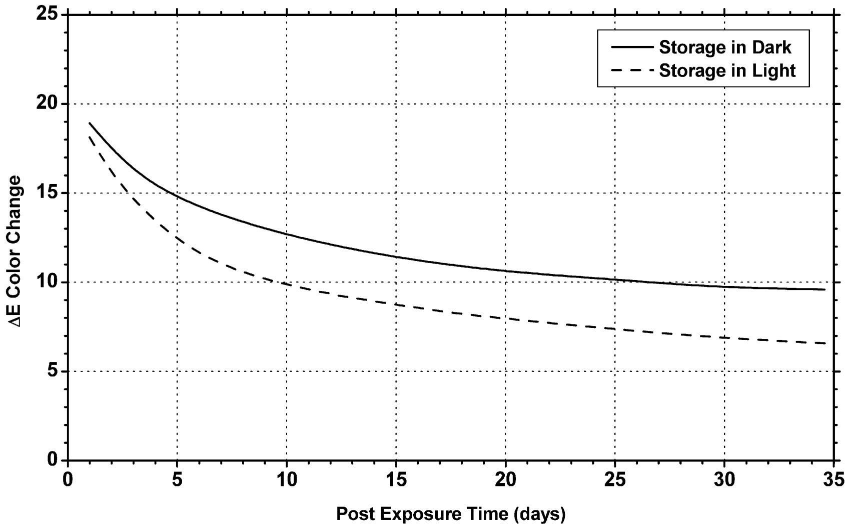


Figure 13.21 Post 10 Mrad gamma radiation exposure time versus ΔE color change of Lubrizol Isoplast® 101 rigid thermoplastic urethane after light and dark storage.[21]

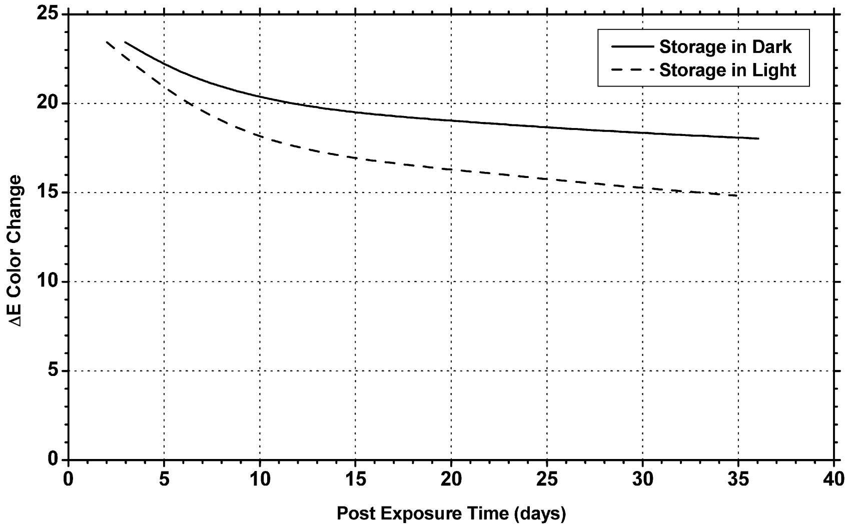
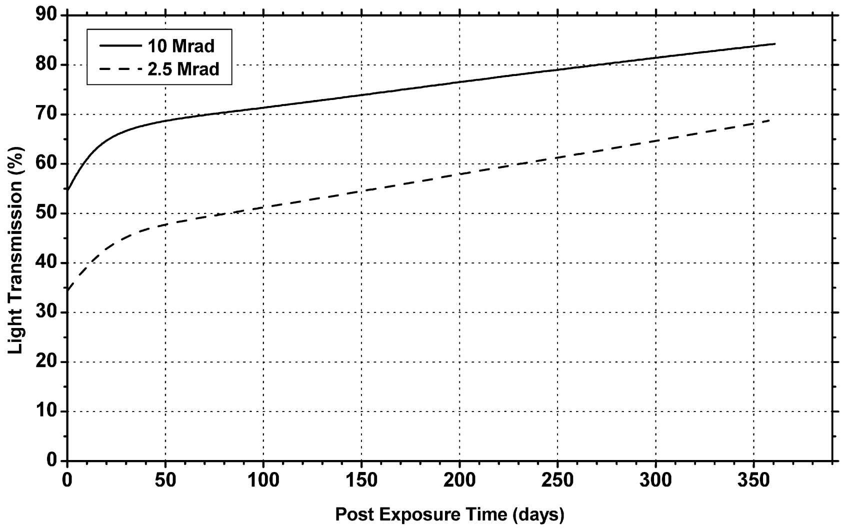


Figure 13.22 Post gamma radiation exposure time versus percent light transmission of Lubrizol rigid thermoplastic urethane.[20]



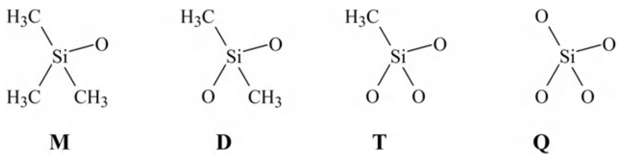


Figure 13.23 Structure of groups that make up polysiloxanes: “M” stands for Me_3SiO; “D” for Me_2SiO_2; “T” for $MeSiO_3$; “Q” for SiO_4; “P” for replace Me with phenyl side groups; “V” for replace Me with vinyl side groups (typically <1%); “F” for replace Me with fluorine.

chemical reactions that lead to this are shown in Fig. 13.24

The curing chemistry affects the properties of silicone rubbers. Three common curatives used (see Figs 13.25−13.39) are:

- Platinum-cured liquid silicone rubber (LSR), Wacker Chemie AG Elastosil LR3003/50 LSR, Part A&B liquid system
- Platinum-cured high-consistency rubber (platinum-cured HCR), Wacker Chemie AG Elastosil R4000/50
- Peroxide-cured high-consistency rubber (peroxide-cured HCR), GE Bayer Silicones GmbH & Co. KG HV3 622, cured by di-2,4-dichlorobenzoylperoxide with 1% loading.

Peroxide curing gives an end product that is more rigid and more resilient, with methyl and vinyl cross-links. Platinum curing gives an end product that is more flexible with better tear, with vinyl/hydride cross-links.

Data for polysiloxane/silicone rubbers are found in Figs. 13.25−13.39.

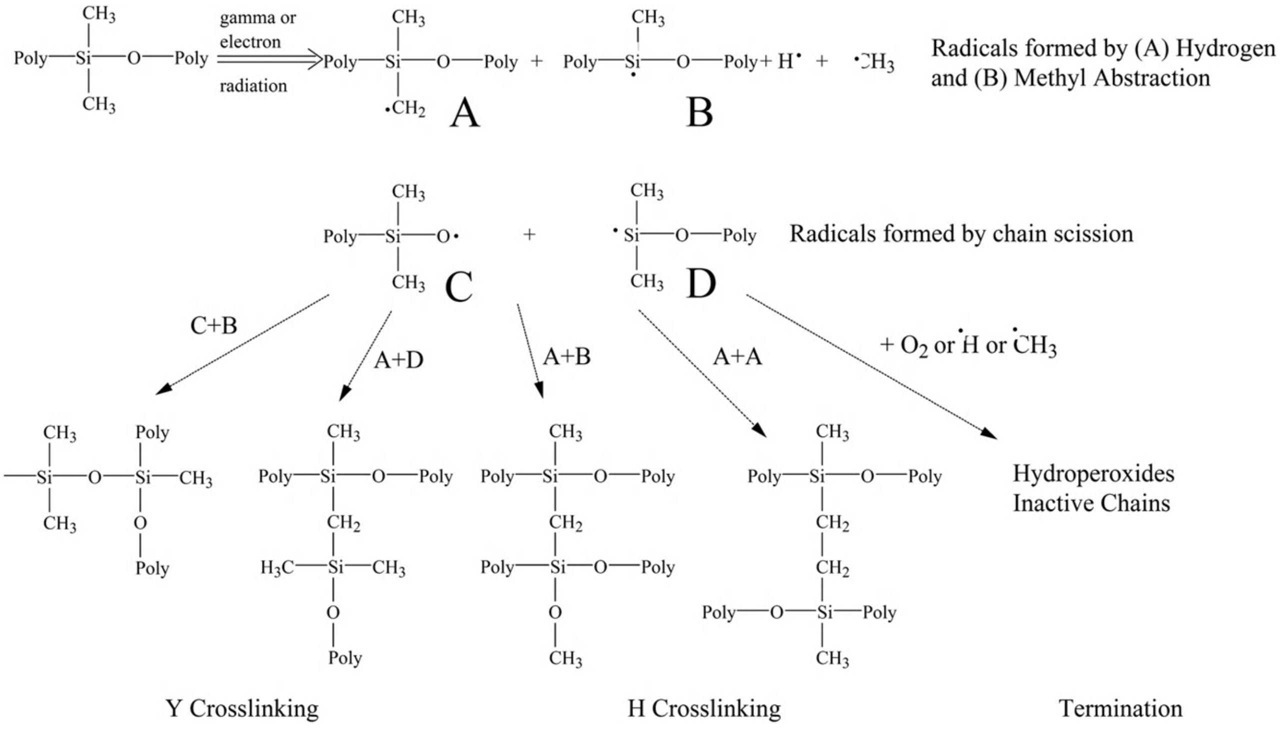


Figure 13.24 Effect of gamma and electron radiations on silicone polymer chains.[25]

Figure 13.25 Effect of gamma radiation on durometer hardness of silicone rubbers.[25]

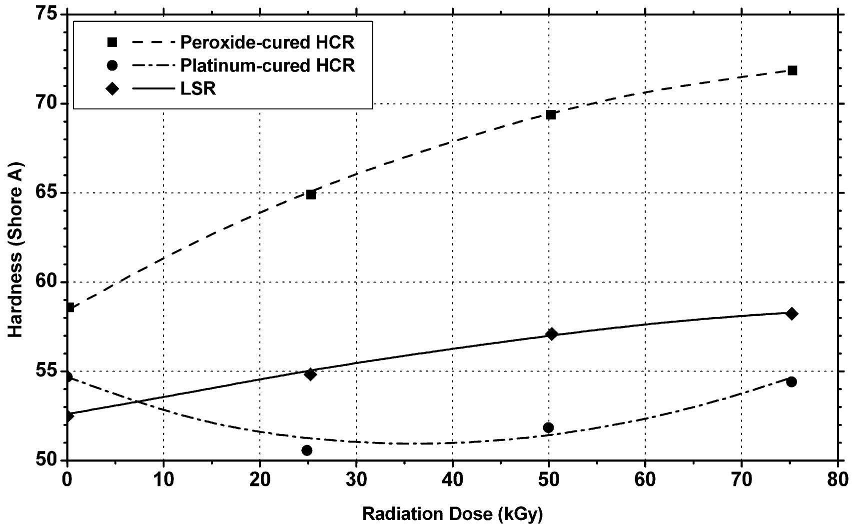


Figure 13.26 Effect of gamma radiation on tensile modulus of silicone rubbers.[25] Note: 100% tensile modulus is the modulus at 100% elongation.

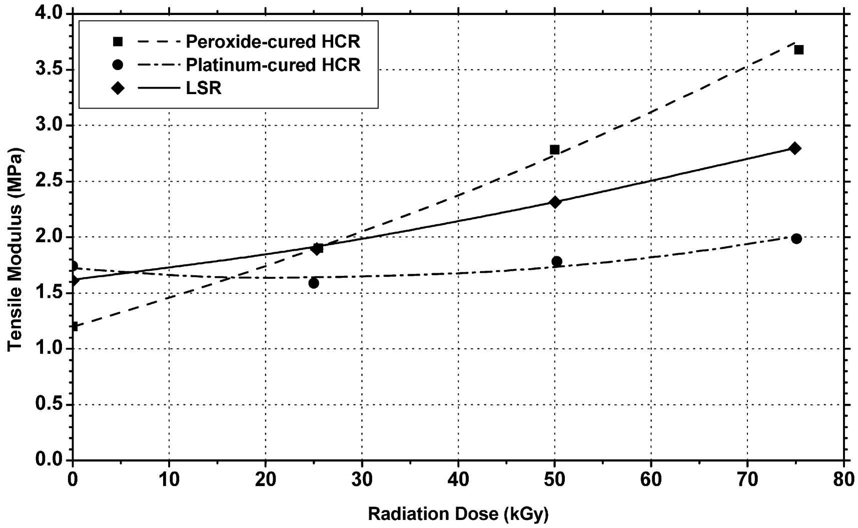
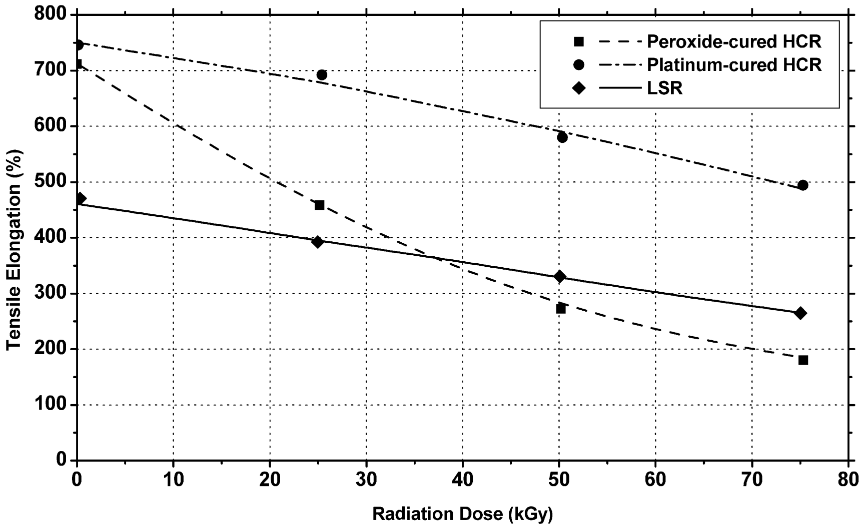


Figure 13.27 Effect of gamma radiation on tensile elongation of silicone rubbers.[25]



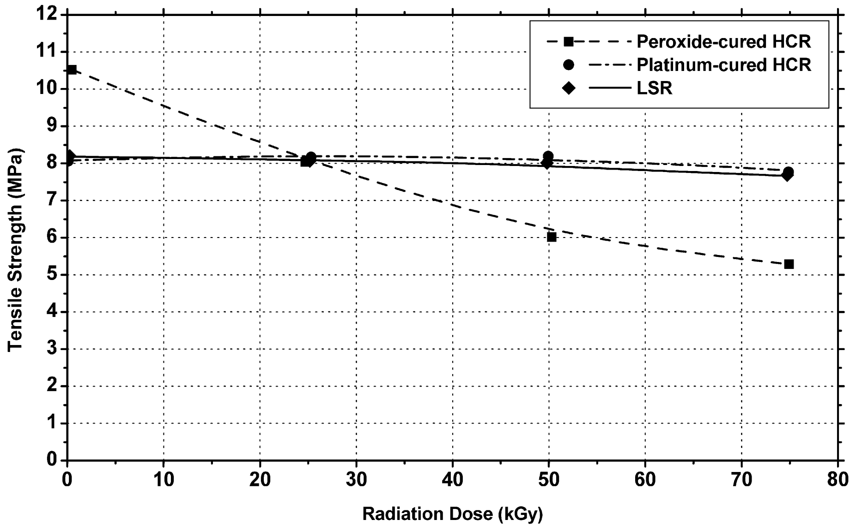


Figure 13.28 Effect of gamma radiation on tensile strength of silicone rubbers.[25]

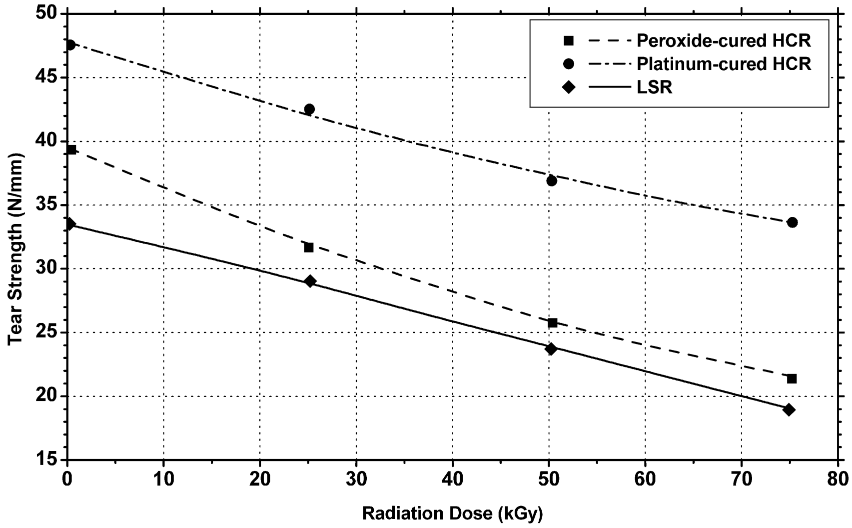


Figure 13.29 Effect of gamma radiation on trouser tear strength of silicone rubbers.[25]

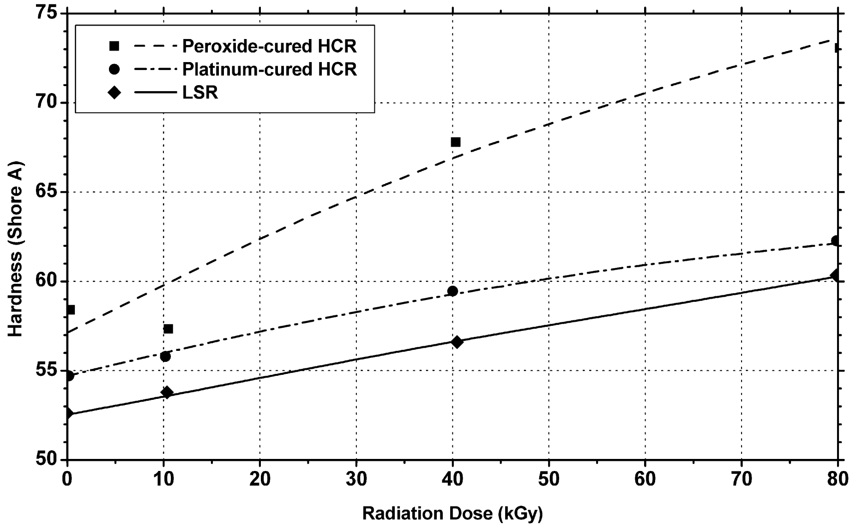


Figure 13.30 Effect of e-beam radiation on durometer hardness of silicone rubbers.[25]

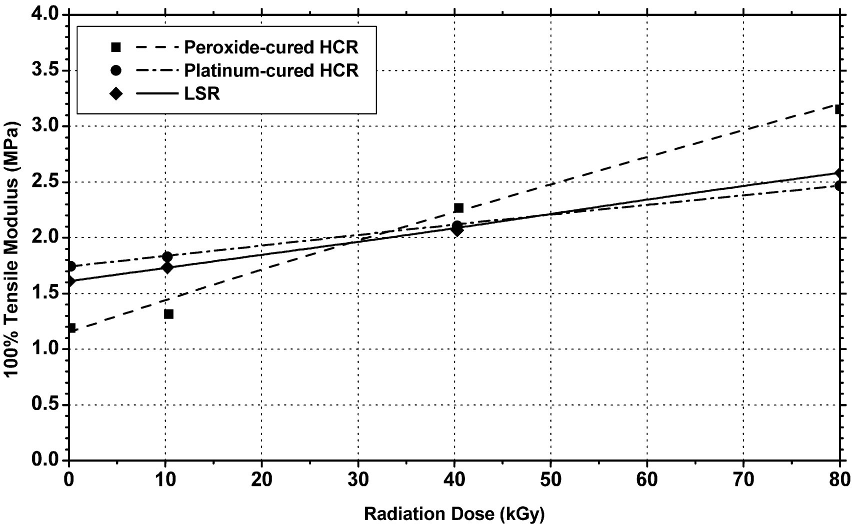


Figure 13.31 Effect of e-beam radiation on tensile modulus of silicone rubbers.[25]

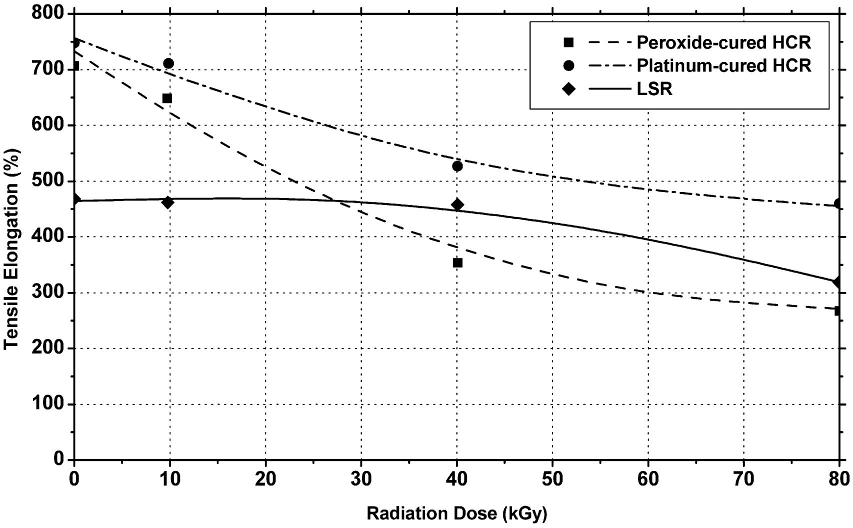


Figure 13.32 Effect of e-beam radiation on tensile elongation of silicone rubbers.[25]

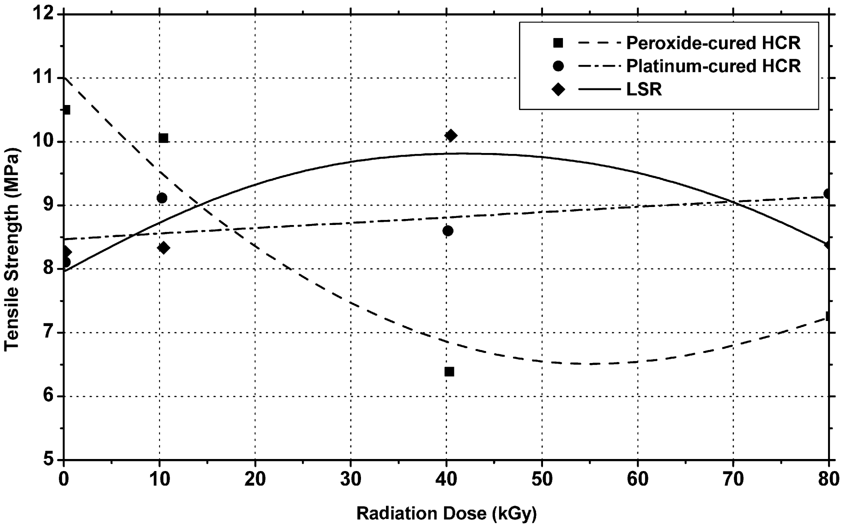


Figure 13.33 Effect of e-beam radiation on tensile strength of silicone rubbers.[25]

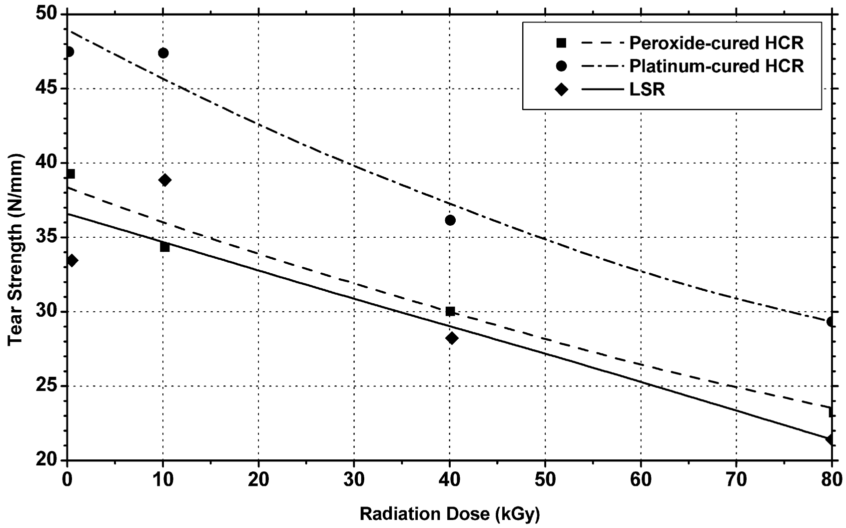


Figure 13.34 Effect of e-beam radiation on trouser tear strength of silicone rubbers.[25]

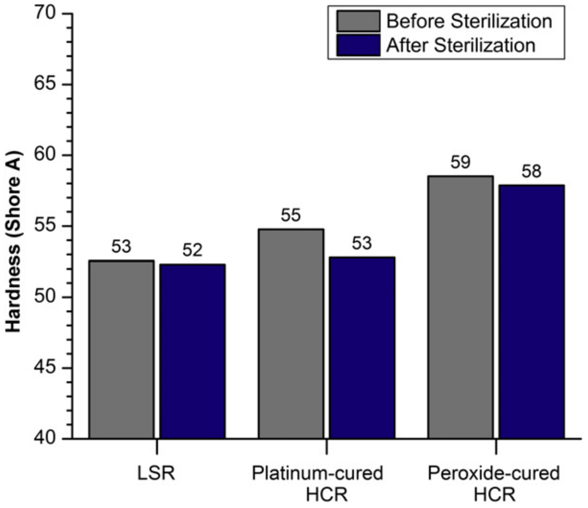


Figure 13.35 Effect of EtO sterilization on durometer hardness of silicone rubbers.[25]

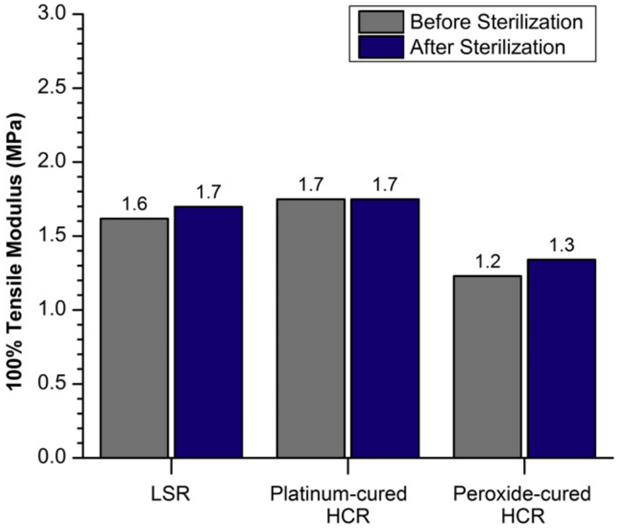


Figure 13.36 Effect of EtO sterilization on tensile modulus of silicone rubbers.[25]

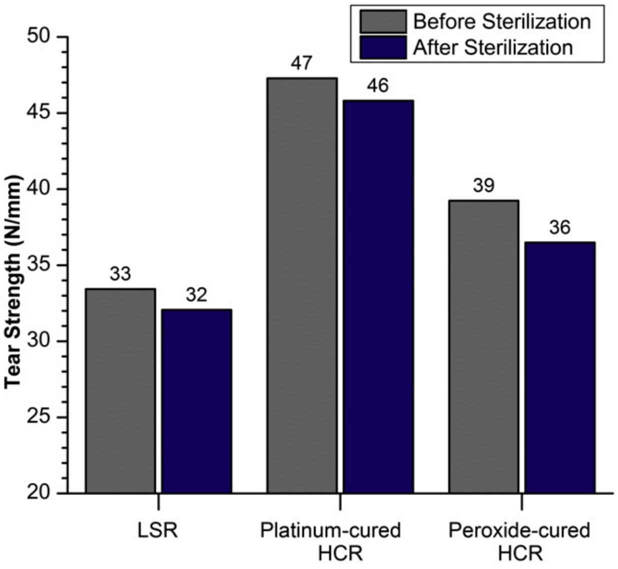


Figure 13.37 Effect of EtO sterilization on trouser tear strength of silicone rubbers.[25]

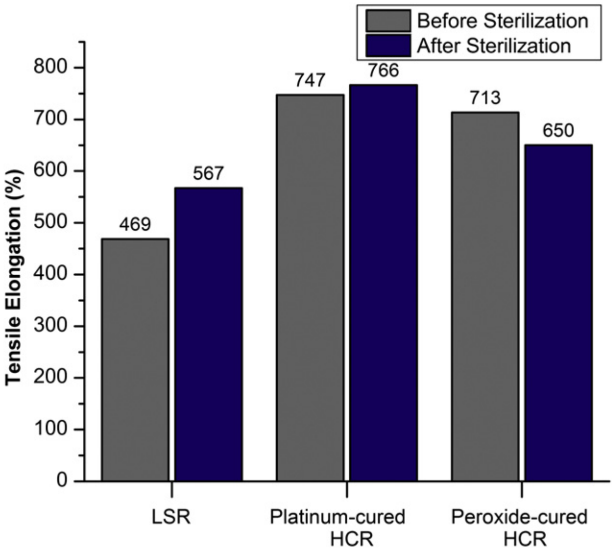


Figure 13.38 Effect of EtO sterilization on tensile elongation of silicone rubbers.[25]

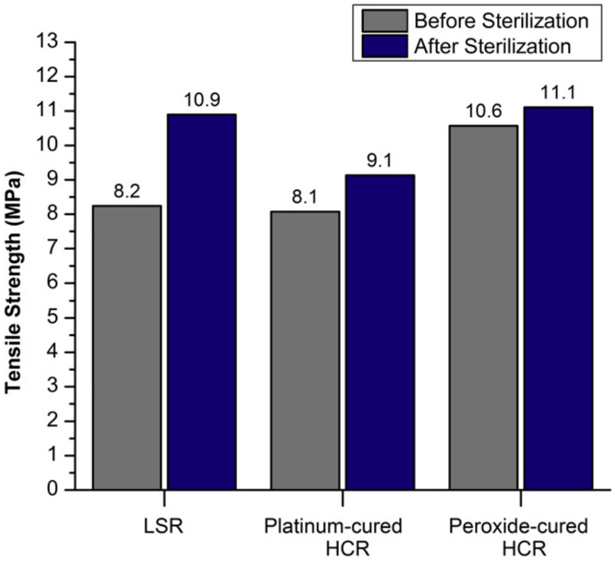


Figure 13.39 Effect of EtO sterilization on tensile strength of silicone rubbers.[25]

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