Elastomer · thermal-ageing · photo-ageing · environmental ageing · cross-linking · chain breaking

This review paper describes the duality between chain breaking and crosslinking reactions which possibly occurs during the ageing of most elastomers. The phenomenon occurs both on crude/not cured rubbers and on fully crosslinked rubbers and is much more important than in other polymer families. As the analytical methods to measure chain scissions are considered to be well known, this paper is more focused on the methods to point out crosslinking reactions derived from thermal or photoageing driven in conditions representative for environmental ageing.

Alterung von Elastomeren durch Umwelteinflüsse - Der Dualismus von Vernetzung und Kettenspaltung

Elastomer · thermische Alterung · Fotoalterung · Alterung durch Umwelteinflüsse · Vernetzung · Kettenspaltung

Dieser Übersichtsartikel beschreibt den Dualismus zwischen Kettenspaltung und Vernetzungsreaktionen, die während der Alterung der meisten Elastomere möglich sind. Dieses Phänomen tritt sowohl bei nicht vulkanisierten als auch bei vollständig vernetzten Kautschuken auf und ist hier deutlich wichtiger als für andere Polymerfamilien. Die berücksichtigten analytischen Methoden zur Messung der Kettenspaltung sind gut bekannt, der Artikel ist daher mehr auf Methoden fokussiert, die die Vernetzung durch Thermo- oder Fotoalterung aufzeigen, welche für Alterung durch Umwelteinflüsse repräsentativ sind.

Figures and Tables:
By a kind approval of the authors.

Environmental Ageing of Elastomers – the Duality of Crosslinking and Chain Scissions

Introduction

Most of polymers present a limited resistance to ageing including the ageings involved by environmental stress (heat, light, etc.). The main reason is their ability to generate macroalkyl radicals (P°) derived themselves from the presence of impurities, in particular those coming from their processing at relatively high temperature (peroxides or hydroperoxides for example).

As it can be seen on the following scheme the main mechanism involves a fast oxidation of macroalkyl radicals resulting in the formation of peroxo radicals (POO°) and various functional polar groups easily revealed by FTIR spectroscopy (hydro peroxides, alcohols, ketones, carboxylic acids). The presence of methyl (chain end) ketones, carboxylic acids and some volatile compounds (methanol, CO_2, H_2O) characterises chain scissions which can also be pointed out by molecular weight or viscosity measurements. In the case of photo ageing, additional chain scissions are produced by the photochemical decomposition of ketones via Norrish reactions (Norrish type I produce essentially shorter chains ketones, aldehydes and carboxylic acids as Norrish type II produce methyl (chain end) ketones and vinyl (end groups) or other unsaturated groups and shorter ketones)[1].

However, and it is particularly the case of elastomers, another route of degradation sometimes occurs, ie crosslinking reactions derived both from the duplication of macroradicals (alkyl, alkoxi or peroxi) and the addition of macroalkyl radicals on residual double bonds (reaction similar to the radical polymerisation of olefins).

It is expected that both chain breakings and crosslinkings observed in elastomers start by the abstraction of an hydrogen atom in α position of a double bond (dienic elastomers including EPDM).

Parallely similar crosslinking reactions (based on peroxide or sulfur reactions) are commonly used in rubber industry to obtain the elasticity (elastic memory), however, conversely, the same peroxide reaction is used in polypropylene industry to reduce the molecular weight (chain scissions). In PP it is expected that the first peroxidation (during ageing or during polymer modification) occurs locally because of the typical position of tertiary carbons [2], then the thermal or the photo-decomposition of the unstable and strongly associated hydro peroxides will generate a lot of chain scissions including low molecular weight compounds like acetone, acetic acid or methanol [3].

Infrared spectroscopy is a fantastic tool to observe oxidation/scissions of polymer chains but, excepted the loss of double bonds which can be observed during the ageing of crude dienic polymers (BR[4], IR [5], SBR [6], ABS [7]), this analytical technique is not very efficient to detect crosslinking (low absorption coefficients and low content of new C-C bonds).

However this loss of double bonds is very limited in the case of highly carbon black filled and crosslinked dienic elastomers.

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This paper will review some experimental techniques able to determine the crosslinking appearing upon the thermal or the photo-ageing of elastomers submitted to environmental stress. Some examples will be given on EPDM, dienic elastomers and silicones ageings.

Experimental aspect of polymer environmental degradation

If we consider the main environmental stress brought by heat and UV light, several methods allow to predict the durability of the polymer/elastomer on the long term.

Thermal ageing

The main way to predict the behavior in the absence of light is to use the Arrhenius approach ($k=Ae^{-Ea/RT}$). The activation energy (Ea) of most oxidation reactions is around 100 KJ mol^{-1} (i.e. the rate is approximatively doubling each 10°C increase) and this value can be used in first approximation to predict the material's lifespan as a function of the conditions for its use (exposure times at different temperatures). However it is better to perform kinetic measurements at three or four different temperatures to check the validity of the Arrhenius law and to determine precise activation

energy for each formulation. The rate can be measured by several analytical techniques (IR, chemiluminescence (CL), UV-VIS, induction period, OIT, etc.). For example the figure **1** shows the determination of Ea for the thermal ageing of EPDM both by CL and OIT/DSC. The correlation coefficient has to be higher than 0.99.

Photoageing

As for thermal ageing it is often not acceptable to wait many years to control the durability during the real life of a material even if, in the case of photo-ageing, some exposures can be done in special places under control of the climatic parameters (for example south of Europe, Florida, Arizona). In most cases it is more convenient to use accelerated photo-ageing in laboratory devices. The main approaches are as follow:

Simulation devices

The light is produced by a filtered Xenon lamp with usually an intensity of 60W. m^{-2} between 300 and 400 nm, equivalent to the maximum energy available on the earth surface; temperature, relative humidity are controlled and water aspersion is also possible to simulate rain. By using a continuous exposure the time needed to simulate one year in south of Europe is roughly 1000 hours (against 8760 hours in 1 year).

Acceleration and ultra-acceleration devices

The light can be produced by mercury lamps (CNEP way) with intensity between 90 (accelerated photo-ageing) and 300 W. m^{-2} (ultra-acceleration); temperature and relative humidity are controlled and water aspersion is also possible. The new instrument (2014) built by Atlas-Ametek in collaboration with CNEP, Renault, PSA and PolyOne offers the two levels of acceleration (SEPAP MHE [8]). The expected exposure times for 1 year exposure in south of Europe are respectively roughly 300 and 100 hours.

For any laboratory device it is necessary to control that the stoechiometry of the polymer degradation and the aspect changes (color, gloss) of the formulated polymer are representative of the situation in real life. This can be done by using non destructive analytical techniques like IR and UV-Vis spectrometries, an approach validated by NF ISO 10640 (2011).
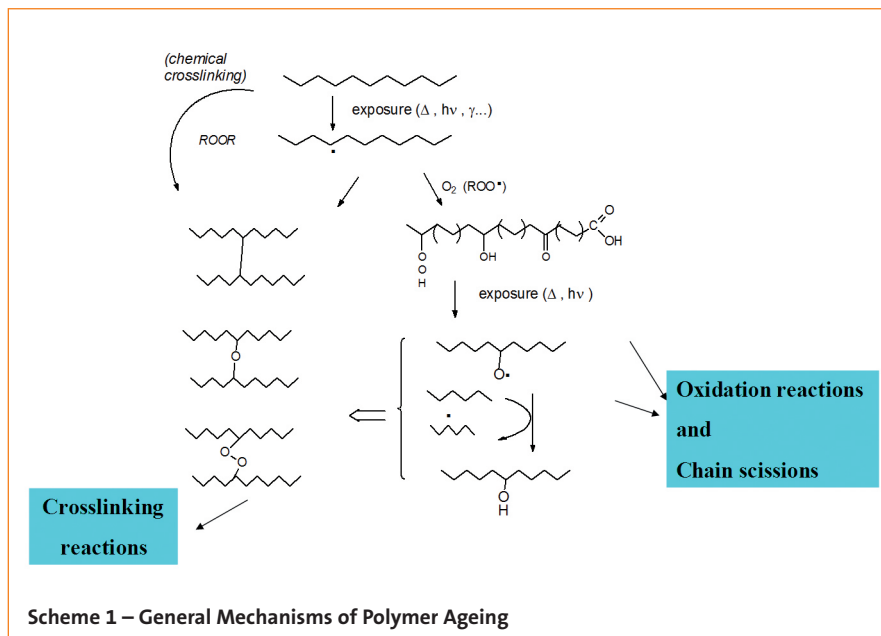
Scheme 1 – General Mechanisms of Polymer Ageing
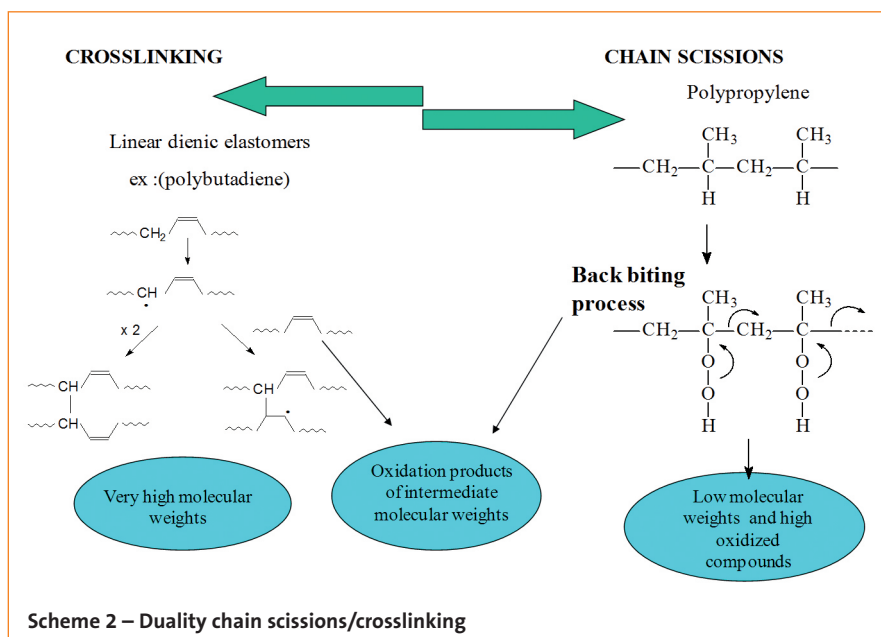
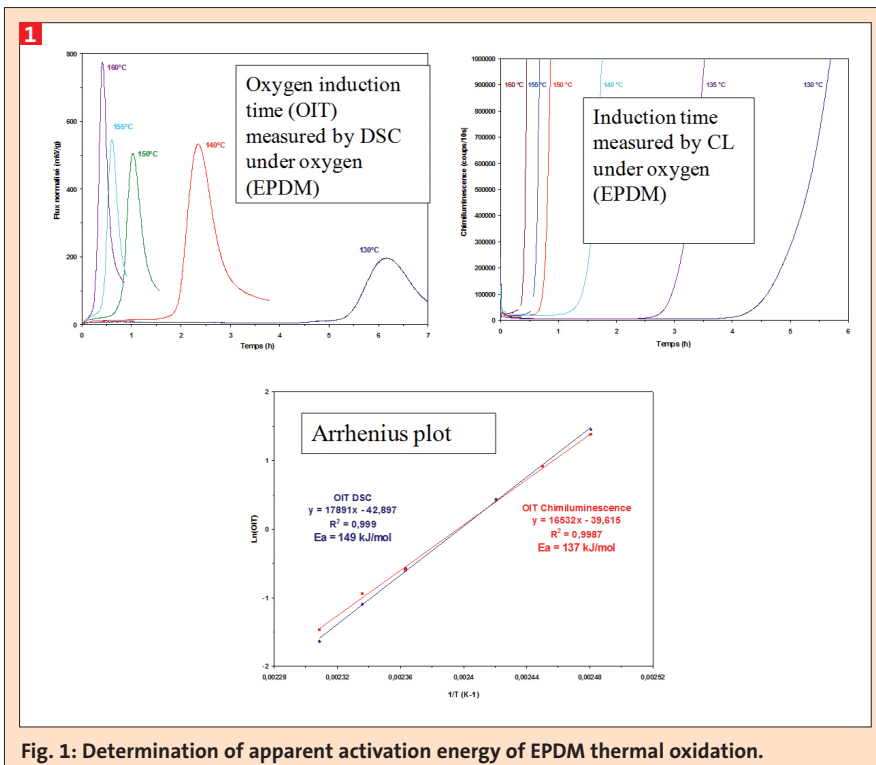Scheme 2 – Duality chain scissions/crosslinking

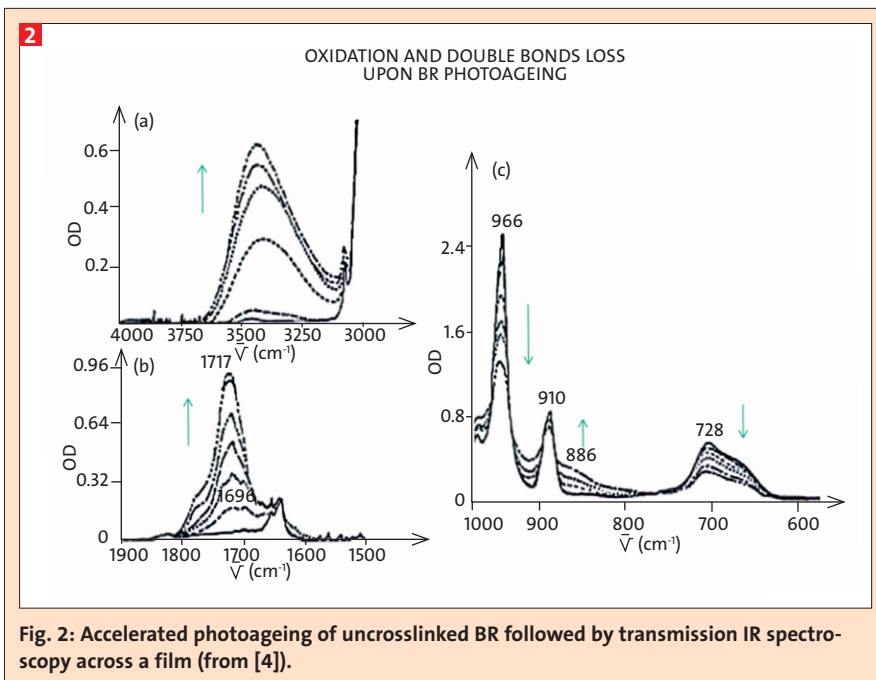Fig. 1: Determination of apparent activation energy of EPDM thermal oxidation.

Fig. 2: Accelerated photoageing of uncrosslinked BR followed by transmission IR spectroscopy across a film (from [4]).

Analytical approach

Chain breaking

As already mentioned Fourier Transformed Infrared (FT-IR) spectroscopy is a well adapted tool to follow both thermal and photoageing (sensitive to polar groups derived from oxidation, non destructive/allowing to follow the same sample upon ageing, with a lot of accessories able to measure both in transmission/reflexion modes and at the microscopic level (analysis of volumes of $1 \times 3 \times 3\ \mu m^3$ is possible).

Figure **2** shows for example the assessment of IR spectrum upon photoageing of crude (uncrosslinked) BR [4]. Together the formation of hydroxylated and carbonylated (oxidation) functional groups and the correlative loss of unsaturations (crosslinking) (t,1-4/966, c,1-4/728 and 1-2/910 cm^{-1}) can be obser-ved. (the thermal ageing and the IR profile across the film thickness are also described in this paper).

Among the oxidated functional groups observed, carboxylic acids absorbing close to 1710 cm^{-1} with high absorption coefficients are typical chain scissions products then the kinetic curve of the formation of total carbonyl groups (wide band) represents a first approach of the determination of chain scissions upon ageing. More precise determination can be done by measuring carboxylic acids after specific reaction with reactive gas or volatile compounds (SF4 or CH_3CO-Cl) shifting the 1710 cm^{-1} through 1800-1840 cm^{-1} (acid fluoride or acid chloride derivative), however the kinetic shape obtained is very similar [9].

According to the polymer, other functional groups detected by FT-IR can also be connected to chain breaking (formiates, vinyl groups, aldehydes, etc...).

Chain breakings can also be revealed by other analytical techniques (size exclusion chromatography, viscosity measurements in solution or at the solid state, NMR for the detection of various chain ends (polymer itself, methyl ketones, etc.). The analysis of volatile products by chromatography techniques is also well documented.

Crosslinking

The assessment of crosslinking is not common in most polymer degradations as it is often a minor process however it is a much more important process in the case of elastomer materials. The following analytical techniques can be used both for the crude/not chemically crosslinked or for fully formulated (filled and cured) elastomers of the rubber industry.

Gel content and swelling

Both those techniques are very common in rubber industry to check the efficiency of curing chemically.

We can see on figure **3** that a quite short exposure in accelerated conditions involves a significant crosslinking of EPDM [10], in fact the efficiency of this crosslinking is similar to this of chemical crosslinking. Oxidation/chain scissions are in fact produced approximatively at the same time even if some differences can be observed according to the polymer involved (see for example [11, 12]). When the exposure is longer, we can see a slow change of the crosslinking values corresponding to the progressive contribution of chain scissions.

Density of a polymer solution

By using a precise densometer (Antonn Paar DMA 58 for example) it is possible to observe (see figure **4**, [13, 14]) that the density of a polymer solution (uncrosslinked polymer + solvent) is decreasing quickly upon accelerated photo-ageing because of the formation of a crosslinked/unsoluble polymer. The final density becomes very close to this of the pure solvent however for longer exposure times we can see again an increase of the solvent density because the formation of short/soluble polymer chains derived from chain scissions.

Ability to crystallise

When a crude uncrosslinked polymer presents initially a crystalline part, its ability to crystallise will be reduced if crosslinking occurs, then analytical techniques like SAXS or DSC can be tools to follow crosslinking upon ageing [15-16]. Figure **5** [15] illustrates for example the loss of cristallinity upon ageing for EPDM and poly-cyclooctene.

DSC of the swelling solvent:

By DSC it is often possible to distinguish the thermodynamic properties of a solvent when it is (confined) or not (free) included in the mesh of a physical network. Then DSC can be used to follow the crosslinking as the temperature shift (freezing point) of the confined solvent is increasing when the crosslinking level increases (another consequence is the decrease of the area of the band upon crosslinking as the mesh being smaller and smaller, the amount of confined solvent is progressively reduced. Figure **6** [11] illustrates the case of cyclohexane used as swelling solvent upon accelerated photo-ageing of crude/uncrosslinked NR and SIR. An advantage of this analytical technique is to be also applicable to the case of initially (chemically) crosslinked polymers. In this case the confined solvent is observed initially and the ageing results in an increase of crosslinking (post-crosslinking). See also [13].

Porous size determination of the mesh:

By using thermodynamic calculations including thermodynamic parameters of the solvent it is possible to convert the DSC shift into a more interesting parameters i.e. the size and the porous distribution of the mesh. The following scheme describe the main results of the papers [18, 19].
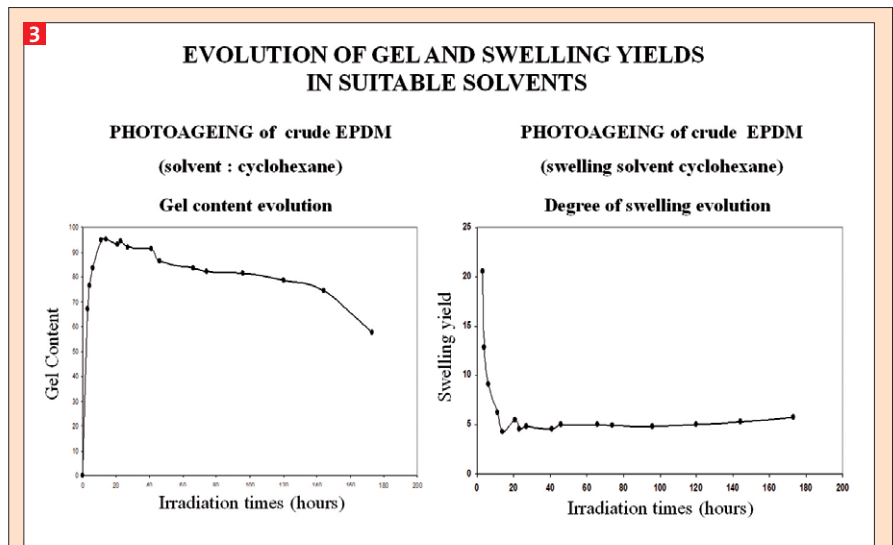

Fig. 3: Gel content and swelling assessment of crude EPDM upon accelerated photoageing (from [10]).
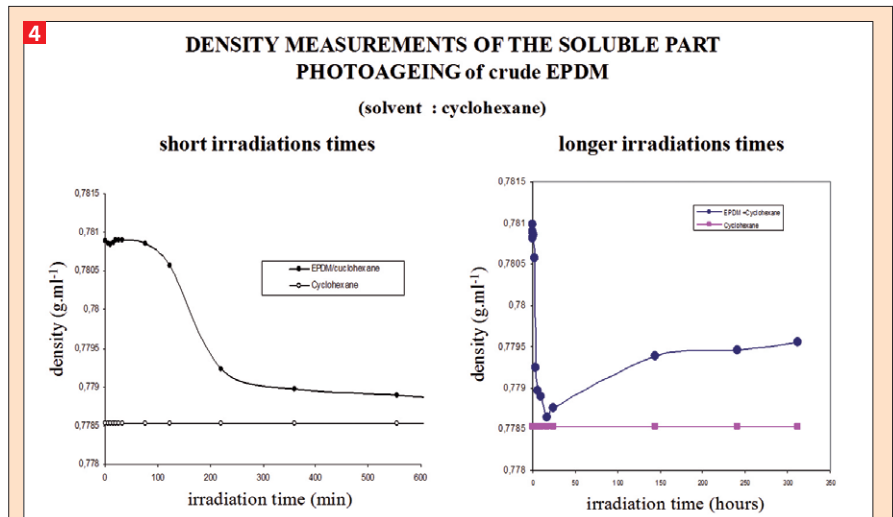

Fig. 4: Assessment of the density of a solution of uncrosslinked EPDM upon accelerated photoageing (from [13]).
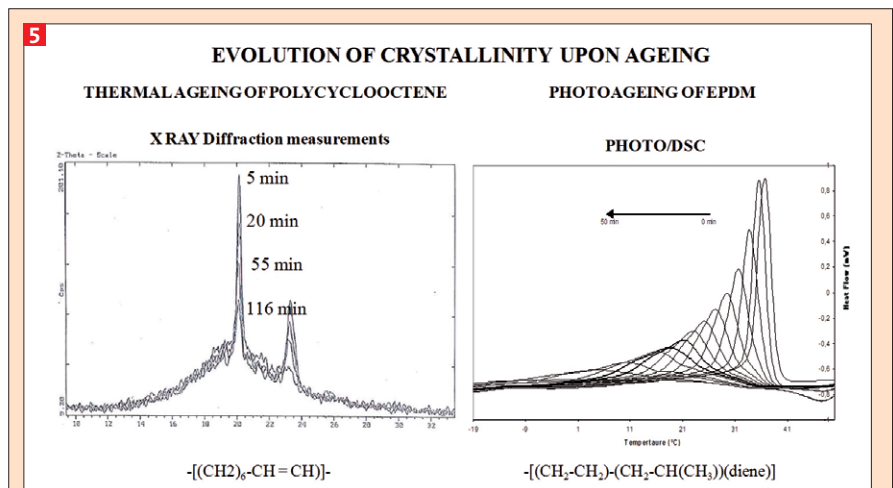

Fig. 5: Assessment of cristalliny of polycyclooctene (SAXS) from [15] and EPDM (PhotoDSC from [17]) on thermal and photoageing.
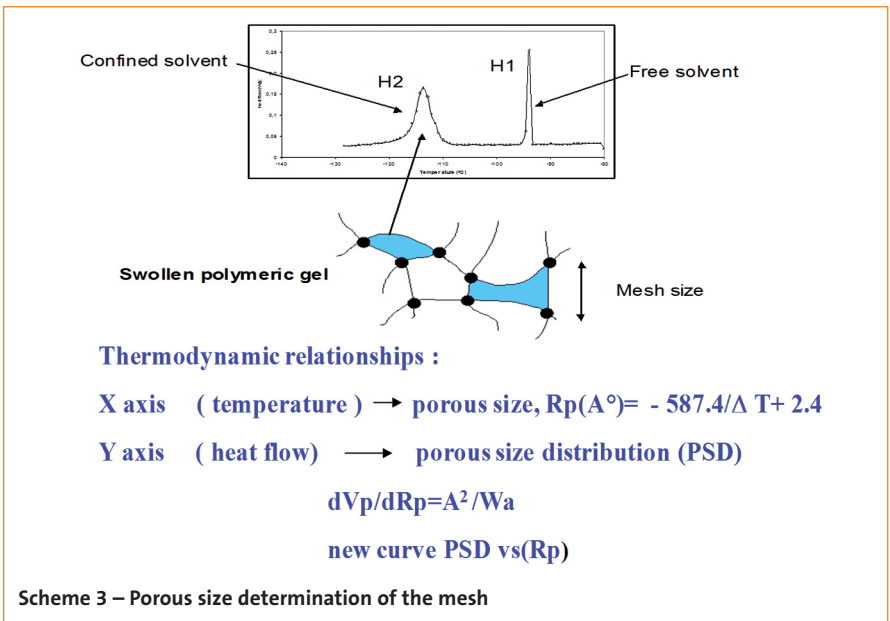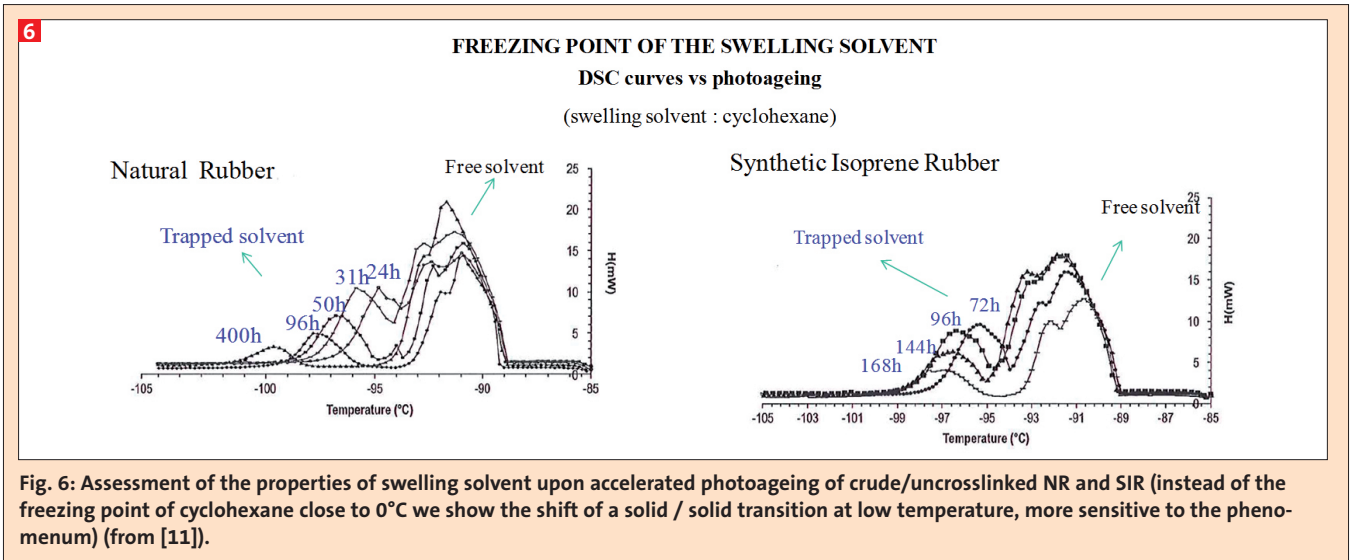
Fig. 6: Assessment of the properties of swelling solvent upon accelerated photoageing of crude/uncrosslinked NR and SIR (instead of the freezing point of cyclohexane close to 0°C we show the shift of a solid / solid transition at low temperature, more sensitive to the phenomenum) (from [11]).

Thermodynamic relationships :

X axis (temperature) ⟶ porous size, $Rp(A°)= - 587.4/\Delta T+ 2.4$

Y axis (heat flow) ⟶ porous size distribution (PSD)

$$dVp/dRp=A^2/Wa$$

new curve PSD vs(Rp)

Scheme 3 – Porous size determination of the mesh

Fig. 7: Porous size distribution of the mesh after accelerated photoaging of crude NR and IR (from [11]).

Figure **7** gives one example on NR and synthetic IR ageings.

Another example is given (figure **8**, [20]) with a chemically (peroxide) cross-linked silicone upon curing time at 170 °C. As expected, porous size is higher for short curing time.

On figure **9** we can see that the method can also be applied to check the profile of crosslinking across the thickness and to check the efficiency of ageing to complete the crosslinking in the core.

Rheological approach:
Melt viscosity measurements can also detect both chain scissions and crosslinking upon ageing. On figure **10** is reported the cases of crude (uncrosslinked) polycyclooctene, SIS and NR elastomers. The gel point can be determined approximately by measurement of tan δ at several frequencies or more accurately by the Cole-Cole approach [21].

Another interesting aspect of the duality of chain scissions/crosslinking in elastomers is their assessment at various temperatures and in the presence of stabilizers.

The following scheme (4) compares the general mechanism of environmental degradation of elastomers (described before) with the main effects of stabilisers currently used in rubber industry. Anti-oxidants for example are expected to inhibit all radical reactions involved both in chain breaking and crosslinking, then their efficiency can be observed in both cases.

On the example given on figure **11** [23] effectively we can check that both the gel time (crosslinking) measured by
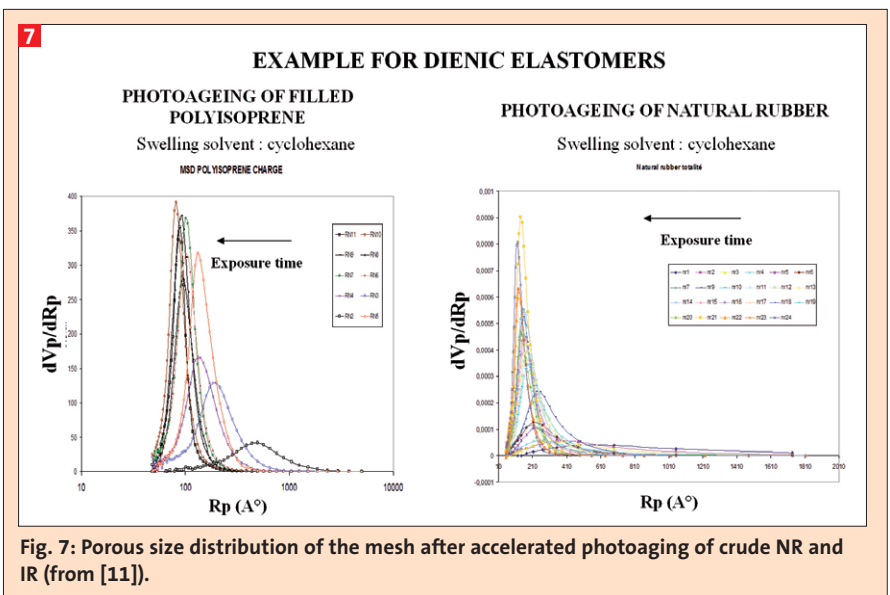
rheology and the induction time (chain scissions) measured by infrared spectroscopy are increasing with temperature decrease or with stabilisers efficiency.

Conclusion

Chain breaking is a general phenomenon occurring during the environmental ageing of any polymer (however negligible in the case of conventional silicones), it can be characterised by a lot of experimental techniques including non destructive methods like FT-IR spectroscopy. The chain breaking is generally characterised by the formation of oxidised functional groups like carboxylic acids, chain end ketones and unsaturated groups and is reinforced in the case of photo-ageing by the photolysis of ketones by Norrish reactions.

Crosslinking is another way of environmental degradation but particularly important in elastomers. Dienic elastomers and EPDM (based on ENB termonomer) develop crosslinking both in thermal and photo-degradation and the level obtained on crude polymers is very similar to this reached by chemical crosslinking (peroxide or sulfur based). The post crosslinking occurs too in the case of already cured elastomers but it can be revealed by a limited number of experimental techniques (DSC/thermoporosimetry, rheology or other physical methods). It can be noticed that crosslinking and post-crosslinking can also be observed in the case of silicones ageing [20, 24, 25]. In addition of elastomers, more and more polymers are suspected to develop crosslinking besides chain breaking during environmental exposure; in our group this property was for example recently pointed out during the ageing of PET [26], PBAT [27] (biodegradable), TMPC [28], PVK [29].

Last but not least it can be proved that both phenomena are concomitant during thermal and photo-ageing. Reducing chain breaking by reducing the thermal ageing temperature or by adding stabilizers results in reducing crosslinking in the same proportion.
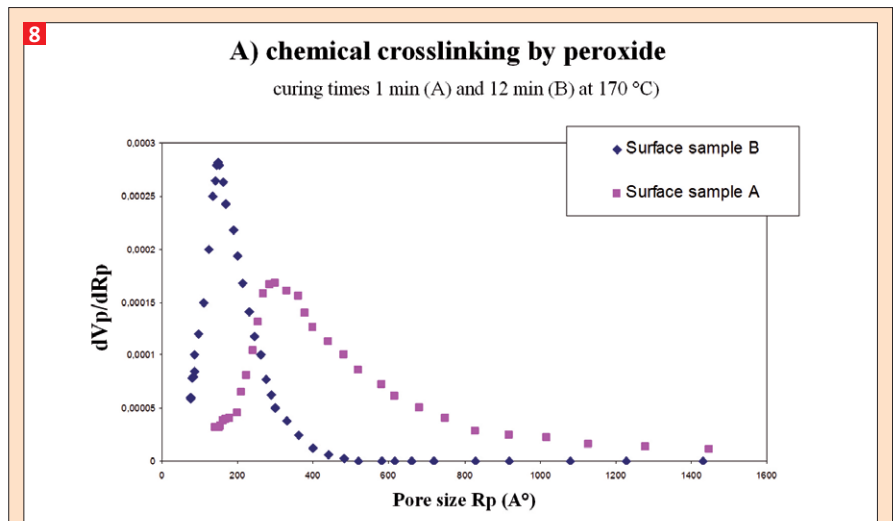
Aknowledgments

Fig. 8: Assessment of porous size distribution upon peroxide ageing of PDMS (from [20]).

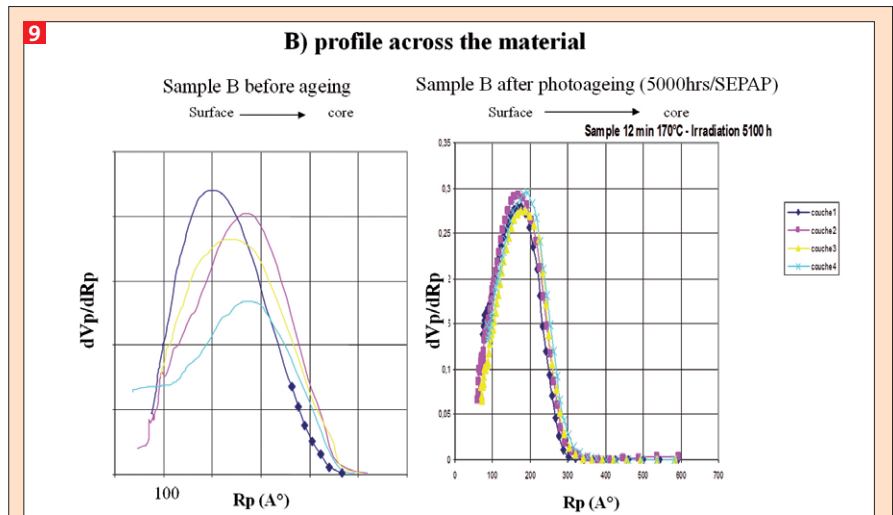**Fig. 9: Profile of the porous size distribution of PDMS across the thickness and effect of accelerated photoageing (from [20]).**

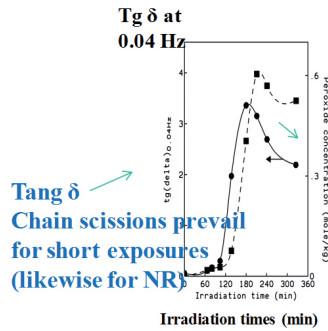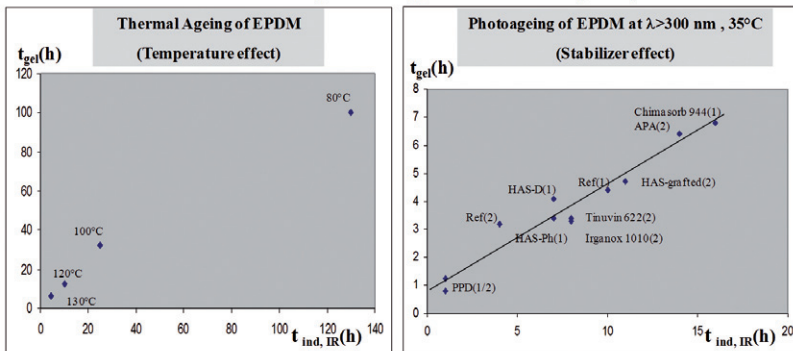Scheme 4 – General Mechanisms of Polymer Ageing – Stabilization Strategy

Fig. 10: Assessment of crosslinking and chain scissions upon accelerated photoageing of polycyclooctene , SIS and NR (from [21-22])

Fig. 11: Effect of temperature and stabilisers on both chain breaking and crosslinking (from [23]).

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