

THE ADHESION OF LSR THERMOPLASTIC COMPOSITES AFTER STORAGE TESTS

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Abstract

The adhesion properties of liquid silicone rubber (LSR) and different thermoplastics (PC, PA, and PP) were examined in this investigation. In order to guarantee the adhesion of both components, an activation (silicization) of the TP surface, which is a conventional method, was carried out. Furthermore, the long-term stability of the silicization (storage of the activated surfaces) as well as the wetting behavior were investigated. Moreover, microscopic investigations were performed to analyze the activated thermoplastic surfaces. The test specimens were produced on a 2-component injection molding machine. In accordance with the guideline VDI 2199, the peeling resistance was determined and the results were compared.

Introduction

Owing to their excellent properties (low weight, inexpensive manufacturing costs, formability and chemical stability), plastics have become indispensable in today's world. Since their introduction, many plastics have been substituted, combined, or modified. Common areas of application for plastics are the electronics, the automotive, and medical technology industries [1] [2].

In addition to conventional components that consist of one plastic, components consisting of multiple components are also a significant group. For example, components manufactured using multiple component injection molding methods replace bonding two materials together. This method has become common for thermoplasts and thermoplastic elastomers. The positive properties of both composite partners can be specifically combined and utilized [3].

One class of multiple-component composites is that of the hard-soft composites. Their range of applications extends from ventilation valves in the automotive industry, shower heads for sanitary fixtures, all the way to components in medical technology [4]. A thermoplastic (TP) is usually employed as the hard component in order to provide the required stiffness. In contrast, an elastic component is suitable for the soft component, since it provides functions such as sealing and damping. For this purpose, materials such as thermoplastic elastomers (TPE) or natural rubber and silicones, i.e., liquid silicone rubber (LSR), are selected [5].

To achieve adhesion in the composite made of a TP and a LSR component, mechanical anchors can be utilized in form of undercut, or, depending on the material compatibility, adhesion mechanisms. The material selection plays a particularly decisive role in regards to adhesion, because selecting a bonding agent that is incompatible with the substrate can lead to insufficient composite adhesion [6]. Various options are available for guaranteeing or increasing adhesion between paired materials.

First, the TP surface can be pre-treated by means of activation. Second, material modifications can be achieved by incorporating additives [7]. Self-adhesive silicone types are very common, and contain additional organofunctional silanes (amino-, epoxy-, glycidoxy-, metacryloxy silanes or others). They function as a bonding agent between the inorganic Si-O chains of the silicone and the functional groups of the thermoplast [8]. They are suitable for polyamides (PA6, PA66) or polybutylterephthalate (PBT) [9].

This enables hard-soft composites with LSR to be produced inexpensively in one step for a wide range of applications. However, in the case of some material combinations, using adhesive LSR types is not effective, and no adhesion occurs between the two components. For instance, this is true for mass plastics like polypropylene (PP), and also partially applies for polycarbonate (PC). This could be attributed to a lack of functional groups on the surface of the thermoplast. Yet, it is also possible that the bonding agent incorporated into the LSR does not possess any functional groups for the development of covalent bonds [10].

In order to increase the adhesion or even achieve adhesion between a LSR and thermoplast, various surface activation methods can be employed, such as flame treatment and plasma activation. Surface activation results in new functional groups on the surface of the thermoplast, which, in turn, lead to an increase in the surface energy. As a result, improved adhesion is attained [11] [12] [13] [14].

Silicization

The silicization method is a modification of flame treatment. Substances containing silicon (precursor) are additionally burned in the flame. Burning the precursor results in particles depositing like ash, which can be regarded as a highly reactive glass layer. The

silicate layer that develops (20-40 nm thick) is created by the deposited product of flame pyrolysis. This leads to an increase in the surface energy, which, in turn, can lead to an increase in the degree of adhesion [15].

Objectives

The adhesive properties of liquid silicone rubber (LSR) and different thermoplastics (PC, PA, and PP) were examined in this investigation. In order to guarantee the adhesion of both components, an activation (silicatization) of the TP surface, which is a conventional method, was carried out. Furthermore, the long-term stability of the silicatization (storage of the activated surfaces) as well as the wetting behavior were investigated. Moreover, microscopic investigations were performed to analyze the activated thermoplastic surfaces. The test specimens were produced on a 2-component injection molding machine. In accordance with VDI 2019, the peeling resistance was determined and the results were compared.

Experimental

Material Selection

Three thermoplasts were selected as the hard component for the following examinations (Table 1). A self-adhesive LSR (Silopren LSR 2742, Momentive Performance Materials, medical grade) was used as the soft component.

Table 1. Employed thermoplasts

Material	Brand Name	Company
Polypropylene	PP Sabic 575P	Sabic
Polyamide	Ultramid B3S	BASF
Polycarbonate	Calibre Meg-arad 2081	Trinseo

Production of Thermoplastic Plates

The thermoplastic plates were produced on the fully electric, multi-component injection molding machine Arburg Allrounder 370A 600-70//70 (600 kN clamping force, Arburg GmbH & Co KG, Loßburg, Germany). The injection unit layout was set up in an L-layout (main axis: liquid, tempered LSR injection aggregate; side axis: thermoplastic aggregate) and included a robotic system. After the thermoplastic plate had been injection molded, it was removed by hand, and, subsequently, silicatized.

Silicatization of the Thermoplastic Plates

Silicatization was carried out using a hand-held flame treatment device (GVE2/HB, SURA Instruments GmbH, Jena, Germany). The employed Pyrosil gas cartridges contain a propane-butane mix with activating components (tetramethylsilane). A flame with a high temperature (1300°C) completely converts the contents of the gas cartridge into silicate particles [16].

A mobile slide was equipped with a flame-proof plate for the following test. The burner of the flame treatment device was attached to a cross bar with an adjustable height. This enabled the testing speeding and distance to the flame to be maintained. A speed of 0.4 m/s was selected for the following tests, as was a distance from the flame of 15 mm.

Microscopy – Confocal Laser Microscope

Microscopic analyses were performed with a confocal laser scanning microscope (confocal scanning laser microscope LEXT, OLS3100/OLS3000, Olympus) in order to examine the roughness of the surface after surface activation. For this purpose, the plates were directly examined with the microscope. Further preparation of the specimens was not required. All of the thermoplasts were examined using the same level of magnification (500x).

Contact Angle Measurements

All activated thermoplasts were stored (0, 1, 3, 7, 14, 21, 28 day(s)) to analyze their long-term stability, and, subsequently, their contact angles on their surfaces were measured with a contact angle measurement device (EasyDrop DSA 20B, Krüss GmbH, Hamburg, Germany) using the drop shape analysis method in order to examine the wetting behavior (DIN 55660-1). For this purpose, a syringe that is attached to the device injects a water droplet onto the surface of the thermoplast. This action is recorded by a camera. The contour of the drop is recorded by the camera, and software determines the three-phase angle (at the solid/liquid/gaseous boundaries of the test liquid).

If the contact angle equals 0°, complete wetting is present. A contact angle ranging between 0° < Θ < 90° (partial to good wetting) is considered defined wetting. No wetting is present if the contact angle is $\Theta \geq 180^\circ$.

FTIR Spectroscopy

Additional examinations of the surface activation prior to and after storage were performed using Fourier transform infrared spectroscopy (FTIR spectroscopy) with an FTIR spectrometer (Shimadzu, IRAffinity -1S). The specimens were examined using attenuated total

reflection (ATR). This method utilizes the total reflection at the boundary between two optically differing media (crystal and specimen). The specimen to be examined is brought into optical contact with a crystal (here ZnSe, 45°), which possesses a higher refraction index than the specimen.

If the IR beam in a crystal touches the boundary of the specimen at a slant, it will be reflected back into the crystal. The intensity of the light reflected back into the crystal is measured, and enables deductions about the absorbing medium to be made.

Non-activated and activated specimens were measured and compared for the following examinations. The measurements of the thermoplastic plates were performed without prior specimen preparation. The specimen was pressed unto the sides of the crystal using a pressing plate and pressing block, and was then measured.

Peeling Test According to VDI 2019

The produced specimens were overmoulded with adhesive LSR in the injection molding machine (measurements of the test specimens: thermoplastic plate: 150 mm x 50 mm x 2 m; LSR loop: 210 mm x 20 mm x 2mm). In accordance with VDI 2019, the peeling resistance of all materials was tested on a tensile testing machine (Hegewald & Pescke 5 kN, speed: 100 mm/min). Five test specimens were tested per batch. Figure 1 shows the employed test specimen geometry utilized in accordance with VDI 2019.

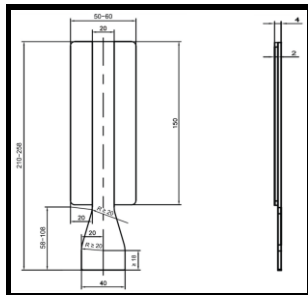


Figure 1. Specimens according to VDI 2019 with 1: hard component, 2: soft component [17].

Results and Discussion

Microscopy – Confocal Laser Scanning Microscope

Figure 2 depicts the microscopy results. The average roughness depth Rz was determined. The silicized PP plates displayed significantly lower values than the untreated plates. An evident regression of the surface roughness after silicization was also verifiable in the

case of PA and PC. The activation of the surface created an alteration in the topography of the surface. The transfer of the contour of the tool onto the component also reduced. A smoother surface might benefit improved adhesion between the thermoplast and the LSR [18].

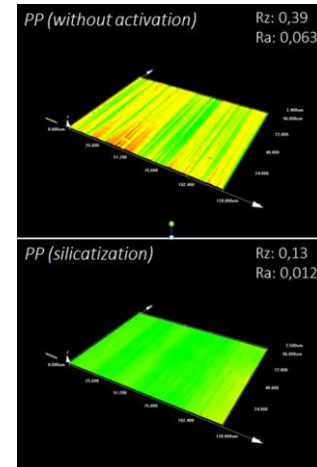


Figure 2. Microscopic image of PP without activation (top) and silicized PP (bottom)

Table 2. Comparison of Surface Roughnesses

Material	Without Silicization	With Silicization
Polypropylene	Rz: 0.39	Rz: 0.13
Polyamide	Rz: 1.21	Rz: 0.99
Polycarbonate	Rz: 0.77	Rz: 0.12

Contact Angle Measurements

Figure 3 provides an overview of all thermoplasts measured prior to and after surface pre-treatment, and includes all images of the contact angles. In the case of untreated specimens, non-polar behavior was observed (high contact angle), which is to be attributed to poor wetting. After silicization, all three thermoplasts displayed a significantly reduced contact angle (indicated with “0 days”, which means measurement directly after surface treatment), which is an indication that the wetting behavior improved. In particular, PP displays a relatively constant wetting behavior for one to three days of storage after pretreatment. After four weeks of storage (28 days), a significant increase in the contact angle was recorded for all materials. However, it was lower than in the inactivated thermoplasts.

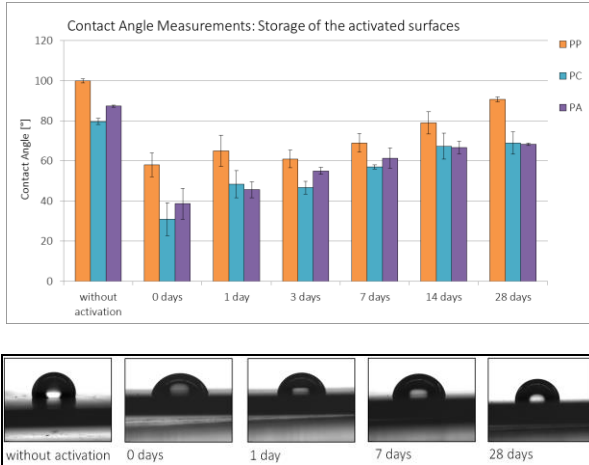


Figure 3. Storage of activated thermoplasts: Measurement of the contact angle

FTIR Spectroscopy

Figure 4 illustrates the results of the FTIR spectroscopy by providing an example of activated PP prior to and after 28 days of storage. After storage, the silicon bonds decreased considerably in the range 1090-1030 $[\text{cm}^{-1}]$, and the Si-NH₂ bonds regressed in the range 1250-1100 $[\text{cm}^{-1}]$. The results for PC were analogous to this, and similar tendencies were observed. In the case of PA, the regression of the bonds was not as pronounced.

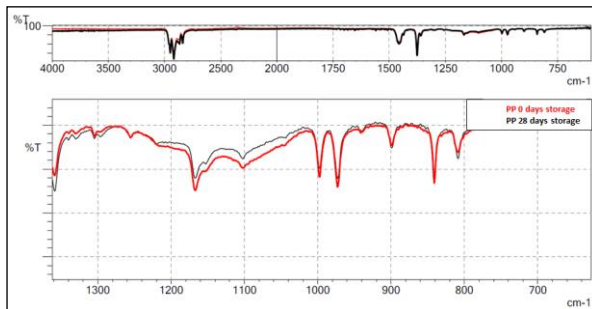


Figure 4. FTIR spectrum of activated PP prior to and after 28 days of storage

Peeling Tests According to VDI 2019

Figure 5 presents the results of the peeling tests performed in accordance with VDI 2019. As was to be expected, an adhesive bond was only able to be achieved for PA with the LSR without activation. After surface activation, all three materials achieved peeling resistances of 3N/mm.

The polypropylene values already began to decline after one day, but remained at a similar level after three to fourteen days of storage. In the case of PA and PC, a small increase in the values was initially observable.

The PC specimens remained stable up to fourteen days, but their values then declined. The PA composites displayed no significant changes during storage, and were still stable after having been stored for four weeks.

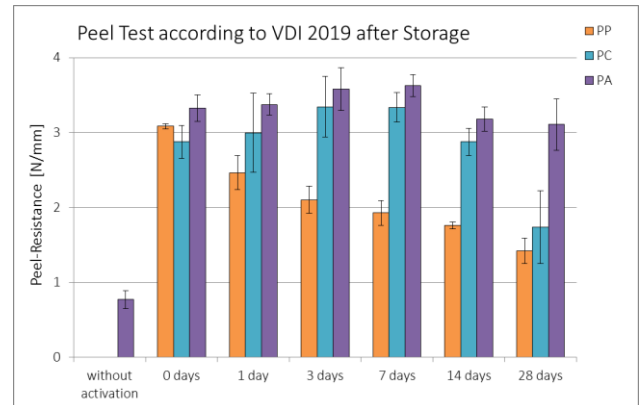


Figure 5. Peeling resistances of activated thermoplasts after storage (no adhesion for PP and PC without activation)

Conclusions

The results illustrate that silicization methods can be used to create adhesive bonds with very good strengths in PP and PC with LSR. The values of the PA specimens were able to be increased considerably by means of surface activation. The microscopic examinations revealed that the surface roughness of all employed thermoplasts declined significantly after surface activation had been performed. The smoother surface enabled better adhesion between the thermoplast and LSR [18].

The results of the contact angle measurements provided proof that the contact angles of all of the employed thermoplasts reduced extensively after activation. The reduction of the contact angle (increase in the surface polarity) increases the surface energy, which, in turn, may have led to an improvement of the adhesive properties on the surface [19]. Furthermore, the contact angle remained stable up to three days after storage. After four weeks of storage, an increase in the values of all thermoplasts was evident.

The FTIR analyses revealed that the created chemical bonds regress in PC and PP after four weeks of storage. In the case of PA, the differences were less pronounced after zero and four weeks of storage.

Of the produced composites, PP displayed sinking values after one day of storage in terms of its peeling resistance. The values remained on one level for up to two weeks. However, after four weeks, a clear regression was observable in comparison to the results obtained directly after injection molding. The peeling resistances of PC remained stable for up to two weeks, but then decreased after a storage period of four weeks.

PA did not display any noteworthy changes throughout the entire storage period.

The results of the FTIR analysis confirmed this as well. They show that composites of LSR and thermoplastics display a high level of potential owing to the silicization method. In addition to the common material pairing of PA with adhesive LSR, surface activation also enables materials like PP and PC to achieve a strong bond.

This opens doors to new areas of application (i.e., replacing bonding of two materials) and represents opportunities to optimize already existing products. Furthermore, new material combinations enable cost savings for materials (compare PP at 2 Euro/kg and PA at 6 Euro/kg) and manufacturing (manufacturing is completed in one step). In the future, the manufacture of new material combinations may create new markets. The continuously newly developed variations create a future-oriented material, which can compete with conventionally employed material groups on the market.

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