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UV Pre-Treatment for Polycarbonate for Bonding LSR in a Multi-Component Injection Molding Process

In this study, the influence of UVC radiation and the influence of ozone on the surface energy of specimens made of polycarbonate were investigated. In an additional step, the peeling resistance of silicone flaps, which were overmolded, onto pre-treated PC plates of multicomponent specimens were analyzed. For this purpose, the samples were exposed to UVC radiation for different lengths of time, ranging from 5 s to 3600 s. To further evaluate the influence of the ozone created by the UVC in the presence of oxygen, treatments were also performed in pure oxygen and nitrogen atmospheres. Contact angle measurements as well as analyses of the surface roughness were carried out to evaluate the effect of the treatment. Two phenomena were identified during the investigations. In room air and oxygen atmospheres, a short-term effect of UVC radiation was observed, which led to an increase in the surface energy, and, therefore, also to an increase in the wettability after an exposure time of only 10 s. In addition, a long-term effect was also found when tests were performed in a nitrogen atmosphere. This effect became visible after at least 60 s, and increased over the course of the duration exposure. The surface roughness of the polycarbonate plates increased up to about 60% after 10 s of UVC exposure time in an air atmosphere, after 300 s of exposure to UVC radiation the roughness values had more than doubled. A modular injection molding tool was designed for the production of multi-component specimens. In this tool, a thermoplastic plate is molded on the one side, and is then automatically transferred by a robot system to be overmolded with silicone on the other side. The employed injection molding technique makes an intermediate treatment, such as surface activation of the thermoplastic plate, possible before it is overmolded. Also, the short-term and long-term effects of UVC treatment were able to be verified again for the peeling resistance of the material. These tests were only carried out for specimens treated in air.

1 Introduction

By using diverse materials, various properties are able to be integrated in multicomponent parts. For example, in these applications there may be hard components that provide the required stability and soft components that function as sealing or shock absorbing elements.

These processes are well-established for the production of thermoplastic components. One of the most common applications are probably tooth brushes, which are made of a hard, solid body that is overmolded with a softer thermoplastic material for a better grip (van Onna, 2003).

When it comes to technical applications that have higher requirements for the employed materials, thermoplastic elastomers (TPEs) reach their limits. Silicones are much better suited for such requirements. They are characterized by highly reversible elastomeric behavior, good temperature resistance (long-term 180 °C, short-term 250 °C), and good flexibility at temperatures as low as -50 °C. Furthermore, silicones show high resistance against chemicals, weather conditions and aging. Additionally, they are harmless from a physiological point of view, which makes them very interesting for medical applications (Briehn, 2011; Clarson, 2009).

Parts consisting of thermoplastic and silicone components can also be produced using multi-component injection molding techniques. There are several variations of these processes, what make them suitable for different applications with their respective requirements. One possibility is the overmolding of previously inserted parts. This approach provides the opportunity to separate both injection molding processes, and to include an intermediate step to enable a pre-treatment of the thermoplastic part before it is overmolded with the silicone (Pruner und Nesch, 2012; Baumgart et al., 2014; Holländer et al., 2010; Mathieson und Bradley, 1996; Roth-Fölsch, 2011).

Due to the varying morphological material characteristics, the creation of a strong bond between the different components is still challenging. Different theories exist that attempt to explain how these combinations could work. For each approach, maximal approximation of both component surfaces is the basic prerequisite (Potente, 2004; Schuck, 2008; Müller and Rath, 2004; Prokop, 2011; Habenicht, 2009).

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2 Objectives

The overall objective of this research was to find ideal conditions for creating multi-component parts consisting of silicone and polycarbonate by bringing their surfaces to maximal approximation to achieve excellent bonding. This study also aimed to activate the surface of polycarbonate specimens using UVC radiation in order to achieve optimized wettability.

For this purpose, a chamber was used in which specimens could be exposed to UVC radiation. The duration of the exposure was set between 5 s and 3600 s. As is well known, ozone is formed by UVC radiation (Wöhrle et al., 1998; Rabek, 1996). This effect was also taken into consideration in the test setup as pre-conditioning took place in different atmospheres. The effect of the exposure to UVC radiation was quantified by contact angle measurements.

3 Experimental

In the following, the employed materials, the test setup with the UVC radiation chamber, the possibility to use different gas atmospheres, the contact angle measurement method, and the multi-component specimen geometry are described.

3.1 Materials

Calibre Megarad 2081 polycarbonate (Trinseo Deutschland GmbH, Boehlen, Germany) was used in this study. Calibre is a medical grade, which can be sterilized by gamma radiation. For this reason, it is used in numerous medical applications and therefore is sought after for use in multi-component parts.

For the peeling tests, the PC plates were overmolded with four different grades of commercially available liquid silicone rubber. They included Silopren LSR 2040 from Momentive Performance Inc., Waterford, NY, USA, QP1-40 from Dow Corning GmbH Schwalbach/Ts., Germany, and Silpuran 6000/40 from Wacker Chemie AG, München, Germany. They are all non-self-bonding grades. Furthermore, Silopren 2740 from Momentive Performance Inc. was used as a self-bonding grade.

3.2 UVC/Ozone Treatment

The UVC/ozone treatment was carried out with a UVC chamber similar to the ELG100 s sold by Dinies Technologies GmbH, Villingendorf, Germany. Figure 1 shows a UVC chamber similar to the one that was used for the treatment performed in this study. It also shows the special sockets which were additionally implemented to flood the interior space with different gases. Figure 2 shows a schematic cross section of the internal setup of the UVC chamber. It is equipped with two U-shaped UVC lamps, where the specimen is placed beneath in the middle in a distance of 21 mm to the lamps. The whole length of the specimen is exposed to the lamps.

Tests were performed with differing exposure times and in different gas atmospheres. Table 1 shows the exposure times of the polycarbonate specimens in the different gas atmo-



Fig. 1. UVC chamber with additional sockets for flooding in gases (Dinies Technologies GmbH, Villingendorf, Germany)

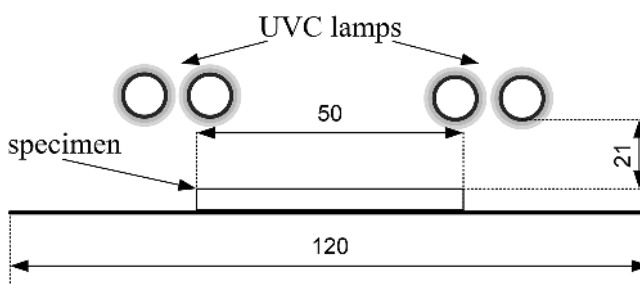


Fig. 2. Scheme of the internal setup of the UVC chamber

Time s	Air	Oxygen	Nitrogen
0	×	×	×
5	×	×	×
10	×	×	×
30	×	×	×
60	×	×	×
120	×	×	×
240	×	×	×
300	×	×	×
600	×	–	–
1800	×	–	–
3600	x	–	–

Table 1. Treatment conditions ($n = 5$)

spheres. Contact angle measurements were performed for special example configurations.

3.3 Test Methods

3.3.1 Contact Angle Measurement

Figure 3 illustrates the degree to which a droplet spreads on a surface. The angle that is formed by the tangent of the droplet and the solid surface at the boundary of the solid, liquid and vapor phase is called contact angle α .

Owing to thermodynamic principles, each phase strives to minimize its surface. Therefore, a specific surface tension between the single phase interfaces is created. At the point of intersection, these tensions – solid/liquid (γ_{sl}), solid/vapor (σ_{sv}) and liquid/vapor (σ_{lv}) – are at an equilibrium in vectorial relation, see Eqs. 1 and 2 (Young, 1805).

$$\sigma_{sv} = \gamma_{sl} + \sigma_{lv} \cdot \cos \alpha, \quad (1)$$

$$\cos \alpha = \frac{\sigma_{sv} - \gamma_{sl}}{\sigma_{lv}}, \quad (2)$$

In accordance with the fundamental interaction forces, these interphase energies can be separated in disperse and polar fractions, see Eq. 3 (Kaelble, 1970; Owens und Wendt, 1969; Rabel, 1971).

$$\sigma_i = \sigma_i^{\text{disp.}} + \sigma_i^{\text{pol.}}. \quad (3)$$

The method of the equation of state according to Neumann was used to calculate the overall surface energy, and the measurements were carried out using distilled water (Li und Neumann, 1992). An EasyDrop device manufactured by Krüss GmbH, Hamburg, Germany, was used for the measurements.

3.3.2 Surface Roughness

Furthermore, the surface roughness of the polycarbonate plates was analyzed. Measurements took place without pretreatment, after 10 s and after 300 s of exposure to UVC radiation in an air atmosphere. For the analysis a confocal laser scanning microscope of the LEXT type from Olympus was used.

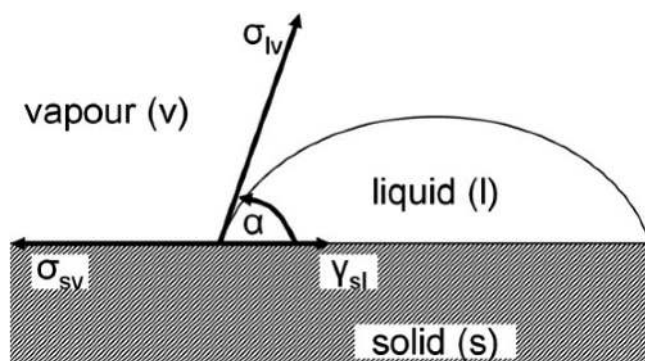


Fig. 3. Illustration of a droplet on a surface and the corresponding contact angle (Young, 1805)

Measurements were performed parallel as well as across the longitudinal axis of the PC plate. Same effects were found for both directions, but due to the machining structure they were even more obvious in the values of the measurements across the longitudinal axis. Therefore in this work only these results are shown.

3.3.3 Peeling Test

The approach presented in the VDI 2019 guideline “Testing the Adhesion of Thermoplastic Elastomers (TPE) on Injection-Molded Substrates” was chosen for testing the material composites, which consisted of thermoplastics and LSR.

VDI 2019 describes the testing of multi-component specimens that consist of a thermoplastic and an elastomeric part, and which were made using injection molding. Other standards, such as DIN ISO 813 or DIN EN 1464, deal with material composites made by means of gluing or other joining techniques (Stenglin, 2011). Although VDI 2019 mainly deals with thermoplastic elastomers, it is applicable for injection molded parts with liquid silicone rubber.

Figure 4 shows the peeling test specimen described in VDI 2019. It consists of a thermoplastic plate that was overmolded with the elastomeric component. The elastomeric component has a flap for clamping it in the testing machine and to perform the peeling test. The thicknesses of the thermoplastic component as well as that of the elastomeric component equals 2 mm.

According to VDI 2019, the adhesive strength between both components is quantified by a peeling test. Figure 5 shows the clamping arrangement the specimens were tested with. A specimen is placed in a tensile testing machine, and the flap of the elastomeric component is clamped in the testing machine.

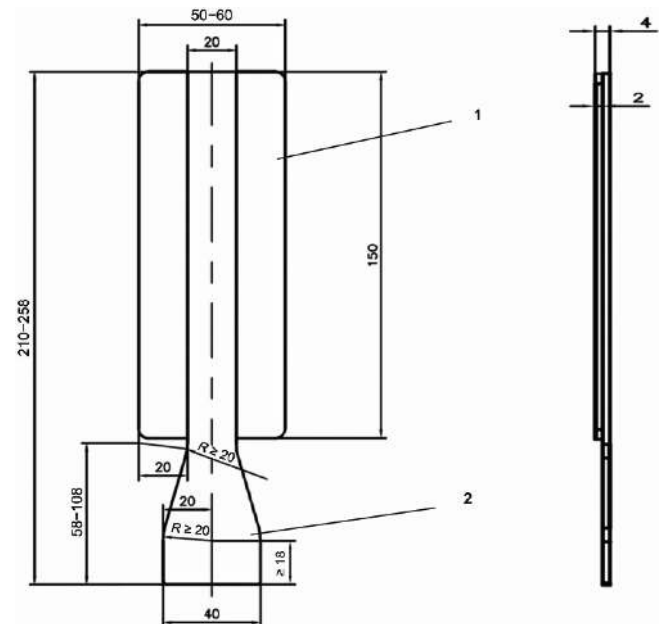


Fig. 4. Drawing of peeling test specimen according to VDI, 2019, 1: thermoplastic component, 2: elastomeric component

As can be seen in Fig. 6, the force of the tensile axis is transmitted by the guide pulley. Owing to this and the moving slide, where the thermoplastic component is fixed, the peeling angle between thermoplastic and elastomeric components is always 90° .

4 Results and Discussion

4.1 Contact Angle and Surface Energy

Figure 7 shows the correlation of the contact angle and the corresponding surface energy with the exposure time of the PC plates to UVC radiation.

The exposure times used for these measurements were the same as those used to produce the peeling test specimen. Furthermore, extreme exposure times of up to one hour were used to better detect the effects occurring within the surface analysis.

It is obvious that the longer the exposure time is, the more the contact angle decreases and, respectively, the surface en-

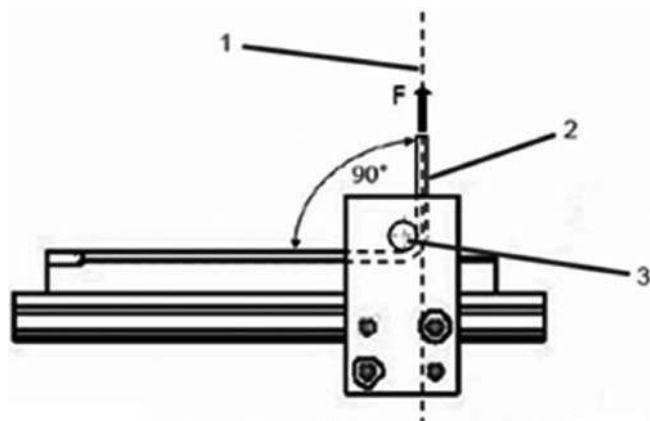


Fig. 5. Specimen/clamping arrangement of VDI, 2019, 1: tensile axis, 2: flap of the elastomeric component for clamping, 3: guide pulley



Fig. 6. Multi-component peeling test according to VDI, 2019

ergy increases. This development takes place until exposure times of up to 1800 s are reached. After that, no further changes in the contact angle or the surface energy can be observed.

In order to clarify whether the surface activation could solely be explained by photochemical reactions, or if the created ozone contributed to the increase in the surface energy, additional tests were performed in oxygen and nitrogen atmospheres. For these studies, the UVC chamber was extended with additional sockets to let in floating gases, as can be seen in Fig. 1.

Therefore, the chamber was flooded with the specific gas for five minutes, then the gas flow was turned off. UVC treatment was started directly thereafter. This approach was chosen to ensure that the treatment took place in a static atmosphere, and in order to exclude flushing processes, which would affect the comparability with the studies performed in room air atmosphere.

Figure 8 shows the contact angle and the surface energy values after different periods of exposure to UVC radiation in an oxygen atmosphere. Previous studies showed that an exposure time of five minutes is sufficient to create relevant effects. Therefore, no tests were performed in this analysis that exceeded an exposure time of five minutes. Figure 9 shows the contact angle and the corresponding surface energy of samples that were treated with UVC radiation in a nitrogen atmosphere. As is evident from the graph provided in Fig. 8, there are only slight differences in the contact angle as well as in the surface energy in specimens exposed to UVC radiation in oxygen compared to those exposed to UVC radiation in air. The progression of the values for the contact angle and surface energy in a nitrogen atmosphere are quite different from those observed in both other environments.

Figure 10 shows the mean value graph of the surface energy of PC plates after UVC treatment in air and oxygen atmospheres and in comparison with the one for treatment in a nitrogen environment.

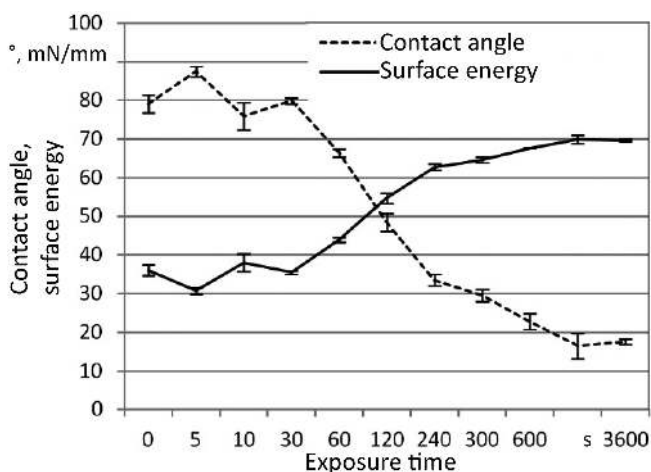


Fig. 7. Contact angle and surface energy in correlation with the period of exposure to UVC radiation in an air atmosphere

Especially for periods of exposure that were shorter than 60 s the progression of both curves is very different. At the beginning a slow decrease of the values can be observed for air and oxygen, then for 10 s of exposure a local maximum is reached. After another small drop the values increase again. For exposure times longer than 120 s the progression of both curves is very similar, while the values of the air and oxygen are about 5 mN/mm higher than for nitrogen.

4.2 Surface Roughness

Figure 11 shows the total as well as the average surface roughness of Polycarbonate plates without exposure to UVC radiation as well as after 10 s and 300 s of exposure in an air atmosphere.

Evidently even 10 s of exposure to UVC radiation leads to a strong increase of the roughness values of about 60%. After 300 s of exposure the roughness values have more than

doubled in comparison to the untreated plates. So not only a chemical, but also a mechanical effect takes place when exposing Polycarbonate to UVC radiation.

4.3 Peeling Resistance of Pre-Treated Multi-Component Specimens

Figure 12 shows the peeling resistance of the silicone flaps of the multi-component specimens originally made from non-self-bonding LSR grades. The polycarbonate plates of these specimens were pre-treated with UVC radiation before over-molding. These UVC radiation pre-treatments were also performed for different periods of exposure, but only in an air atmosphere.

As can be seen, there is a local maximum of the peeling resistance values. This local maximum was recorded for the originally non-self-bonding LSR grades also in the case of a UVC radiation pre-treatment time of 10 s. These grades show

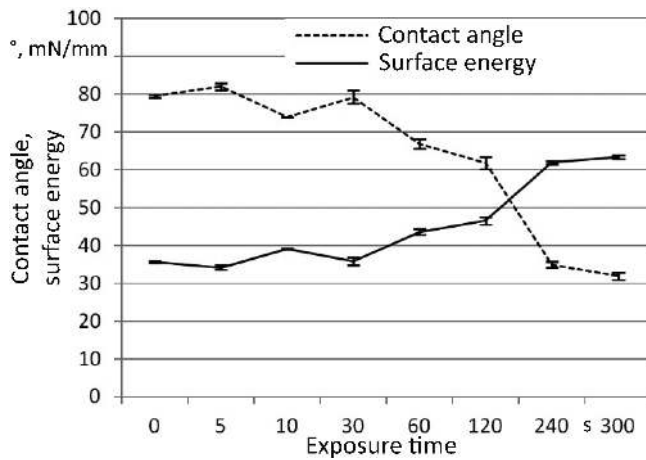


Fig. 8. Contact angle and surface energy in correlation with the period of exposure to UVC light in an oxygen atmosphere

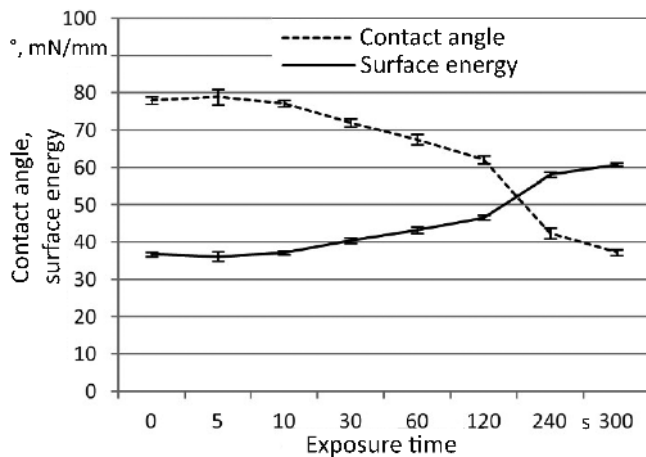


Fig. 9. Contact angle and surface energy in correlation with the period of exposure to UVC radiation in a nitrogen atmosphere

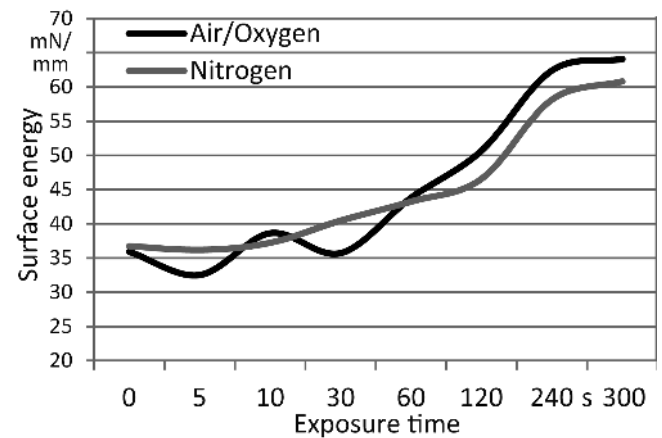


Fig. 10. Surface energy in a nitrogen and the mean value in an air and oxygen atmosphere in correlation with the period of exposure to UVC radiation

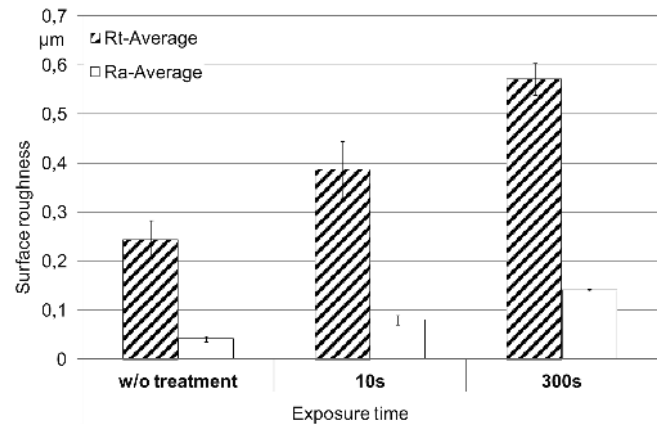


Fig. 11. Surface roughness of PC plates after different periods of exposure

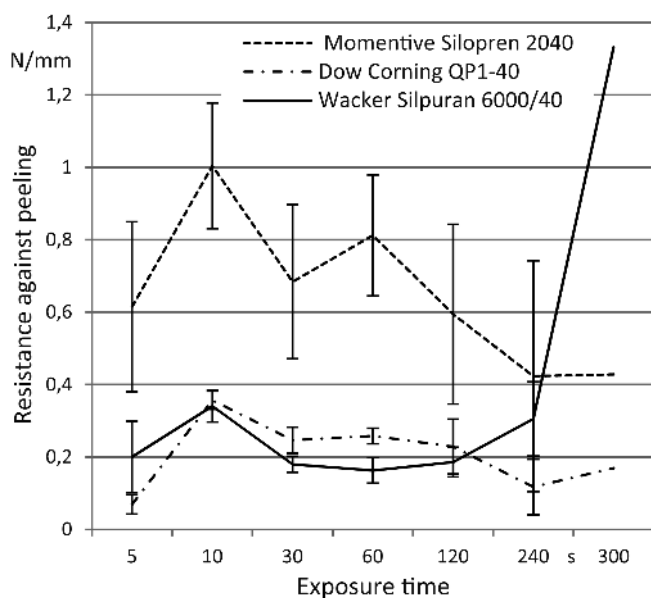


Fig. 12. Peeling resistance of non-self-bonding LSR grades in correlation with the period of exposure

no bonding at all without pre-treatment of the polycarbonate plates, which means the specimens could not be ejected off the mold without being separated. Furthermore, there is a relatively high standard deviation in the results, especially for the values of the Silopren 2040 samples. This standard deviation increases with longer exposure times. In the case of values recorded after 300 s of pre-treatment, the standard deviation is not shown in the graph, because it was manifold larger than the mean values. This tremendous standard deviation results from the fact that cohesive failure takes place in some samples after 300 s of UVC radiation exposure, thus leading to the wide range of the single values.

Apart from the results of the non-self-bonding LSR grades shown in Fig. 12, Momentive Silopren 2740 was also tested. Silopren 2740 is a self-bonding type, which is known to show good bonding when used with engineering plastics like polyamide and polybutylene terephthalate, but it only shows poor bonding when combined with polycarbonate that has not been pre-treated. Cohesive failure occurred in every sample pre-treated with UVC radiation after the peeling test was performed. This means that the silicone itself failed, but not the bond between the silicone and the polycarbonate. The peeling resistance measured for each sample was >3.3 N/mm.

4.4 Discussion

The results of these UVC pre-treatment studies show that there are primary photochemical as well as secondary oxidative reactions that influence the polycarbonate surface, and lead to an increase in the surface energy.

The tests in a nitrogen atmosphere showed that long-term surface activation takes place although no oxygen is present. However, no local maximum was observed in the case of very short exposure times. This local maximum occurred when test-

ing in air as well as in oxygen atmospheres, and can be explained by the presence of oxygen, which reacts due to the UVC radiation impact, creating ozone (Wöhrle et al., 1998). This ozone causes further surface activation.

The long-term effect can be explained by the so-called photo-Fries rearrangement. Due to the photochemical processes that take place, in two different steps phenol groups form (Rabek, 1996). Kim et al. (2013) also investigated the impact of UV radiation on polycarbonate. They treated samples with UVC radiation using a wavelength of 254 nm. By means of x-ray photoelectron spectroscopy, they were able to verify an increase in the number of C-O-H groups (286,5 eV), which is strong evidence of the described photo-Fries rearrangement. Furthermore, they found additional carbon-oxygen cleavage products (C=O at 287,6 eV and O-C=O at 288,8 eV), which is additional proof of strong surface activation.

Measurements of the surface roughness of untreated plates and of plates exposed to UVC radiation showed that there is also a mechanical impact on the surface. An exposure of only 10 s leads to an increase of the surface roughness of about 60%. After 300 s of exposure time the roughness values have more than doubled.

The peeling tests showed that very short UVC radiation treatment leads to a resistance against peeling that increases from 0 N/mm up to nearly 1 N/mm. That increase can be explained by a better wettability of the polycarbonate surface caused by an enhanced surface energy in combination with a higher surface roughness. Both lead to a better mechanical bonding of the silicone to the polycarbonate. But as the impact of that short term effect caused by the ozone that resulted from the oxygen and UVC radiation is that high it needs to be further investigated.

Furthermore, long-term effects were found that lead to cohesive failure between the polycarbonate plate and the non-self-bonding silicone after 300 s of UVC radiation pre-treatment. These effects can be explained by strong activation induced by the UVC radiation and thus triggered photo-Fries rearrangements.

5 Conclusion

This study has shown that standard LSR grades can be used for multi-component parts by integrating UVC radiation pre-treatment of the polycarbonate.

Since a local maximum in the surface energy of the polycarbonate plate is reached after a short exposure of 5 to 10 s which goes together with an increase of the surface roughness of about 60%, the peeling resistance increases from 0 N/mm up to nearly 1 N/mm. Although, in these cases, only physical bonding takes place, this resistance against peeling could be sufficient to fix the silicone component during transportation processes in production until the final assembly takes place.

Furthermore, longer UVC radiation pre-treatment of the polycarbonate plates led to composites that showed cohesive failure after peeling. However, these processes last at least 300 s. Consequently, the utilization of such effects will have to be evaluated while taking economic factors into account.

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