Release properties of plasma polymeric coated polymer films and adhesive strength of transferred polyurethane coatings to fiber-reinforced thermosets

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ABSTRACT
An investigation of plasma-polymeric coatings on stretchable polymer films utilizing hexamethyldisiloxane and oxygen has been performed. The influence of the plasma parameters on release properties to polyurethane paints as well as the unpreventable transfer of traces of plasma-polymeric coatings to paints or thermosets were investigated. The elemental composition and physical properties have been analyzed using contact angle measurement and X-ray photoelectron spectroscopy (XPS) with peak fitting. The release properties of the coatings are discussed. The results show that a higher ratio of oxygen to hexamethyldisiloxane during the plasma process leads to an increase of peel forces to polyurethane paints. The XPS shows that the transfer of plasma coating to the paint is on average below 0.4 at% of silicon, which is below the critical fraction of 2 at% silicon reported in the literature. Therefore, the clear-coat paint shows no difference in its adhesion to thermosets between untreated and pretreated surfaces.

GRAPHICAL ABSTRACT

1. Introduction
Fiber-reinforced plastics (FRP) produced by resin transfer molding (RTM) are often covered by polyurethane paint for appearance, increased durability, and weather resistance [1, 2]. In some cases, in-mold basecoats are used, which are applied to the mold before the preform is inserted and the injection is started. In general, manufacturing molds for closed mold processes require high investment costs, whereby in-mold coatings that occupy the mold due to their application and drying inside of the mold are mostly inefficient. Kim et al. present an alternative technique for plastic plates that allows injection of the coating and the plastic part inside of one mold [2]. Nevertheless, molds utilizing this technique are complex in design and the shapes of the part are limited. A novel approach to coat fiber-reinforced thermosets is the use of stretchable polyurethane-based coatings, which are applied to plasma polymer coated transfer films.

The painted transfer film is stretch drawn at room temperature with a vacuum into the mold’s cavity before the preform is inserted. For an automated application of the thin films on tempered RTM molds, a reusable sealing frame can be used [3]. Afterward, the state-of-the-art process chain for RTM parts is performed. The polyurethane-based coating is transferred from the plasma polymer coated transfer film to the FRP by curing the resin on a coating similar to in-mold coatings. After demolding the coated FRP part, the plasma polymer coated transfer film can be peeled off from the painted FRP part. The surface roughness of the polymer film majorly determines the surface roughness of the painted FRP because the...
plasma coating is deposited on the polymer film and the paint as well as fiber-reinforced thermoset cure on top of them. Figure 1 shows a schematic layup after demolding and a possible overpainting with a clear coat, which will be important for the experiments presented in chapter 2.

This process to paint is not restricted to fiber-reinforced thermosets. It is likely to work for fiber-reinforced thermoplastics too. The paint must allow for sufficient adhesion to the thermoplastic because the fibers themselves do not lead to adhesion to the paint. In addition, the polymer film must have a temperature resistance to the process temperatures and at the same time, a sufficient low deformation resistance to stretch draw the transfer film on a mold with a vacuum.

The release of epoxy-based FRP parts from the mold is commonly ensured by semi-permanent release agents [4]. The interfacial properties, such as the adhesion between the substrate’s surface and the coating, are influenced by the wetting of the substrate’s surface and therefore it’s surface free energy [5]. Hence, the transfer of small amounts of silicon-based release agents to the demolded reinforced plastic’s surface leads to a decrease wettability and weak bonding [6, 7]. Also, Markatos et al. showed that the defects resulting from the contamination at the interface between the substrate and reactive substance cannot be detected by conventional non-destructive techniques [6, 8]. Therefore, mechanical or chemical surface treatment methods, are important to achieve an adequate interfacial bond [9].

By using the plasma polymer coated transfer films for the transfer of the coating, we expect surface treatment methods not to be necessary before the application of an additional layer of paint. The plasma polymeric coatings on the polymer films are deposited by plasma-enhanced chemical vapor deposition (PECVD) utilizing oxygen and hexamethyldisiloxane (HMDSO). Several studies showed that a stable hydrophobic surface can be obtained by using the pure monomer of HMDSO in plasma processes because of the high retention of methyl groups [10, 11]. Polyimide films coated in a low frequency powered plasma reactor with pure HMDSO were found to increase the water contact angle from 63° to 115° after 10 min of coating [12]. By increasing the power input per monomer flow to increase the fragmentation of HMDSO molecules or adding oxygen to the plasma process, SiO2-like coatings can be created [13]. These coatings can be used as protection for metals and polymers [14, 15] or oxygen barriers for polymer films [16]. No study investigated the influences of hydrophobic plasma coatings to highly stretchable polymer films (elongations above 100%) on the transfer of paints to thermosets and the influence of the unpreventable transfer of traces of plasma coating on the adhesive strength of thermosets. Only the transfer of macroscopic structures of plasma polymeric coated films to FRP was shown [17].

When using painted and plasma polymeric coated films, it appears that the plasma polymeric coated film will be discarded. In comparison, in-mold coatings do not require additional plastic films. The advantage of the painted and plasma coated films is the fast application on tempered RTM mold. Thus, the RTM tool does not need to be cooled down or tempered for a longer time to apply the in-mold coating. For a comparison of the ecological balance, the CO2 emission for heating the mold and the amount of waste by the polymer film needs to be validated according to the use case. An argument in favor of the painted and plasma polymeric coated film is that the polymer films used for this technology can be recycled. Similar to a subsequent painting, the painted transfer film can be more eco-friendly, when the paint on the transfer film is solvent-free as e.g. water-based paints or powders.

For a better understanding of plasma polymeric coatings utilizing oxygen and HMDSO for the transfer of polyurethane paints to FRP created with different plasma parameters, we manufactured and investigated the properties of different plasma
coatings. Based on the plasma coated films, this study aims to create a deeper understanding of the paint transfer for the FRP production utilizing RTM. For this purpose, the effect of the inserted gas composition in the plasma reactor on the plasma coating is investigated. The usage of these plasma coated films as transfer and release films are investigated regarding their adhesive strength between the plasma polymeric coated film and the paint. Also, the possible transfer of the plasma coating to the surface of the RTM part after peeling the transfer film off is quantified. The influence of the transferred amount of plasma coating on the adhesive strength between the painted FRP part and an over-painted clear coat is investigated. We expect that the fiber volume fraction and the surface roughness of the polymer film have a negligible influence on these parameters. Nevertheless, we performed all the experiments with one polymer film to keep the surface roughness constant as well as one preform layup to keep the fiber volume fraction constant (see chapters 2.1 and 2.4).

Different theories aim to explain adhesion. Even though these theories are mostly confirmed, none of them by itself can fully explain the adhesion. The theories can be differentiated into mechanical and specific adhesion theories. The mechanical theory is based on the idea that the coating or adhesive permeates the substrate. This theory is of importance for wood and paper but not for plasma coatings on polymer surfaces. Subdivision of the specific adhesion theory leads to the theory of polarization, electrostatic theory, diffusion theory, interfacial thermodynamics, and chemical bonds. The theory of polarization states that adhesion only occurs between partners with the same polarization. Therefore, the coating or adhesive as well as the substrate need to have functional groups to create dipole forces or hydrogen bonds. The diffusion of the coating into the substrate is temperature-dependent and limited to polymeric substrates. The electrostatic theory states that an electrical double layer is formed between polymer and metal when there are thermodynamic potential differences between them. Interfacial thermodynamics are based on the wetting process and the surface free energy of the contacting phases. Based on this theory, Tadmor et al. established a direct measurement for the work needed to separate a liquid from a solid [18]. Last, the adhesion can be created by chemical bonds as covalent and ionic bonds [19].

2. Materials and methods

2.1. Plasma reactor and its coatings

All investigated plasma coatings were deposited on the same polymer film. The 50 µm thick polyamide film Stretch VAC 3000 from Solvay with a width of 2000 mm was used. The film itself does not have any release properties. In this study, the release properties are adjusted by varying the ratio of O₂ to HMDSO. The plasma coating acts as an unconventional release medium.

The plasma polymeric coatings were deposited by plasma-enhanced chemical vapor deposition by a roll-to-roll process in a low-pressure, radio-frequency plasma reactor of Fraunhofer IFAM with a size of 15 m³. During the plasma coating process, the polyamide film passed vertically 40 mm in front of two plate electrodes with a width of 2640 mm and a height of 1640 mm each. The web guidance was chosen in such a way that the polyamide film faced the first electrode with one side and then the second electrode with the other side. In this way, the film was coated on both sides. The winding apparatus was on floating potential.

Before the plasma coating process, the polyamide film was dried by rewinding it several times in the evacuated plasma reactor. The plasma coating was performed with a web speed of 4 m/min and a pressure of 2.5 Pa. Each electrode was powered with 3000 W at 13.56 MHz. These parameters were kept constant for all the plasma coatings. The pressure was kept constant by adjusting the position of butterfly valves, which controlled the suction of the gas. The gas supplies for the different plasma coatings are shown in Table 1. The gas flow is stated in standard cubic centimeters per minute (sccm). This unit indicates cubic centimeters per minute (cm³/min) in standard conditions of the gas (0 °C, 1013 hPa).

| Coating-no. | O₂ supply [sccm] | HMDSO supply [sccm] | O₂/HMDSO |
|------------|------------------|---------------------|----------|
| 1          | 100              | 380                 | 0.26     |
| 2          | 140              | 340                 | 0.41     |
| 3          | 180              | 300                 | 0.60     |
| 4          | 205              | 275                 | 0.75     |
| 5          | 240              | 240                 | 1.00     |
| 6          | 275              | 205                 | 1.34     |
| 7          | 300              | 180                 | 1.67     |
| 8          | 340              | 140                 | 2.43     |
| 9          | 380              | 100                 | 3.80     |
| 10         | 410              | 70                  | 5.86     |

2.2. Surface free energy by contact angle measurement

The measurement of the contact angle is an indirect method to determine the surface free energy of a solid surface. The calculation of the surface free energy is based on the Young-Dupré’s equation with \( \sigma_{sv} \) as the surface free energy of the solid against saturated vapor, \( \sigma_{lv} \) as the surface tension of the liquid against saturated vapor, \( \sigma_{dl} \) as the
interfacial tension between solid and liquid, and \( \theta \) as the contact angle [20]:

\[
\sigma_{sv} = \sigma_{sl} + \sigma_{lv} \cdot \cos \theta
\]  

(2.1)

There are different approaches for the calculation of the interfacial tension [21–23]. In this study, the calculation is done by the method of Owens, Wendt, Rabel, and Kaelble by assuming that the vapor pressure is negligible [22, 24]:

\[
1 + \cos \theta = \frac{2}{\sigma_l} \left( \sqrt{\sigma_l^d \cdot \sigma_s^d + \sqrt{\sigma_l^d \cdot \sigma_s^d}} \right)
\]  

(2.2)

The approach assumes that the interaction between solid and liquid can be calculated by the average of the disperse (\( \sigma_l^d \) for the solid and \( \sigma_s^d \) for the liquid) and polar (\( \sigma_l^p \) for the solid and \( \sigma_s^p \) for the liquid) amount. The sum of disperse and polar amounts are equal to the surface free energy [20, 22]:

\[
\sigma_s = \sigma_s^d + \sigma_s^p
\]  

(2.3)

\[
\sigma_l = \sigma_l^d + \sigma_l^p
\]  

(2.4)

The requirement to solve the equations to get the surface free energy of the solid is to test two liquids with known disperse and polar amounts. In this study, water and diiodomethane were chosen with the disperse and polar amounts shown in Table 2.

| Liquid          | \( \sigma_1 \) [mN/m] | \( \sigma_d^l \) [mN/m] | \( \sigma_p^l \) [mN/m] |
|-----------------|----------------------|----------------------|----------------------|
| Water           | 72.8                 | 21.8                 | 51.0                 |
| Diiodomethane   | 50.8                 | 50.8                 | 0.0                  |

Table 2. Disperse and polar amounts of the surface tension of water and diiodomethane [25].

2.4. RTM plate production

The resin and painting surfaces for the XPS measurements were produced by glass fiber reinforced plastic plates with the RTM tool that is shown in supplementary data 1. The upper mold was equipped with a porous aluminum METAPOR® HD 210 AL, which has a total porosity of 16% and a mean pore diameter of 12 \( \mu \)m. Through the porosity, the aluminum is gas permeable and therefore usable to stretch draw the painted and plasma polymeric coated film. Vacuum-assisted resin transfer molding utilizing porous aluminum shows that the quality and mechanical properties of the cured plates are satisfactory and reproducible [27]. A release agent always covered the lower mold. The release agent used in this study is a wax called Rexco PARTALL® Hi-Temp Wax. It was applied with a microfiber cloth, and the mold’s surface was polished before further usage. Afterwards, a plain preform made of 26 layers of glass fiber non crimp fabrics (article no. 30003671 and 30003912 by SAERTEX) with dimensions of 400 \( \times \) 265 \( \times \) 5 mm was inserted. The necessary external clamping force of 200 kN to close the mold was ensured by a Langzauner press type LZT-OK-140-L. The premixed resin Biresin CR141 with the hardener Biresin CH135-4 from Sika were injected using a custom made injection pot from Bolle&Cords Elektrotechnik GmbH.

The process started by preheating the resin to 35°C. At the same time, the mold was heated to 60°C. The injection started by opening the inlet leading the resin to flow through a rising pipe. By the vacuum inside of the mold, the resin was sucked into the mold. The riser pipe was in the resin pot and at the outside of the injection pot connected with the RTM tool by a silicon tube (article no. 222104120350) from Tecnoplast Industrietechnik GmbH. After 4 min, the absolute pressure of the injection pot was increased to 200 kPa. By applying pressure inside of the resin pot, the resin was pushed through the rising pipe into the RTM tool and therefore supported a fast filling. When the resin started to flow out of the outlet, the outlet was closed. To ensure no fiber disorientation by too high initial injection pressure [28], the pressure was increased to 400 kPa within 5 min. As soon as 400 kPa was achieved, the pressure of the inlet was kept for another 10 min. Then, the inlet was closed too and the curing phase at 80°C for 60 min started.
After cooling down, the painted and plasma polymeric coated film was detached from the upper mold and then the mold was opened.

2.5. Chemical composition by X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS) enables a quantitative determination of the chemical composition of a solid surface [29]. For the XPS investigations in this study, a K-alpha K1102 by Thermo Scientific with an upstream argon glovebox was used. The angle of the photoelectrons was 0°. The source was a monochromatic Al Kα. The pass energy to determine the chemical composition was about 150 eV. For high-resolution spectra, a pass energy of about 40 eV was chosen. The analyzed area has an area of approximately 0.1 mm². To compensate for charging effects during the evaluation, the C-C and C-H species in the C1s photoemission line were set to 285 eV, whereby the positions of the other photo lines were shifted accordingly. The unit for the amount of elements is given in atomic percent and refers to all elements except hydrogen and helium.

To determine the distribution of silicon structures, the Si2p peak was deconvoluted with fixed distances between the Si-structures according to Brenner and Vissing [30]. Primary Si-structures are represented by one silicon linked with one oxygen and three R-groups [31]. Secondary Si-structures are represented by one silicon linked with two oxygen and two R-groups [31]. Tertiary and quaternary Si-structures are linked respectively [31]. We assume that the R-groups are mainly methyl groups from the HMDSO molecule. In reality, the Si2p binding energy can be influenced by various combinations of carbon and hydrogen atoms bonded to the silicon, i.e. \(-\text{H}, -\text{CH}_2-, =\text{CH}_2, -\text{CH} = \text{CH}_-, -\text{CH} = \text{CH}_2, -\text{CH}_3, \text{and } -\text{CH}_2-\text{O-} [31]\). We assume that these influences on the Si2p binding energy are small in comparison to the shift caused by oxygen. Therefore, the Si2p peak was divided only into four silicon structures each represented by a doublet. The amount of the doublet peaks was set to 1: 2 with a distance of 0.61 eV. The half-width was kept variable in the calculation, but set to the same value for all peaks. Also, the peak for the primary Si-structure was variable between 101.4 eV and 101.6 eV. The distances to the following Si-structures were kept constant. According to Brenner and Vissing, the binding energies are +0.9 eV for secondary silicon structures, +0.7 eV for tertiary silicon structures, and +0.7 eV for quaternary silicon structures [30]. All data on the atomic fraction (at%) in XPS refer to atoms other than hydrogen.

2.6. Pull-off test based on DIN EN ISO 4624

Regarding DIN EN ISO 4624, the pull-off test allows for the quantification of the adhesive strength of a coating utilizing a stamp [32]. The maximum force divided by the measured area calculates the adhesive strength. In this study, the pull-off tests are used to quantify the adhesive strength between a clear coat and the surface of the RTM plate for different manufacturing and pretreatment routines.

The surfaces of the RTM plates, which needed to be analyzed, were coated with the clear coat VP 7550 D/7/4-026 and hardener 28/13 from Bomix. The clear coat was applied with a 150 µm squeegee. After the application, the clear coat was dried for 30 min and cured at 80 °C for 30 min. Martínez-Landeros et al. [33] investigate different treatments for high adhesive strength. They found that a mechanical removal by an abrasive paper combined with a solvent-based cleaning led to the highest adhesive strength compared to pure solvent-based cleaning, acid treatment, etching, or peel ply removal [33]. Therefore, in the case of pretreatment, the surface was ground with a P400 abrasive paper and cleaned with isopropyl alcohol. Loose particles were removed with de-oiled pressurized air. As required in DIN EN ISO 4624, the stamps with a diameter of 20 mm made of steel were glued to the clear coat [32]. For this purpose, the clear coat was ground with a P400 abrasive paper, cleaned with isopropyl alcohol, and loose particles were removed with de-oiled pressurized air. The stamps were then glued to the clean clear coat with the epoxy adhesive Araldite 2011 from Huntsman. The adhesive was cured at 80 °C for 30 min and the pull-off test was performed more than 48 h after the curing of the adhesive. Each coated surface was tested at least five times.

3. Results and discussion

3.1. Effect of O₂ to HMDSO ratio on the surface free energy

Figure 2 shows that the contact angle of water decreases constantly with a higher ratio of oxygen to HMDSO in the gas supply of the plasma coating process.

For solvent-based liquids, the contact angle of water is not enough to consider since solvents spread differently than water. Exceptions of organic liquids which not spread on surfaces with a high surface free energy can for example be liquids containing a dissolved polar-nonpolar compound [23]. In the general, a high surface free energy increases the wetting with liquids [23].

It must be considered that the thin plasma coating of about 20 nm has no relevant influence on the
surface roughness of the film. All measurements were performed on the same polymer film, but with different plasma coatings. This is important to consider because the surface roughness significantly influences the surface free energy [34]. Sekvakumar et al. found that increased surface roughness of superhydrophobic PTFE coatings increases the dispersive surface free energy which is part of the surface free energy (see equation 2.3) [34].

Figure 3 shows that the surface free energy can be adjusted by the gas supply while plasma coating. A higher ratio of oxygen to HMDSO led to higher surface free energy. A possible explanation for the increase in the surface free energy can be that methyl groups decrease the surface free energy. Zisman reported that the surface free energy of surfaces with methyl groups decreases when the molecules are close-packed and oriented [23]. Therefore, a higher density of methyl groups at the surface leads to low surface free energies. In the plasma process, the fragmented HMDSO molecules find more oxygen to react with. Therefore, a shift from primary and secondary Si-structures towards tertiary and quaternary Si-structures should be formed. This would lead to higher crosslinking and fewer methyl groups at the surface. The Si-structures of the different plasma coatings are presented in the next chapter.

3.2. Effect of O₂ to HMDSO ratio on the chemical composition of the plasma coating

Figure 4 shows the amount of silicon, oxygen, and carbon of plasma coating with different ratios of O₂ to HMDSO as determined by XPS. As expected, it can be seen that the amount of oxygen in the plasma coating increases when more O₂ is inserted in the process because the possibility of a fragmented molecule reacting with oxygen is increased. Due to the detailed C1s signal, we expect that preferably carbon is linked as a methyl group to the silicon. Silicon which would be linked to oxygen would result in a shift of the carbon signal due to the greater electronegativity compared to links between silicon and carbon. The decrease of carbon with an increased ratio of O₂ to HMDSO as seen in Figure 4 indicates that fewer methyl groups (-CH₃) are present in the plasma coating. This expectation is confirmed by the decrease of secondary Si-structures with an increased ratio of O₂ to HMDSO as can be seen in Figure 5.

Brenner and Vissing found that the power supply does not affect the chemical composition [30]. In their study, a power between 1000 and 3400 W has almost no influence on the distribution of Si-structures [30]. In contrast, the distribution of the Si-structures can significantly be influenced by the gas supply, as can be seen in Figure 5. This finding is consistent with XPS measurements of plasma coating with O₂ and HMDSO in the literature [31]. Even at a low amount of oxygen in the gas supply (O₂/HMDSO = 0.26) the fraction of primary Si-structures is quite low with 6.6 ± 3.3%. The major Si-structure is secondary with 87.0 ± 5.7%. Repeating secondary Si-structures are represented by polydimethylsiloxane (PDMS) which can have many thousands of secondary Si-O units terminated typically with two primary Si-structures. Due to many primary and secondary structures, and therefore methyl groups, it is expected to create low adhesive forces towards polyurethane paints. The peeling forces for an adhering polyurethane paint will be presented in chapter 3.3. Figure 5 shows that with an increased gas supply ratio of O₂/HMDSO the secondary Si-structures in the coating decrease in favor of tertiary Si-structures. The highest gas supply ratio of O₂/HMDSO of 5.86 led to 17.0 ± 4.7% quaternary Si-structures with four oxygen atoms surrounding the silicon and 64.6 ± 3.6% tertiary Si-structures with three oxygen atoms surrounding the silicon, meaning the coating was highly cross-linked in comparison to the other plasma coatings. Even though all coatings are cross-linked by tertiary and quaternary Si-structures, they are expected to show good release properties due to primary and secondary Si-structures of 18.4 ± 1.2% and more.

3.3. Effect of O₂ to HMDSO gas supply ratio on the release properties

The peel test is a well-suited test to quantify the adhesive strength between the plasma polymeric
coated film and the paint. First, the peel test is easier and faster to perform than other tests like the pull-off test. Second, the peel forces have high reproducibility, which can be seen by the low standard deviation of the results presented in this chapter. Third, the peel test is close to the practical handling where the plasma polymeric coated film will be peeled off the paint.

Both partners influence the peel forces of the plasma polymeric coated films on polyurethane paints. For instance, the peel forces differ from 0.02 ± 0.01 N/25 mm for the Bomix VP 7550 D/7/4-026 over 0.86 ± 0.06 N/25 mm for the Bomix VP 82360005 CHP up to 9.40 ± 0.36 N/25 mm for the Mankiewicz Alexit FlexPrimer 493-23 on the same plasma coating (gas supply O₂/HMDSO of 1.67). The FlexPrimer even results in a mixed failure of cohesion break inside of the paint and adhesion break at the interface between plasma coating and paint. All samples of the Bomix VP 7550 D/7/4-026 and Bomix VP 82360005 CHP with the different plasma polymeric coatings (gas supply O₂/HMDSO from 0.26 to 5.86) result in adhesion breaks.

Figure 6 shows that the plasma coating can significantly influence the peel forces. The peel forces increase proportionally with the gas supply ratio of O₂ to HMDSO. Therefore, the peel force of a polyurethane paint on plasma polymeric coatings with different gas supply ratios of O₂ to HMDSO can be predicted with a few peel tests of the paint with a small number of plasma polymeric coatings.

Since all plasma coatings were deposited on the same polymer film, the topography does not explain the increase of peel force. Due to the shift of the plasma coating towards higher crosslinked structures, as shown in Figure 4, the increase in peel force is unlikely attributable to diffusion. Also, an electrical double layer is unlikely to appear since no
metal is involved. Furthermore, the thermodynamic theory tries to explain the work which is needed to separate a liquid from a solid [18], which is not the case for a cured paint of the plasma coating. Most likely, the peel forces between the paint and the plasma coating can be explained by the polarization theory and the chemical bonds. Either covalent bonds or dipole forces are likely to affect the adhesion.

3.4. Surface composition of polyurethane in-mold coating and resin on the composite part utilizing the plasma coated film or wax

Markatos et al. found that silicone-based release agents significantly decrease the Mode-I fracture toughness of bonded joints. The degradation was significant for silicon fractions, determined by XPS, of more than 5 at%. Silicon fractions of more than 7 at% resulted in a complete lack of adhesion [6]. A similar study was performed by Wadowski et al. [35] who investigated the influence of the silicone-based release agents while the fabrication of carbon fiber reinforced plastics (CFRP). They found that the shear strength decreased dramatically with Si-fraction of the CFRP surface more than 4 at%. The Si-fraction is an indicator for the amount of silicone transferred to the surface of the CFRP. At 2 at% Si on the surface, a difference in the fracture pattern could still be observed even though the shear strength was not influenced [35]. Therefore, a transfer of the plasma coating to the paint or resin surface of less than 2 at% seems tolerable and should not influence the adhesive strength when the surface is painted with a clear coat (see 3.5).

Table 3 shows the elemental composition of the reference materials, determined by XPS. The two surfaces, either the paint or the resin, are silicon-free, which simplifies the discussion of the results if some amounts of the plasma coating with high fractions of silicon are transferred to the surface. Since the wax is almost silicon-free, the comparison needs to be done by the composition of oxygen and carbon.

For further investigation, RTM parts were prepared either with wax or plasma-coated films on the mold surface. Figure 7 shows the amount of oxygen and carbon of the demolded RTM part comparing resin and paint surfaces after the use of wax as a release agent. The reference measurements of the wax, resin, and paint are shown respectively. It can be seen that the amount of oxygen and carbon of the RTM part are almost in the middle of the references, both for the resin as well as the paint surface. Therefore, it is very likely that large amounts of waxes are transferred to the surface of the part. This should lead to a decrease in adhesive strength (see chapter 3.5).

By looking at the plasma coated films at a light microscope when the films are stretched, it can be seen that the plasma coating breaks at elongations between 20 and 50%. The plasma coating seems to have very good adhesion to the polymer film because no detachments can be observed. To verify the transfer of the plasma coating to the part surface, the plasma coated films were bidirectionally elongated to 50 × 50% to simulate a worst-case scenario. Also, it needs to be taken into account that the paint is applied to the plasma coated film before it is elongated. In comparison, the resin got in contact with the plasma coated film after it was elongated. Hereby, the liquid resin can enter the cracks of the elongated plasma coating while the paint, which is cured on the unstretched film, cannot enter the

Figure 6. Peel force per width from Bomix VP 82360005 CHP for the gas supply with different ratios of O2/HMDSO while plasma coating.

Table 3. Element composition of the references.

| Reference materials | C [at%]   | O [at%]   | Si [at%] |
|---------------------|-----------|-----------|----------|
| Plasma coating with gas supply ratio O2/HMDSO of 0.60 | 49.1 ± 0.3 | 25.6 ± 0.3 | 25.3 ± 0.0 |
| Plasma coating with gas supply ratio O2/HMDSO of 1.67 | 44.4 ± 0.5 | 31.3 ± 0.3 | 24.4 ± 0.2 |
| Resin (Sika Biresin CR141 + CH135-4) | 83.3 ± 0.0 | 12.8 ± 0.0 | 0.0 ± 0.0 |
| Paint (Bomix VP 82360006 CHP) | 84.9 ± 1.4 | 11.1 ± 1.1 | 0.0 ± 0.0 |
| Wax (Rexco PARTALL Hi-Temp Wax) | 98.9 ± 0.7 | 0.7 ± 0.6 | 0.2 ± 0.1 |
cracks. For this reason, it was expected that the contamination of the resin’s surface would be higher than the paint’s surface. The XPS measurements showed that the transfer of plasma coating to the surfaces of the RTM part was for both surfaces so low that the difference was negligible. The paint’s surface had a Si-amount of 0.4 ± 0.1 at% and the resin’s surface had a Si-amount of 0.3 ± 0.1 at%. Both Si-amounts were significantly below the critical 2 at% reported by Wandowski et al. [35].

### 3.5. Adhesive strength of a polyurethane topcoat to surfaces created with the plasma coated film or wax

In order to determine the adhesion of the subsequently applied clear coat, tear-off tests were carried out. The results are shown in Figure 8. It can be seen that the measured tensions on the paint and the resin lead to similar values. As expected, a direct application of the clear coat to the untreated surfaces demolded with the wax led to a significant decrease in the pull-off tension. This result is in accordance with the measured transfer of the wax to the surfaces as shown in Figure 7. When comparing the pull-off tensions after pretreatment, it can be seen that there is no difference between the surfaces after demolding with wax and the plasma polymeric coated film. Therefore, the result of Martínez-Landeros et al. [33] that a great adhesion is created by a mechanical removal with an abrasive paper combined with a solvent-based cleaning can be confirmed. As shown in chapter 3.4 the transfers of the plasma coating to the paint’s as well as resin’s surface are below the critical 2 at% for Si. Therefore, the transfer of the plasma coating should not influence the adhesive strength to the clear coat. Figure 8 shows that the pull-off tension for the untreated
as well as for the pretreated surfaces created by the plasma polymeric coated film is similar. As expected, the small amount of silicon does not influence the pull-off tension. In addition, the different plasma coatings did not lead to differences in the pull-off tension. After the pull-off test, the optical examination of the test specimens demolded from wax without pretreatment showed 100% adhesion failure between the clear coat and the underlying paint. All the other test specimens showed more than 90% cohesion failure within the FRP.

4. Conclusion

Different plasma polymeric coatings utilizing O\textsubscript{2} and HMDSO deposited on polymer films were demonstrated as a tool to transfer paints to the surface of a FRP part produced by RTM. The effect of the plasma coating on the adhesive strength was determined. It was found that the surface free energy increases when the gas supply ratio of O\textsubscript{2} to HMDSO in the plasma reactor is increased. A possible explanation for the increase in the surface free energy can be the decreased density of methyl groups. The deconvolution of the Si2p peaks of the different plasma coatings supports this theory because the amount of secondary Si-structures decreases and the tertiary Si-structures increase respectively when the ratio of O\textsubscript{2}/HMDSO in the plasma process was increased.

The peel tests revealed that the plasma coating can significantly influence the adhesive strength to a polyurethane paint. The peel force of the polyurethane paint Bomix VP 82360005 CHP increases almost proportional to the gas supply ratio of O\textsubscript{2}/HMDSO. This indicates that the adhesive strength of polyurethane paints and plasma coatings by O\textsubscript{2} and HMDSO can be predicted by a few peel tests determining the gradient of the linear increase between peel force and gas flow ratio. Nevertheless, the adhesive strength will always be a parameter determined by both interacting partners. The results showed that the same plasma coating can lead to peel forces, which differ by a factor of more than 100 for different polyurethane paints.

XPS measurements showed that only negligible traces of the plasma coating are transferred to the polyurethane paint or the epoxy resin. Even after the films were elongated to 50\%\% the paint’s surface only had a Si-amount of 0.4±0.1 at\% and the resin’s surface only had a Si-amount of 0.3±0.1 at\% after peeling off the plasma coated film. In the literature, a Si-fraction of 2 at\% was found to affect the adhesion [35].

It was shown that the transfer of the plasma coating does not influence the adhesive strength to a subsequently applied clear coat. The pull-off tension for the surfaces, which were treated with an abrasive paper combined with a solvent-based cleaning led to the same value as the untreated surfaces after peeling off the plasma coated film. In contrast, the untreated surface demolded from a wax led to a significant decrease in the pull-off tension.

The study gives new insights into the production technology of painting fiber reinforced thermosets. The elemental composition, chemical network, and resulting physical properties of plasma polymeric coatings were determined. The effects of the plasma parameters on the peeling forces, transfer of plasma coating to the FRP surface, and the resulting adhesive strength by eliminating pretreatments for paints were presented and discussed for production purposes.

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Disclosure statement

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