Applied Adhesion Science

RESEARCH Open Access

Investigation of fluorine-based release agents for structural adhesive bonding of carbon fibre reinforced plastics

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Abstract

Peel plies can be used during the manufacture of fibre-reinforced plastics for two reasons: to protect the surface during transport and storing the parts as well as during subsequent work steps, such as adhesive bonding, the removal of the peel ply can result in bondable surface with required surface characteristics. However, the use of peel plies is not straightforward. It can be difficult to remove peel plies and a surface produced by a peel ply is altered in terms of roughness and elemental composition. In the present work, the influence of fluorine-based release agents on adhesive joining of carbon fibre reinforced composites is investigated. Within the scope of the screening, 14 fluorine-based release agents—ETFE release films, PTFE coated glass fabrics as well as fabrics made of PTFE fibres—were investigated. Preliminary studies (Meer, in: Deutscher Luft- und Raumfahrtkongress 2014, Augsburg, 2015) have shown that ETFE films have advantages in terms of adhesion. The study covers a number of aspects: the determination of the tear strength of the release agent by peel test; the determination of the element composition (XPS) and surface characteristics (SEM) before and after atmospheric pressure plasma pre-treatment, characterization the topology and the characterization of the adhesive strength by centrifugal adhesion test.

Keywords: CFRP, Release agent, Contamination, Adhesion

Introduction

Adhesive joining is increasingly used in many industries because of the advantages it provides compared to conventional structural joining methods (e.g. riveting). This applies in particular to fibre-reinforced composites, as a rivet hole interrupts the fibres and thus weakens the mechanical properties of the laminate. In aerostructures, adhesive bonding is applied in metal-to-metal joints, composite-to-composite joints and composite-to-metal joints both for assembling parts and for patch-repairing.

The quality of a bonded joint depends on the adhesive, the manufacturing process, the environmental and loading conditions, as well as from the surface of the substrates to be joined. The surfaces of CFRP components to be joined by adhesive bonding are often textured surfaces resulting from the used peel plies during production or mechanical pre-treatment such a sanding or milling.

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In the production of CFRP with prepreg materials, peel plies have been used for years for several reasons. The peel ply layer on top of the laminate absorbs excess resin during manufacturing [1] and is meant to protect the surface during handling as well as to create a fresh surface after peeling it off [2]. In order to ease the release of the fabrics from the composite surface after curing the laminate, the materials are sometimes coated with release agents. A weak interaction between peel ply and the laminate is desired as it should be easy to remove. The peeling force must not exceed the laminar strength to avoid fibre tear. Hence, after removal of the peel ply, residues of the release agent often remain on the surface [2, 3], whereby the concentration can fluctuate due to the production process. This transfer of a contamination can have consequences for the quality of the adhesive bond [4–6] and might require additional surface treatment [7]. Holtmannspoetter et al. [8] showed in an investigation with six different peel plies that creating a reproducible, highly activated surface by peel ply removal only could not achieved. It was only possible to achieve a reproducible but finally contaminated surface.

In the case of liquid release agents, it has been shown that after the demolding process, remaining release agent on the surface can significantly affect the performance of an adhesive joint depending on amongst others the concentration of the release agent and the adhesive. Markatos et al. [9, 10] found a significantly affect on the fracture toughness (G_{IC}) for Si concentrations over 5 at.% (60% reduction in G_{IC}). For double lap joints, Jeenjitkaew et al. [11] found a 27% reduction in joint strength for a silicone release agent. For CFRP laminates that were moulded against release cloths or metal plates coated with release agents, Parker et al. [12] found that remaining surface contamination with release agent resulted in significant reduced strengths for adhesively bonded single lap joints.

Atmospheric pressure plasma (APP) pre-treatment can modify the chemistry and topography of a CFRP surface [7, 8]. Preliminary studies [7] have shown that ETFE films have advantages in terms of adhesive bonding. Due to the smaller thickness of the contamination on the CFRP surface, fluorine residues could be removed by a plasma process. However, the high separating ability of the film leads to the fact that it detaches very easily from the CFRP surface and thus the surface to be bonded cannot be protected until immediately before activation or bonding.

The scope of the following study was to investigate the influence of fluorine-based release agents for the bonding of CFRP components. In the screening a total of 14 different fluorine-based release agents, including materials that were not originally produced as release fabrics, were examined.

Centrifugal adhesion test

An effective and frequently used method to determine quantitative results in terms of normal force per area is the standardized pull-off test which gives the adhesion strength by means of tension [13]. The standardized conventional adhesion tests exhibit a number of disadvantages. Due to sample misalignment they develop shear stresses [14], a clamping at two-sides is required [15, 16], and they are, as single-sample test, time-consuming. A few year ago, a new test method has been proposed for measuring the adhesion strength of adhesive joints, which exploits the centrifuge force. The principle has been used for many years for the separation process of solids from liquids or liquids from liquids [17, 18] in various applications.

Table 1 Overview of the release agents tested

Sample	Product	Type	Material
01-01	Setex PTFE[a]	Peel Ply	PTFE yarn
01-02	PTG 76[b]	Release-Ply	Glass fibre fabric
01-03	Sefar 24-4-500[c]	Peel Ply	PTFE yarn
01-04	Vac-Pac A6200[d]	Foil	ETFE
02-01	MR1[d]	Foil	PTFE
02-02	8940[e]	Peel Ply	Glass fibre fabric
02-03	60 BR[f]	Release-Ply	Glass fibre fabric
02-04	MR2[d]	Foil	PTFE
03-01	RE 234 TFP[d]	Release-Ply	Glass fibre fabric
03-02	Sefar 1100-SK 012[c]	Peel Ply	PTFE yarn
03-03	Sefar 1100-K 020[c]	Peel Ply	PTFE yarn
03-04	RE 234 TFNP[d]	Release-Ply	Glass fibre fabric
04-01	WL 4500C[d]	Foil	PFV
04-02	TFG 125[f]	Release-Ply	Glass fibre fabric
04-03	TFGS 075 PS[f]	Release-Ply	Glass fibre fabric
04-04	Setex Kalandert[a]	Peel Ply	PTFE yarn

The samples 02-02 and 02-03 are a wax- and silicone-based fabric, respectively; all other samples are a fluorine-based release agent

Manufacturer: [a]Setex; [b]Precision; [c]Sefar; [d]Airtech; [e]UTT; [f]Tygavac

For the measurement of the adhesion strength, the centrifuge test is a multi-sample, single-lap fast test that is still rather new and under evaluation. In the field of composites it was recently used to investigate the effect of pre-bond contamination scenarios related to production and repair processes on the adhesion strength of composite-to-metal joints [19].

Methods

Materials and specimen preparation

Release agents

A total of 16 various release agents were chosen for investigation. Altogether five peel plies of PTFE yarn, five release plies (glass fibre fabric) with a PTFE coating and four foil materials (2x PTFE, 1x ETFE, 1x PVF) were tested. In addition, two peel ply fabrics, one with a silicone finish and one with a wax finish, were examined. Table 1 gives an overview of the considered materials and some of their properties.

CFRP samples

The CFRP panels were manufactured from 8552/IM7 (12K) UD prepreg material. The lay-up sequence of the panels was $[90/0/135/452/135/0/90]_S$. The lay-up of the plies was applied by hand. According to the planned investigations, the required samples are arranged on the surface of the panels for each release agent (Fig. 1). Table 2 summarizes the used methods together with their respective section on the panel as well as the resulting sample number. After curing in the autoclave, the panels were cut into the individual sample segments using a circular saw with diamond blade. As some of the specimens are relatively small (10 × 10 mm), the individual specimens are cut to oversize and then brought to their final size with a belt sander.

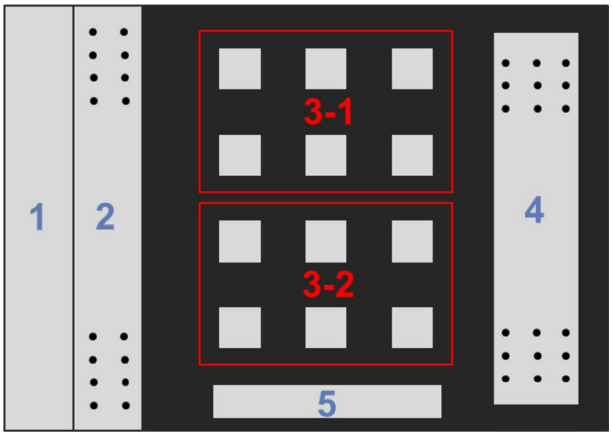

Fig. 1 Layout of the CFRP panels (width 210 mm, height 150 mm). Section 1: peel resistance; 2 and 4: confocal laser scanning microscopy; 3-1 and 3-2: centrifugal adhesion test; 5: scanning electron microscopy and photoelectron spectroscopy

Table 2 Sample placement and used methods for each release agent

Section	Method	Number of samples
Whole panel	Ultrasound	
1	Peel resistance	1
2 and 4	Confocal laser scanning microscopy	2
3-1 and 3-2	Centrifugal adhesion test	6 / 6[a]
5	Scanning electron microscopy	2 / 2[a]
5	Photoelectron spectroscopy	2 / 2[a]

[a] With and without pre-treatment, respectively

As for the samples for the centrifugal adhesion test, a thickness of 5 mm is required in order to minimize bending during testing, these samples were reinforced using an additional CFRP panel with a thickness of 3 mm. The reinforcing panel with a quasi-isotropic layer structure (24 layers) was bonded to the panel with the samples using the film adhesive Henkel Hysol 9695.050 PSF NW and surface pre-treatment by atmospheric pressure plasma.

Centrifugal adhesion test samples

The specimens used in the centrifugal adhesion test had a stamp-to-plate configuration (Fig. 2). The modular test stamps bonded to the CFRP adherends consist of the aluminum adherend (EN AW-2007) screwed onto a mass body made of copper (Fig. 2). The test stamps had a diameter of 10 mm on the bonding face and were anodized in phosphoric-sulfuric acid (PSA, 120 g/l H_3PO_4/ 80 g/l H_2SO_4). Prior to anodizing, all specimens were de-greased (Turco 4215 NC from Henkel), etched (Aluminetch No. 2 from Henkel) and pickled (Turco Liquid Smutgo NC from Henkel).

For the bonding of the samples, a mixture of the two two-component adhesives Henkel Hysol EA 9395 and Henkel Hysol EA 9396 was used. The samples were cured

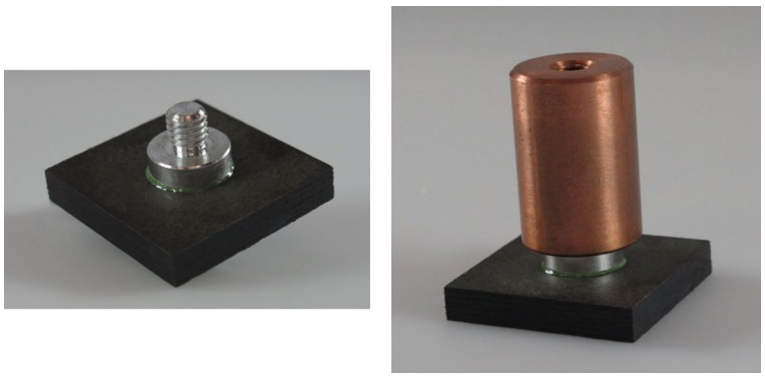

Fig. 2 The stamp-to-plate specimen used in the centrifuge tests: (left) metallic stamp bonded to the CFRP adherend; (right) specimen with copper mass body

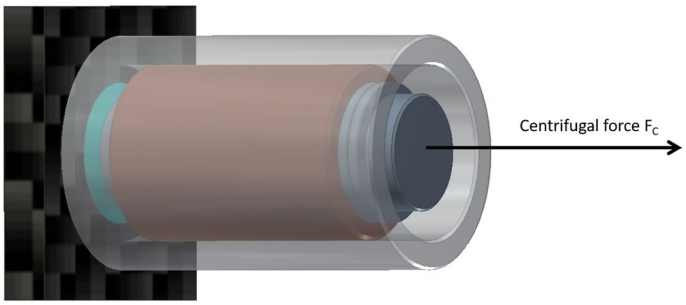

Fig. 3 Measurement principle of the centrifugal adhesion test (CAT) for the determination of the adhesive strength; black: CFRP adherend, turquoise: adhesive, red: copper mass body, grey: aluminium adherend, transparent: guiding sleeve

for 60 min at RT, for 60 min at 66 °C (heating rate 2 K/min) and cooled down to RT with rate of 2 K/min.

Plasma pre-treatment

The plasma pre-treatment is carried out using an atmospheric plasma device from Plasmatreat with a RD1004 plasma nozzle, a FG5002S generator and a HTR12 transformer. The generator voltage was 280 V, the used gas was air at a pressure of 58 mbar. A nozzle spacing of 6 mm, a feed rate of 3 m/min and a line spacing of 6 mm was used.

Mechanical testing

Centrifugal adhesion test

The centrifugal adhesion test (CAT) rests upon the physical law of inertia of a body [20]. A successively increasing radial centrifugal force is applied to the sample as a results of the rotation. The load increase is regulated by the variation of the rotational speed. The CAT principle for the bonded joints is demonstrated in Fig. 3.

The sample comprises of the adherend (composite panel) bonded to a metallic cylindrical stamp. The axial centrifugal force acts as a normal tensile force in the bondline.

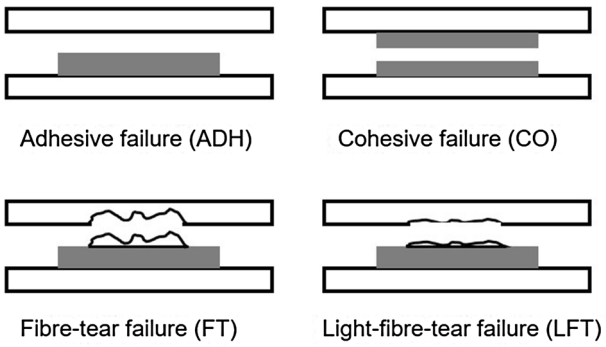

Fig. 4 Schematic representation of failure modes used in the present investigation

When the applied load exceeds the tensile strength of the assembly, the test stamp changes its position within the guiding sleeve. The detachment of the test stamp from the adherend at the time of rupture is automatically detected and the current rotor speed as well as rupture time is recorded [21].

The centrifugal force F_c [N] is derived from:

$$F_c = m\omega^2 r \tag{1}$$

with m [kg] as the mass of the stamp, r [m] as the distance of the test stamp to the rotational axis and ω [rad/s] as the angular velocity connected to the frequency ν via:

$$\omega = 2\pi\nu \tag{2}$$

The tensile strength σ [MPa] is then derived by dividing the centrifugal force F_c by the area of the adhesive bond A [mm^2],

$$\sigma = \frac{F_c}{A} \tag{3}$$

The centrifugal adhesion tests were carried out using a LUMiFrac desktop adhesion analyser equipped with a LSFR-ST: 200.42 drum rotor of up to eight testing units. The fully loaded rotor allows for a maximum rotational speed ω of 13,000 rpm [21]. During the experiment, the test stamp are supported within the testing unit by a guiding sleeve to avoid the development of shear forces [13, 22]. The experiment were conducted with a controlled load increase rate of 20 N/s.

Failure characterisation

After determination of the adhesive bond strength, high resolution microscope images of the failure surfaces of the CFRP adherend and the test stamp were taken and analysed to characterize the failure patterns. The observed main failure modes are schematically shown in Fig. 4. Adhesive failure (ADH) occurs when the rupture takes place at the adhesive/adherend interface, cohesive failure (CO) when the rupture takes place within the adhesive, fiber-tear failure (FT) when the failure occurs within the CFRP matrix revealing fibres on both ruptured surfaces and light-fibre-tear failure (LFT) when the rupture occurs within the adherend, near the interface characterized by a thin layer of the matrix on the surface with few or no fibres transferred

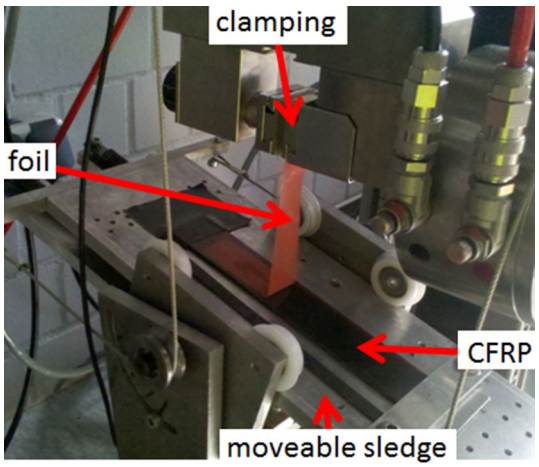

Fig. 5 Test set-up for the determination of the peel resistance showing a sample clamped into a moveable sledge to keep the peeling angle constant at 105°. The unbonded end of the release agent (foil or peel ply) is attached to the load cell via a clamping device

from the CFRP to the adhesive. The classification, identification and characterization of the failure modes of the joints were conducted according to the ASTM D5573 [23].

Peel resistance

The peel resistance was determined using a universal testing machine Zwick/ Roell Z020. The release agent is peeled from the laminate by means of a fixture shown in Fig. 5 [24].

The sample, consisting of the CFRP substrate with the release agent applied, is inserted into the peel fixture movable in one plane. On one side of the sample the release agent is removed from the surface to form the unbonded end, which is in turn gripped in the free jaw of the testing machine. The movement of the fixture is controlled by two wire ropes that are attached to the cross beam of the universal testing machine. As the peel resistance is strongly dependent on the peel angle, the direct coupling between the path of the fixture and the traverse path ensures that the angle remains constant during the measurement.

A peel velocity of 500 mm/min, a peeling angle of 105° and a strip width of 24 mm was used. The maximum peel strength and the average peel strength over the distance peeled was determined.

Surface characterisation

Scanning electron microscopy (SEM)

The SEM examinations were performed with a Zeiss Ultra Plus system (bean energy 1 kV, working distance about 5 mm). The images were recorded with 2000-, 5000-, 20,000- and, as far as there were no charges on the surface of the samples, also with 50,000-times magnification.

Table 3 Peel strength (max / average) for the investigated release agents

Sample	Product	Max peel strength [N/24mm]	Average peel strength [N/24mm]
01-01	Setex PTFE	11.1	8.7
01-02	PTG 76	0.6	0.2
01-03	Sefar 24-4-500	9.6	7.6
01-04	Vac-Pac A6200	0.7	0.1
02-01	MR1	0.6	0.1
02-02	8940	35.1	26.7
02-03	60 BR	14.6	8.4
02-04	MR2	0.7	0.2
03-01	RE 234 TFP	2.7	2.2
03-02	Sefar 1100-SK 012	6.6	5.8
03-03	Sefar 1100-K 020	25.6	22.7
03-04	RE 234 TFNP	0.8	0.2
04-01	WL 4500C	13.6	3.7
04-02	TFG 125	0.9	0.1
04-03	TFGS 075 PS	1.7	1.0
04-04	Setex Kalandert	5.7	3.6

Photoelectronspectroscopy (XPS)

The XPS measurements were performed on a Thermo K-Alpha instrument with attached argon glovebox for the handling of air sensitive samples applying the following acquisition parameters: take off angle of electrons 0°, excitation of photoelectrons by monochromatic Al K_{alpha} radiation, constant analyser energy mode (CAE), pass energy 40 eV in high resolution spectra and 150 eV in survey spectra, analysis area: 0.40 mm ∅, charge compensation of non-conduction samples by dual beam Argon / electron source with ultra-low energy beam neutralisation. To compensate for charging effects, the C1s main emission line is set to a binding energy of 285 eV during evaluation, so that the positions of the binding energies of the other photolines shift accordingly.

Confocal laser scanning microscopy (CLSM)

The measurement of the surface roughness was carried out by means of a Keyence VK-X200 microscope. The roughness values R_a and R_z were determined at 20× magnification.

Results and discussion

Peel resistance

The determined peel strength are shown in Table 3. As expected, very low peel strength are found for the release films. For the fabrics, the maximum peel strength varies in a broad range from < 1 N/24 mm up to > 35 N/24 mm. High peel strength (> 10 N/24 mm) increasingly lead to fibre tearing and accordingly damaged laminate surfaces; with a peel strength of 25 N and above, the fibre tearing is very frequent and leads to high rejects.

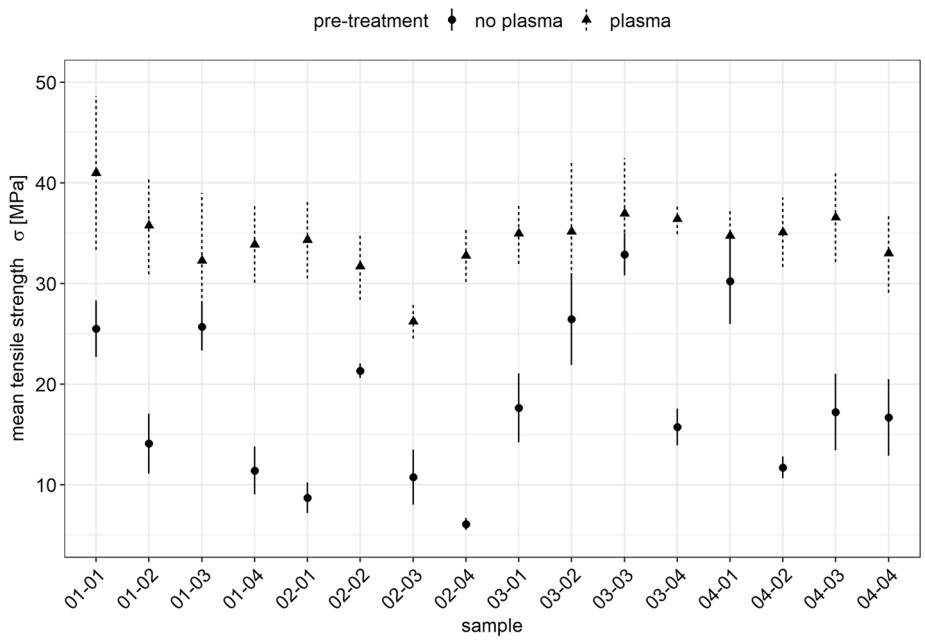

Fig. 6 Adhesive strength with and without plasma pre-treatment for the investigated release agents

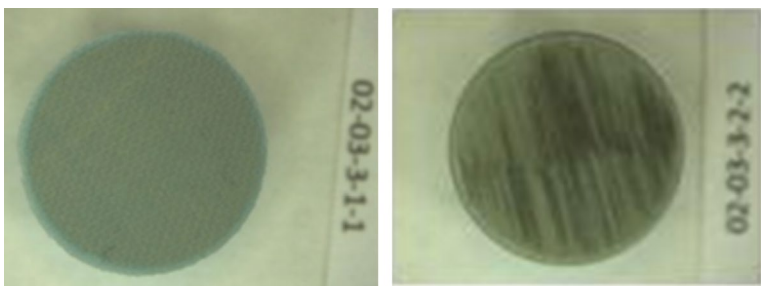

Fig. 7 Representative microscope picture of the fracture surface after centrifugal adhesion test for the release agent 60 BR (sample 02-03) without plasma pre-treatment (left) and with plasma pre-treatment (right). Shown is the stamp side of the fracture surface; the left picture shows 100% adhesive failure (ADH) as the turquoise-colored adhesive is clearly visible over the whole stamp surface; the right picture shows a failure in the laminate characterized by light fibre tear (LFT); fibres from the substrate are visible on about 50% of the surface

Adhesive strength

The determined mean tensile strength and corresponding standard deviation for the investigated release agents are shown in Fig. 6.

The mean tensile strength varies from approx. 6 MPa to approx. 33 MPa for samples without plasma pre-treatment. For almost all release agents, adhesive failure (ADH) between laminate and adhesive is observed [exemplarily shown in Fig. 7 (left)]. Only for the Sefar 1100-K 020 Peel Ply (sample 03-03), the fracture surfaces showed a near-surface cohesive failure (CO) and light fibre tear (LFT), respectively. This is also the release agent with the highest found adhesion strength for the samples without pre-treatment.

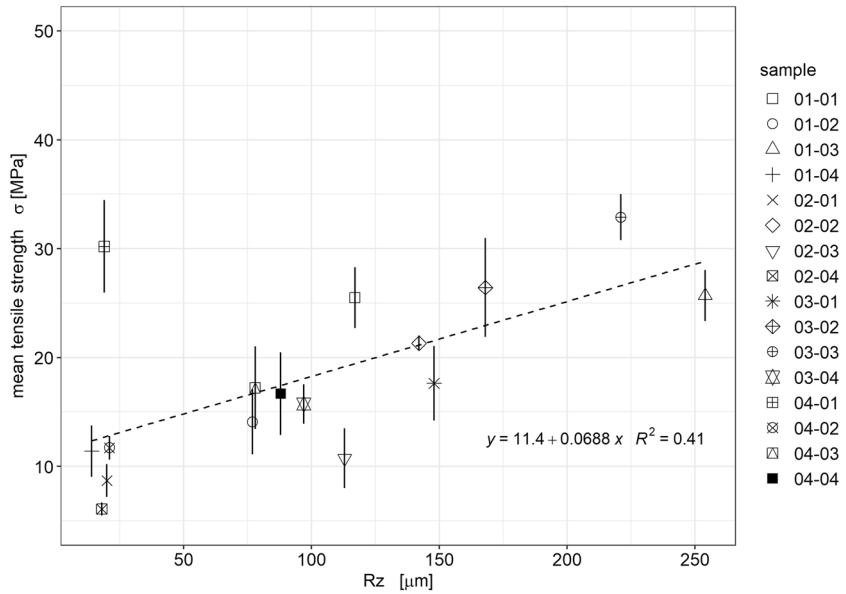

Fig. 8 Dependence of the tensile strength from the roughness (R_Z) for the samples without plasma pre-treatment

For all pre-treated samples, a failure in the boundary layer to the laminate characterized by light fibre tear (LFT) is found in the centrifugal adhesion test. Figure 7 (right) shows a typical fracture pattern. The average tensile strength lies between 26 and 41 MPa and thus significantly above the values found for the untreated samples. For almost all pre-treated samples, the mean tensile strength is very similar, in particular if the standard deviation is considered too. However, for these samples, the failure of the first laminate layer is the dominant failure mode. Hence the laminate strength is actually evaluated.

For the Peel Ply Setex PTFE, the highest overall tensile strength was measured. For all investigated release agents, an increase in tensile strength could be achieved by the plasma pre-treatment.

Some of the samples show a high standard deviation (about 15–20%) for the mean tensile strength. This concerns in particular samples without pre-treatment. The considerable high standard deviation could be attributed to the inhomogeneity of the contamination.

Surface roughness and surface topography

The laminates produced by means of foils show a clearly low roughness (R_z < 20 µm) compared to samples manufactured using fabrics that exhibit R_z values up to 260 µm.

Regarding the adhesion, an increased macroscopic roughness can have a positive effect on the tensile strength for samples without plasma pre-treatment (see Fig. 8). However, this in turn does not mean that smooth surfaces show a lower adhesion strength in general (cf. sample 04-01).

Figure 9 shows the dependence of the tensile strength from the R_z value for the samples with plasma pre-treatment. The macroscopic roughness is hardly changed by the

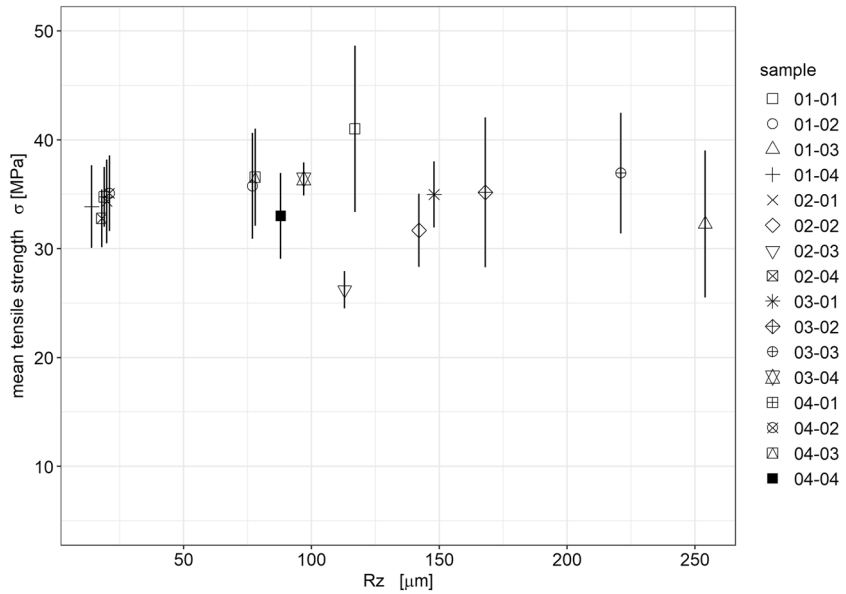

Fig. 9 Dependence of the tensile strength from the roughness (R_Z) for the samples with plasma pre-treatment

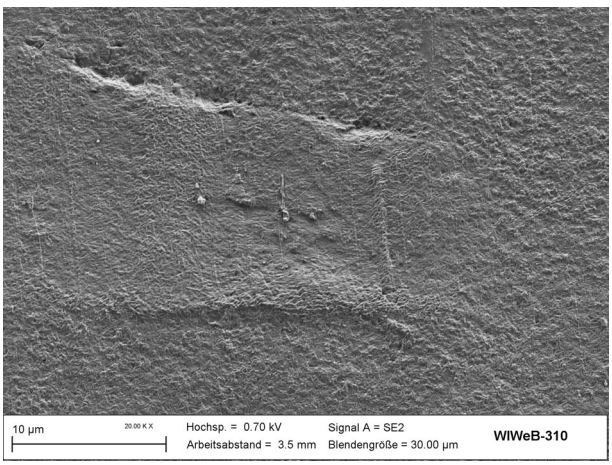

Fig. 10 Sheet-like, relatively even distribution of residues on the laminate surface produced with MR1

pre-treatment, but the tensile strengths is increased significantly as outlined above. As a results, the influence of the roughness on the tensile strength vanishes.

The form and distribution of residues of the release agent on the laminate surface was analysed by SEM down to the nanometer range. The observed structures are either of sheet-like nature (Fig. 10), fibrous (Fig. 11) or compact (Fig. 12). The fibrous residues are usually evenly distributed over the entire surface, while the compact structures are usually formed locally on smaller areas (see Table 4).

Despite local differences on a microscopic scale (µm-, nm-range), an inhomogeneous distribution of residues on a macroscopic scale (mm range) can not be detected in the SEM examinations.

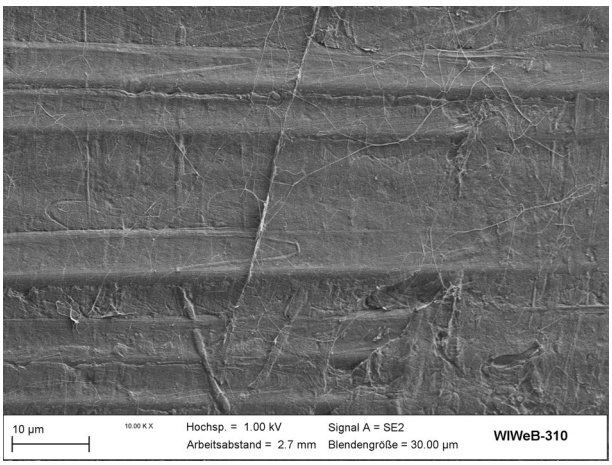

Fig. 11 Fibrous structures on the laminate surface produced with Setex Kalandert. The structures are irregular but evenly distributed

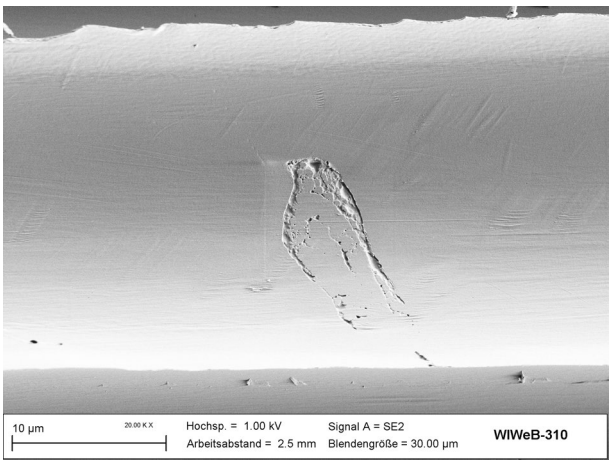

Fig. 12 Compact structure on the laminate surface produced with TFGS 075 PS. The structures are locally limited and therefore not evenly distributed on the surface

The laminate surfaces manufactured with various release agents react differently to the plasma pre-treatment. The shape and distribution are often not noticeably influenced. The amount of residues (cf. XPS results) and, in particular, the structure of the laminate surfaces are, however, sometimes modified. Exemplarily this is shown in Fig. 13 for the release agent MR2. After the plasma pre-treatment, the epoxy areas of the laminate surface show a fine structured surface that is not present before the pre-treatment. Thus a modification of the surface in the microscopic scale (nm-range) through the plasma pretreatment can be concluded for this sample.

Surface composition

For the XPS analysis, the specimens were examined directly after removal of the release film and peel ply as well as after the plasma pre-treatment. As outlined above, different fracture patterns could be observed after the removal of the peel ply indicating different

Table 4 Results of the SEM analysis of the laminate surfaces

Sample	Product	Shape of residues	Distribution of residues
01-01	Setex PTFE	Fibrous	Even
01-02	PTG 76	Compact	Local
01-03	Sefar 24-4-500	Fibrous	Even
01-04	Vac-Pac A6200	Compact	Even
02-01	MR1	Sheet	Even
02-02	8940	Sheet	Even
02-03	60 BR	Sheet	Even
02-04	MR2	Fibrous	Even
03-01	RE 234 TFP	Compact	Local
03-02	Sefar 1100-SK 012	Fibrous	Even
03-03	Sefar 1100-K 020	Fibrous	Even
03-04	RE 234 TFNP	Compact	Local
04-01	WL 4500C	Sheet	Even
04-02	TFG 125	Compact	Local
04-03	TFGS 075 PS	Compact	Local
04-04	Setex Kalandert	Fibrous	Even

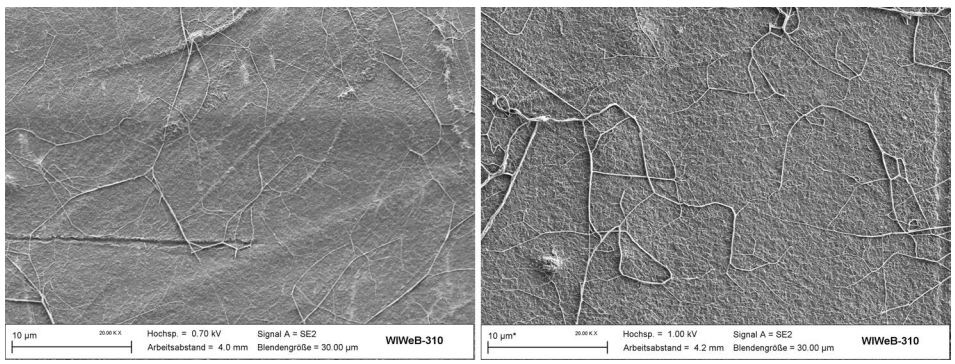

Fig. 13 Surface of the laminate produced with MR2 before (left) and after (right) plasma treatment. Fibrous residues of the release agent remain on the surface after plasma treatment. The fine structuring, which is visible in the epoxy areas, indicates a clear modification of the surface by plasma treatment

adhesion of the peel ply to the laminate. For the XPS analysis of mixed fracture surfaces (ADH/LFT), areas that do not show fibre tear were selected.

Based on the measured spectra, the element composition of the surface is determined.[1] The determined element compositions are shown in Fig. 14 for the samples without plasma pre-treatment and in Fig. 15 for the samples with plasma pre-treatment.

The main components of the composite material—carbon, oxygen and nitrogen—are clearly visible. In addition, a clear signal for the element fluorine is visible indicating a transfer from the release agent to the laminate surface. The results show that the transfer of fluorine to the surface fluctuates considerably between the investigated release agents. While for example for MR1 (sample 02-01) a fraction of about 5 at.% is found, the Sefar

[1] The element composition results from the integration of the corresponding element signals and is given in atomic%.

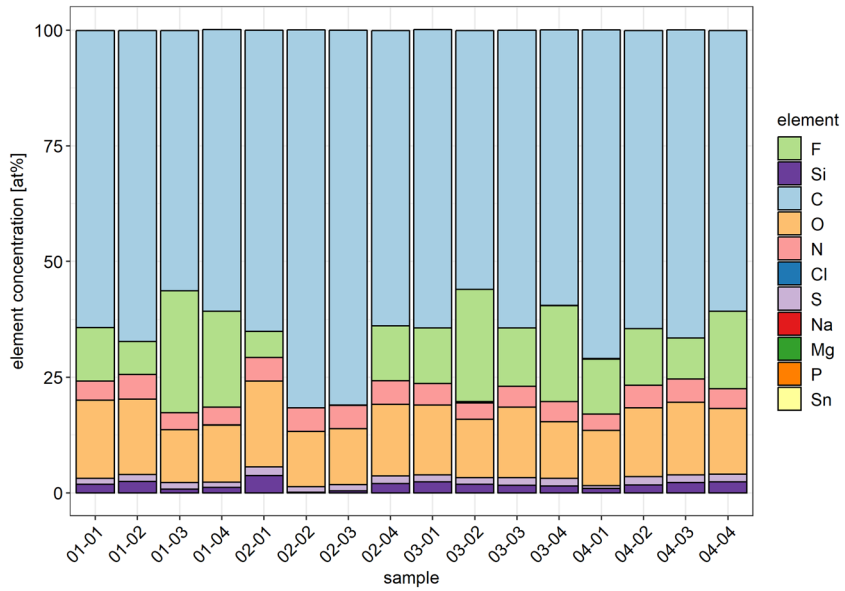

Fig. 14 Surface composition (atomic precent) of investigated laminate surfaces without plasma pre-treatment by XPS analysis

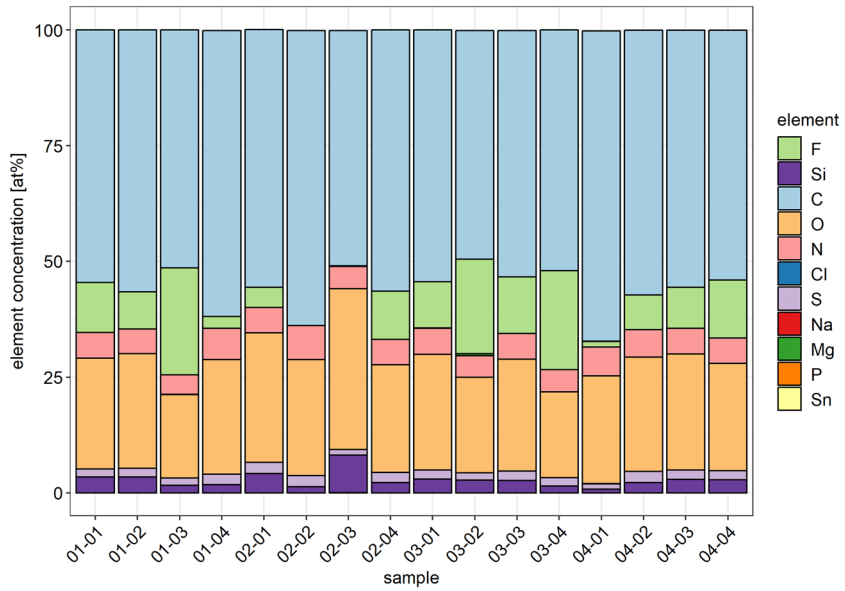

Fig. 15 Surface composition (atomic percent) of investigated laminate surfaces with plasma pre-treatment by XPS analysis

products (e.g. 01-03) show a fraction of 20–25 at.%. For most products, however, a fraction of about 10–15 at.% was found. A fluorine concentration, significantly lower than 10 at.% is only found for PTG 76, TFGS 075 PS and the already mentioned MR1. The materials UTT 8940 (02-02) and Tygavac 60 BR (02-03) do not show a contamination with fluorine, as the products are not fluorine-based and thus serve as a negative sample.

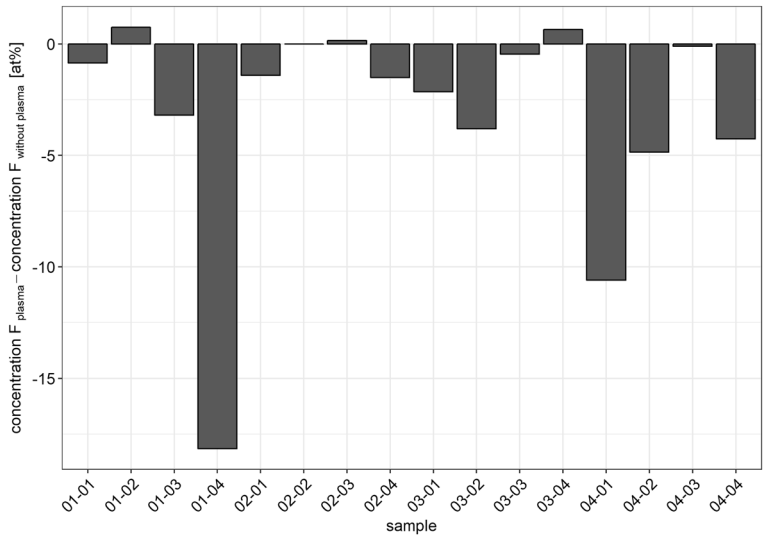

Fig. 16 Difference of the fluorine content in the sample surface due to the plasma pre-treatment by XPS analysis

In order to illustrate the effect of the plasma pre-treatment, the differences of the fluorine content on the surface (concentration F_{plasma}–concentration $F_{without\ plasma}$) are summarized in Fig. 16. As can be seen, the influence of the plasma pre-treatment on the fluorine content on the surface differs significantly for the samples. For most samples (e.g. Setex PTFE, Sefar 1100-K 020), there is only minor change in the fluorine content on the surface. For two samples, a slight increase of the fluorine content is being observed. The reason for this effect is that it is not possible to measure the identical location before and after plasma pre-treatment in combination with an inhomogeneous transfer of fluorine from the release agent to the surface. For some samples, however, a significant change in the fluorine content is found: (i) for WL 4500C, a decrease of approx. 10 at.% which results in an almost complete removal of the contamination; (ii) for Vac-PAC A6200, a decrease of approx. 17 at.% which also results in a significant removal of the contamination; (iii) for TFG 125 and Setex Kalandert, a reduction of approx. 5 at.% is found.

In the following, the fluorine content and the carbon-to-oxygen ratio are related to the determined adhesive strengths. Figure 17 summarizes the dependency of the tensile strength from the fluorine concentration on the surface. As the results show, there is no correlation between the amount of fluorine on the surface and the tensile strength neither before nor after plasma pre-treatment. Only, the tensile strength increases significantly after the plasma pre-treatment for all samples as outlined above.

To overcome the apparent contradiction—improved adhesive strength despite still existing contamination—the ratio of the concentration of oxygen to the concentration of carbon on the surface before and after the plasma pre-treatment (concentration O/ concentration C) is evaluated. A higher value for this ratio means the proportion of active oxygen species, which play an important role for the adhesion of the adhesive,

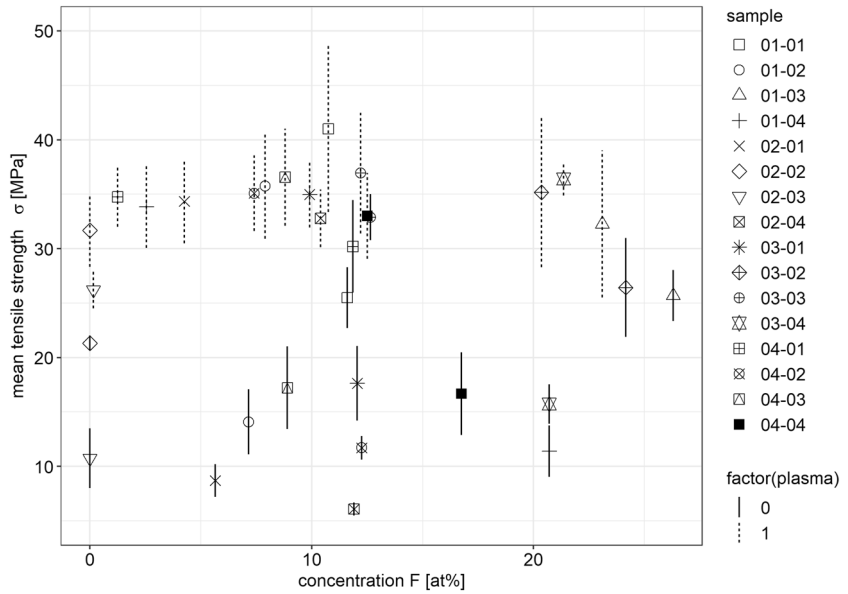

Fig. 17 Dependence of the tensile strength with and without plasma pre-treatment from the concentration of fluorine on the sample surface by XPS analysis

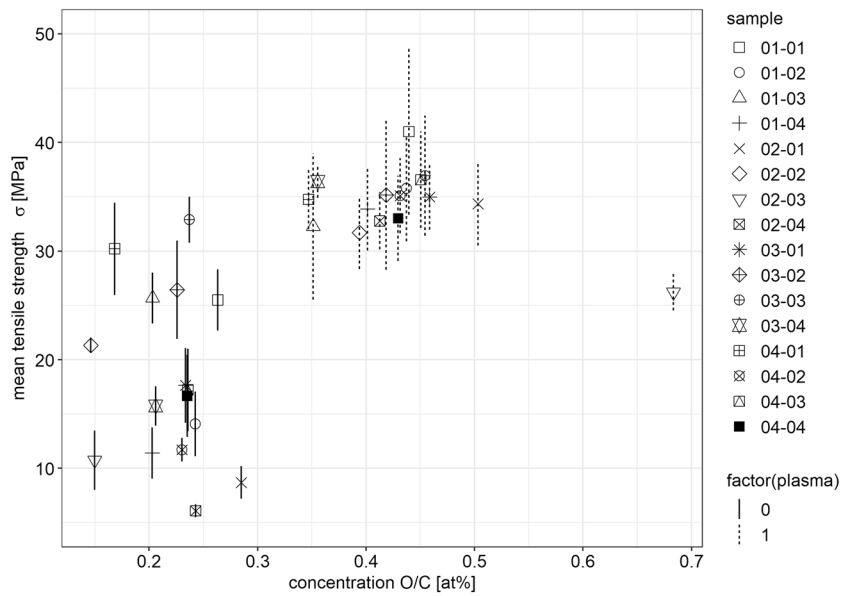

Fig. 18 Dependence of the tensile strength with and without plasma pre-treatment from the O-to-C ratio on the sample surface by XPS analysis

is higher and therefore an improved adhesion can be expected. Due to the plasma pre-treatment, the O-to-C ratio increases significantly for all tested samples. The increase is relatively uniform in the range of 0.2, with the exception of the sample prepared with the release agent Tygavac 60 BR (increase approx 0.5). The dependency of the tensile strength from the O-to-C ratio is shown in Fig. 18.

As for the fluorine concentration, the results show that there is no clear correlation between the O-to-C ratio on the surface and the tensile strength. Before the plasma pre-treatment the O-to-C ratio scatters over a rather large range (0.1–0.3); after the plasma pre-treatment the absolute value of the O-to-C ratio is increased for all samples, as outlined above, and the range of the values is slightly decreased.

Conclusion

The study shows that the use of many fluorine-based release agent in combination with a subsequent plasma pre-treatment after demolding can have no detrimental impact on the adhesive bonding performance of CFRP components.

The release properties of the release agents are an important factor to ensure reliable protection of the component surface without fibre cracks when the fabric or film is removed. It was shown that with a peel strength between 1 and 10 N/24mm, the adhesion to the laminate surface is good and there is hardly any fibre tear during removal.

With larger peel strength, fibre tears are more frequent. However, as Buchmann et al. showed, the occurrence of defects can be beneficially influenced by optimizing peel angle, peel ply orientation, and peel ply material [25].

Furthermore, the results showed that the roughness of the pristine surface can have a considerable influence on the adhesive strength and should therefore not be neglected. A positive effect on the bond strength can partially be identified when an adhesive failure is dominant for untreated samples. However, as soon as the samples are pre-treated and a complete cohesive rupture is reached, the positive effect vanishes. Similar results were found by Benard et al. [26] for a series of polyester and polyamide based peel ply treatments.

In the context of this work, a correlation between a contamination of the laminate surface by fluorine residues and the adhesive strength could not be found.[2] By means of the atmospheric pressure plasma pre-treatment, the fluorine residues on the surface could be reduced (for some samples significantly), but with the selected plasma parameters the contamination could not be removed completely. Regarding the plasma treatment, a similar results was found by Encinas et al. [27], whereby it unclear which peel ply or release agent was used for the manufacturing of their laminates.

However, a large amount of oxygen could be incorporated into the surface, so that an oxygen-to-carbon ratio in the range of 0.35–0.5 could be achieved. As a result, a significant increase in tensile strength (up to 42 MPa) was found together with fibre tear fracture patterns. With tensile strength of 30 MPa and above, the failure of the first laminate layer is thus the most dominant failure mode and hence the laminate strength is evaluated in the end.

Of particular interest here is the fact that some peel-plies made from PTFE yarn, although not originally produced as release fabrics, fulfil the requirements of a release agent better than conventional release agent. For example Sefar 1100-K 020 peel ply is the only release agent that leads to a boundary layer break in the laminate without a plasma pre-treatment. This means by using a selected fabric, the initial, untreated state

[2] Parker et al. [12] found in their study a connection between concentration of fluorinated contaminant and single lap shear strength. However, in their study, the concentration was up to 90 at.% F.

can be significantly improved, which, together with a pre-treatment, can make the entire bonding process much more robust and secure.

Beside the fluorine-based release agents, the peel ply UTT 8940 and the silicone-based release-ply Tygavac 60 BR, both of which are used in the production of CFRP components, were investigated as reference samples. In the case of the UTT 8940, the poor release property (highest peel strength), which in the majority of the samples leads to fibre tears in the laminate, is particularly critical. For the Tygavac 60 BR, the lowest tensile strength was found in the entire field with and without plasma pre-treatment.

This work thus contributes to the future targeted development of release agents regarding their impact on preparation of fibre composite surfaces to ensure a reliable adhesive bonding process.

Abbreviations

CFRP: carbon fibre reinforced plastic; XPS: X-ray photoelectron spectroscopy; SEM: scanning electron microscopy; CLSM: confocal laser scanning microscopy; CAT: centrifuge adhesion test; PTFE: polytetrafluoroethylene; ETFE: ethylene tetrafluoroethylene; PVF: polyvinyl fluoride; APP: atmospheric pressure plasma.

Acknowledgements

The authors acknowledge the financial support by the Federal Ministry for Economic Affairs and Energy of Germany in the project SCHACH (project number 20W1303F).

Authors' contributions

MH (Last and corresponding author) was responsible for drafting and completing the article, the surface characterisation by XPS and contributed to the data analysis. TH, FZ and JH were responsible for the surface characterization by SEM, CLSM and the measurement of the peel resistance and supported with expertise on adhesion and surface analysis. DF was responsible for sample preparation, mechanical characterisation by CAT and contributed to the design of the work. TK contributed to the conception and design of the work. All authors read and approved the final manuscript.

Funding

This is an article based on parts of research performed within the project SCHACH. The project was funded by the Federal Ministry for Economic Affairs and Energy of Germany.

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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Received: 1 March 2019 Accepted: 15 May 2019
Published online: 28 May 2019

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