

Influence of Plasma activation on surface energy and adhesive properties of RTM6-CFRP

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Abstract

In aircraft construction, carbon fiber reinforced composites (CFRP) with RTM6 matrices are commonly used in combination with bonding. Requirements for this joining technique are good adhesion properties along with high surface energies of adherends. RTM6-CFRP do not meet these requirements. The effectiveness of plasma activation in case of improving surface energies has already been proven for various materials. For RTM6-CFRP no results are available yet. For this reason, two methods of plasma activation (low and atmospheric pressure plasma) will be compared and optimal parameters for this joining technique will be determined. Summarizing this, for both activation processes a significant increase of surface energy is recognizable. Proven by lap-shear tests a rise of adhesion properties through plasma activation is detectable as well. In future, aerospace and other industrial sectors are able to benefit from these findings, which can contribute to improve the reliability of adhesive joints for mentioned material.

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Introduction

Weight reduction plays a major role in aerospace industries. For example, 10 kg saving in weight in an Airbus A320 already means a 1.75 liter fuel reduction per flight. This adds up to a total of €6.7 million cost savings in one year for the whole fleet. Nowadays, in a commercial aircraft frictional and keyed connections in joint zones are still predominant, which implies additional weight. A substitution by adhesive bonds enables substantial weight loss, which results in economic gain. But because of insufficient inspection of bonding joints and restricted reliability this will be a challenging task.

A series of pre-treatment techniques have already been established, that lead to an improvement of quality in bonding. In this context several techniques may be distinguished, thermic, chemical, mechanical and electric methods.

Plasma activation (electric method) is already being applied in manufacturing of medical equipment, tubes and consumables. By applying functional groups on the surface of specimens, these techniques result in an increase of surface energy that has a beneficial impact to adhesion properties. Various types of plasma activation methods can be distinguished, which have, in each case, process-related advantages and disadvantages. For large structures and three-dimensional-shapes atmospheric pressure plasma (APP) is suitable because of its inline-capability. In contrast, low pressure plasma (LPP) is well known for careful and also effective processing.

In the present study the influence of these plasma treatment techniques on surface energy of aircrafts using RTM6 carbon fiber reinforced composites (CFRP) is investigated. Therefore, these two techniques will be compared with regard to their effectiveness and processing properties. Additionally, optimal parameters will be determined for the abovementioned matrix material. Finally, these

parameters will be estimated relating to their adhesion influence through lap shear test series. It is worthwhile to mention that this study presents exclusively lap shear results for APP parameter researches. Further investigations of parameters are in progress. Another point that will be discussed is the technological need of surface cleaning before the plasma activation process. This is relevant especially for the RTM6-CFRP material.

Experimental

Materials

In this study the CFRP specimens were produced using the following materials:

1. HexFlow® RTM 6, 1K-epoxy resin
2. Saertex (NCF) biaxial, 4 layers, Fiber Tenax-E-HTS40 F13 12K, 0/90° weight per unit area 557 g/cm²; ±45° weight per unit area 540 g/cm².
3. Precision Fabrics Group Inc., Greensboro Peel ply Style 56009 Polyester
4. Mikon 705 MC release agent

Specimens manufacturing

Specimens were produced per vacuum infusion onto an aluminum hotplate. Infusion was processed by use of the standard injection cycle as specified by Hexcel. Fiber volume content of all specimens was continuously at 60%. For tailoring a water jet cutting plant was used. Sample dimensions were 75x25 mm. Before starting surface investigations, each specimen was cleaned by compressed air (oil-free).

Used equipment

- Drop Shape Analyser DSA25, Krüss GmbH (Germany); measuring method OWRK; measuring fluids distilled water, diiodmethan 99%, ethylene glycol 99,5%; for sample cleaning isopropyl 99,8%; Krüss software ADVANCE; for determinations of surface energy following measurement

parameters were defined: droplet size 2 μl , drop dispense velocity 0.16 ml/min; Temperature 22-24°C at laboratory ambient air.

- Notation on measuring method OWRK: this method allows to calculate the surface energy with one polar and one disperse fluid. For matching the results of these two fluids, additional tests were run with a third fluid (ethylene glycol).
- *Low pressure plasma device, Tetra Duo Femto 30*, Diener electronic GmbH (Germany), Low frequency-generator 300 watt; frequency 40 kHz; alternating current; vacuum chamber arranged as double plate reactor.
- *Atmospheric pressure plasma RD1004*, openair-plasma, Plasmatreat GmbH (Germany); rotating plasma jet; generator FG 5001; rotation nozzle speed 2500 rpm; nozzle width 28 mm; gas flow rate 30 slm; frequency 19-23 kHz; working gas compressed air (oil-free). Sample holder movement with velocities from 1-60 m/min.
- *X-ray photoelectrical spectroscopy (XPS)* performed by using an Omicron XM1000 mono-chromatized X-ray source with Al K α radiation (1486.7 eV) and Omicron EA125 hemispherical analyzer with pass energy of 50eV and pass energy of 17 eV for C1s peaks.
- *Zwick/Roell Zmart.pro (1464)* 50 kN; lap shear test according to EN DIN 1465
- *j. Keyence VHX-5000*, digital microscope, Keyence GmbH (Germany), progressive scanning, optical resolution 4800 (H) x3600 (V) (pixel size 18 millions), up to 2500x magnification
- *Advanced development profiler, VeecoDektak 8*, New York (USA), contact-based 2D/3D topography measurement to samples up to 200mm; 262 μm vertical range with 1 Å vertical resolution at 6.55 μm range
- *Scanning electron microscope ESEM XL30 FEG*, FEI company (USA), operating pressure: high vacuum to 20 mbar
- *HIOKI LR 8400-20*, Memory Hilogger, temperature measurement device, thermocouple type J, wire width 0.25 mm

Investigated parameters

Preliminary investigations

During preliminary investigations different types of surface cleaning methods on surface energy were tested. Surface energies of specimen treated with compressed air or isopropyl are compared to grinded samples. The results can be looked up in chapter 3.1.

Low pressure plasma treatment

The effect of LPP treatment can be influenced by varying the input parameters like generator power, pressure, time and the type of gas. Generator power can be modified from 0 to 100% (maximal power equals 300 watt). For researching the influence of generator power, 50% (=150 watt) and 100% (=300 watt) were selected. The range of plasma treatment durations has been subject to various publications. Paynter [1] describes a 12-14% increase of oxygen concentration on polystyrene surface after 30 sec in oxygen plasma. Min Ho Kim et al. [2] suggest 60 sec for carbon/epoxy Prepreg. Gleich [3] points out that 60 to 300 sec are suitable for polypropylene samples exposed to oxygen plasma. With reference to these previous investigations the time range was chosen from 10 to 300 sec. That means 10 sec – 30 sec – 60 sec – 300 sec. Despite of [3] who mentioned 10 sec as an insufficient time for the activation because of transient response of plasma processes and non-equilibrium of contained particles (electrons, ions, atoms and furthermore neutral and radical components), 10 sec will be set within the scheduled measurements. The pressure in the vacuum chamber was varied from low pressure, which means 0.1 mbar, to a mid-value 0.4 mbar and additionally to a high pressure (0.8 mbar). These values range within the threshold of the low

frequency generator zone. Thus, the entire scope of pressure – high, middle, low – could be covered. Other publications deal with equal pressure ranges (10 to 500 Pa maximum) as described in [4]. All measurements were done with oxygen-plasma but in order to have a comparative value for APP treatment, which works with compressed air, air-based plasma has also been used. The results of this comparison are discussed in chapter 3.2.3.

Atmospheric pressure plasma treatment

To determine the beneficial settings for APP treatment some parameters were varied. At first the parameters of generator frequency and plasma cycle time (PCT) were considered. A frequency range between 19-23 kHz is feasible. At 23 kHz, the plasma pulses more often as at 19 kHz. In chapter 3.3.1 the influence of minimal and maximal frequency on surface energy is examined. The PCT represents the duration of the plasma pulse. It can be modified in a range from 0 to 100%. For the following experiments a PCT of 50% and 100% were chosen. The results are contained in chapter 3.3.2., were further parameter, the distance of the plasma nozzle to sample surface and the speed of sample holder were studied. The fabricator suggests a distance between 5 to 18 mm. Another publicized work [5] refers to 5 mm distance. Therefore those mentioned distances and further the middle distance range of 10 mm was selected. The sample holder speed can be changed from 0.1 m/min to 60 m/min. For testing different values, two lower speeds (1 m/min and 5 m/min), a middle speed (27 m/min) and the maximum (60 m/min), were chosen. The influence of these parameter variations can also be abstracted from chapter 3.3.

Results and Discussion

Influence of plasma activation on surface energy

Results of preliminary investigations

Today several technologies for manufacturing of carbon fiber reinforced composites are available. According to the type of production varying kinds of chemical consumables are applied, which leave remnants on composites more or less. For processing by vacuum infusion these are peel ply, release film, release agent and fabric sheet [6], [7].

Produced RTM6-CFRP specimen were investigated by the use of three pretreatment methods, compressed air (oil-free), solvent wipe (isopropyl), 1000 grade grit paper. The influence on surface energy is demonstrated in Fig. 1.

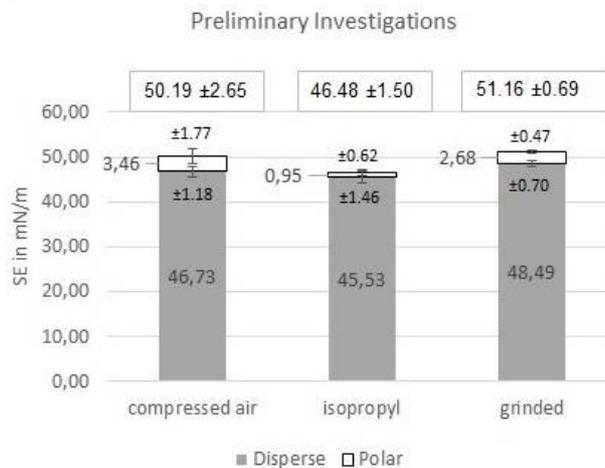


Figure 1: Pretreatment of CFRP-RTM6-specimen

As seen above, the compressed air treated specimen presents values with highest polarity, 3.46 mN/m. The use of isopropyl decreases polar and disperse parts, additionally. Responsible for this result could be the chain length and reactivity that enables the isopropyl to interact with disperse groups. Grit paper causes a small increase of surface energy, but the polar part shows with 2.68 mN/m a lower value as compressed air. For preliminary trials the height of disperse parts differ between 46-49 mN/m.

Published works on pretreatment describe similar results with grit paper and their reduction of polarity [8] and furthermore a decrease of lap shear strength of isopropyl treated specimens [9], that could explain the decrease in surface energy.

Resulting from preliminary trials the pretreatment of specimens with solvent wipe and grit paper is not necessary. Further measurements will be run with compressed air treatment and use values of compressed air as a comparison to plasma activation.

Results of low pressure plasma activation

Hereafter the results of investigations on low pressure plasma (LPP) are described. The LPP was produced by the low pressure plasma system Femto Duo Tetra 30.

Different from APP researches no temperature parameters were modified. The temperature in the used device ranges from nearly room temperature to up to 38°C maximum. The low frequency generator does not have any effect on temperature in the vacuum chamber. The maximum temperature of 38 °C was reached after 20 minutes of treatment.

See below the results of parameter variation.

Influence of generator power

The low frequency generator was specified with 300 watt total power. First investigations were carried out at equivalent pressure (0.4 mbar) and varying times (60 and 300 sec) with the aim to draw conclusions about the output influence. Therefore, two parameters 300 watt as 100% generator power and 150 watt as 50% were chosen. Surface energy measurements should reveal a difference between 100% and 50% generator output during the plasma activation of RTM6-CFRP-specimens.

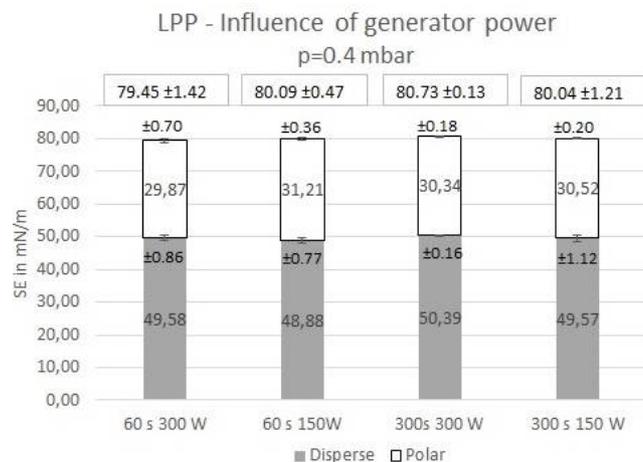


Figure 2: Separation of surface energy in polar-disperse parts for mentioned parameters

As is visible in Fig. 2 the variation of the abovementioned parameters do not significantly influence the surface energy of the specimens. At 60 sec the surface energy is 79.45 mN/m at 100% generator power and runs up to 80.09 mN/m at 50%. For 300 sec the value of surface energy is about 80.73 mN/m at 100% and

80.04 mN/m at 50%. Besides, the surface energy is divided into polar and disperse, where you can see small variations in both parts. Standard deviation of data was negligible as shown above. Changing the generator power seems to have a smaller influence than presumed. There is a difference of 0.81% deviation in surface energy for both output settings. According to these small differences, the generator output can be disregarded. Furthermore value variance could be caused by measurement inconsistency as well.

The result of these first investigation suggests to decide for only one generator power for following trials. In this particular case, the 100% output was determined as final parameter setting.

Influence of pressure and time

The parameters of pressure and time were investigated simultaneously. As it is already described in chapter 2.4 three pressures (0.1, 0.4 and 0.8 mbar) and four time steps (10 s, 30 s, 60 s and 300 s) were combined.

The results of variation in pressure and time are listed below and start with an overview in Fig. 3. Afterward, the settings which yield the highest level of surface energy will be illustrated and discussed.

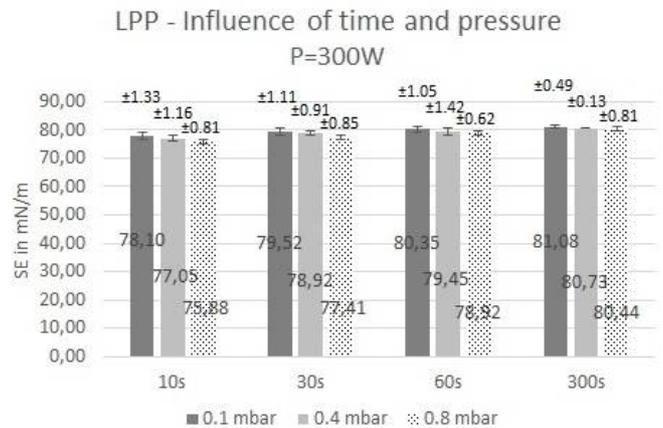


Figure 3: Overview of different pressures and times with their influence of surface energy

For a comparison to surface energy of untreated RTM6-CFRP-specimens see Fig. 1, chapter 3.1, the reference surface value was about 50.19 mN/m. As is visible above, the increase depends on plasma pressure. Low pressure (0.1 mbar) steadily raises the surface energy and shows higher values than medium pressure (0.4 mbar) and high pressure (0.8 mbar). This shows a linear correlation between pressure ranges and surface activation. Additionally, there is a proportional correlation between the rise of surface energy and the length of plasma exposure. That means a 300 sec activation process causes maximum energy on specimen surfaces. To see at the bar graph above all values increase over time. A longer plasma exposure time leads to a minimizing of value differences. The reason for this value approximation is a saturation effect on sample surfaces, which is described more detailed in the discussion part. In sum of these LPP researches the 300 sec duration at the lowest pressure elevates the surface energy to 81.08 mN/m, this is a 61.5 % rise.

By regarding the disperse part separately in Fig. 4, it remains constant between 49-51 mN/m, compared to the disperse part of untreated specimens (Fig. 6). The polar part, however, increases up to 30.52 mN/m, that is a rise of 782% in comparison to the reference specimen. As mentioned before, the LPP treatment always shows slightly higher values in polar parts. This persists for other measurement variations as well.

Fig. 4 also shows the plasma parameters, which generate the highest result in surface energy and polarity. In conclusion, it can be said that the 300 sec oxygen exposure at 0.1 mbar delivers promising results for activation levels. It should be proved in further tests on variation in material, component geometry (undercut) and inline process implementation, particularly, on shortening the evacuation time of the plasma chamber.

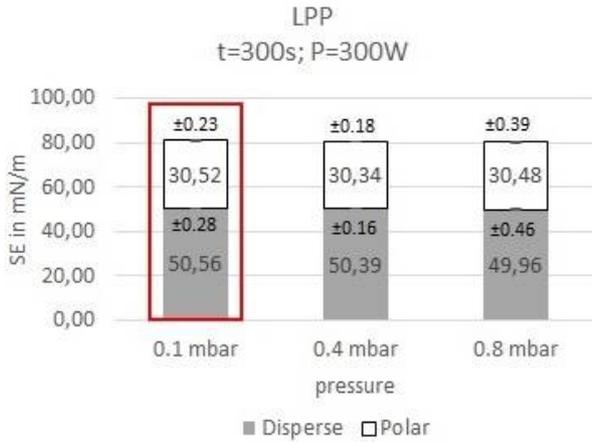


Figure 4: 300 sec oxygen-plasma exposure, generator power 100%

The comparison of untreated RTM6-CFRP (reference) and LPP settings with highest polarity are pictured in Fig. 5/6.

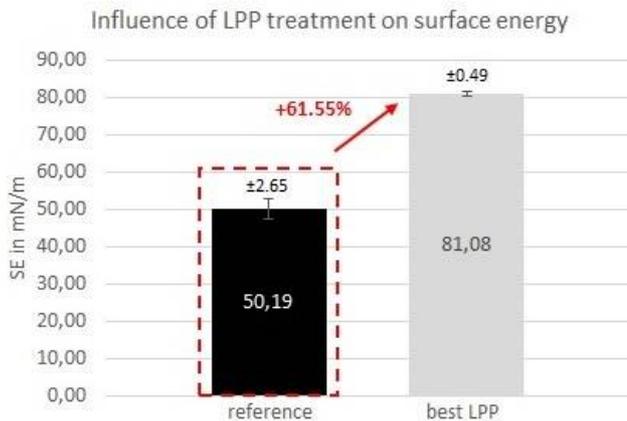


Figure 5: Reference surface value and best activation parameter at LPP

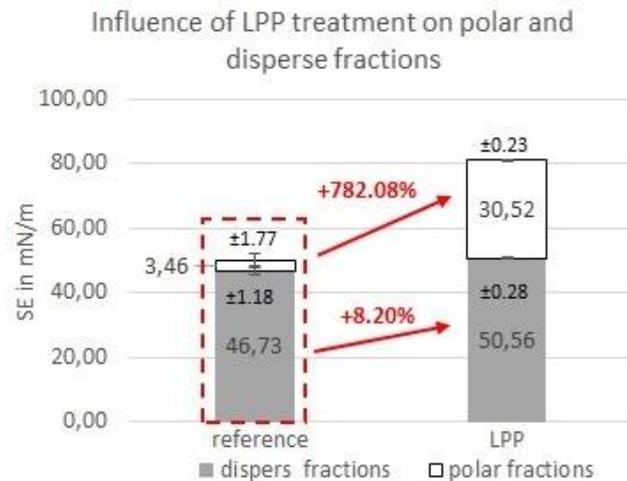


Figure 6: Summarized surface energy polar/disperse of reference and LPP treatment

Finally, Fig. 7 presents the summary of data pictured by design of experiment (DOE), Design Expert 10:

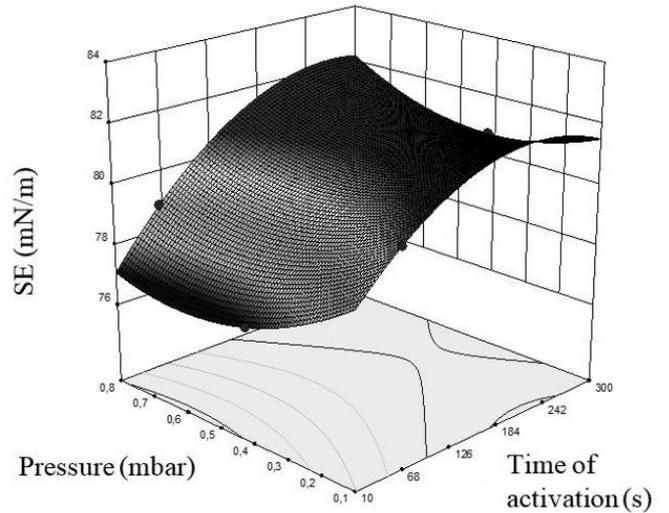


Figure 7: DOE graphical overview of LPP results

Investigations on air-plasma

To ensure a better comparability between oxygen LPP and APP activation by use of compressed air (oil-free), an investigation on air plasma exposure was done. Parameters like generator power, pressure and plasma duration time were chosen as described above from results which generated highest surface energy and polarity (marked in Fig. 4, bar on the left with 0.1 mbar, 300 sec). The used air in the vacuum chamber was not precleared, but from laboratory environment. Values of surface energy and polar/disperse parts can be found below.

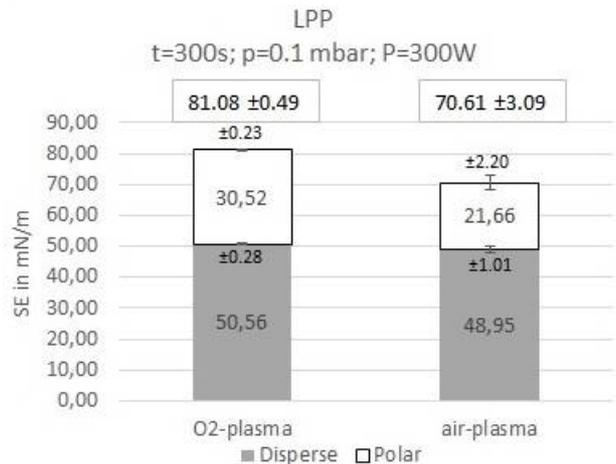


Figure 8: Polar/disperse parts of surface energy for air and oxygen plasma

The result is a difference of surface energy of about 13 percent. Attention should be paid to the higher deviation in measurement data by the use of air plasma. The separation of surface energy into polar and disperse parts is also visible in Fig. 8. Clearly recognizable is that the polar part of air plasma (21.66 mN/m) is 29% less than the polar part of oxygen plasma (30.52 mN/m). Besides, disperse parts of specimens also rise minimally, as was the case in previous measurements. In summary, it can be stated that at LPP all kinds of gaseous elements have an apparently great influence on surface energy and their polar part level. Eventually, the surface can be modified depending on required polarity, surface chemical groups and reactivity.

Results of atmospheric pressure plasma activation

In this chapter, the results of the APP treatment are summarized. As already described in chapter 2.3 we used a plasma-jet built by Plasmatrete GmbH to activate the specimens with APP. At first, the influence of this sample treatment on surface energy was examined. The Plasma generator allows two parameters to vary, frequency and plasma cycle time (PCT), so their effects will be determined. Additionally, the influence of the plasma nozzle distance to specimen and the speed of the moveable sample holder were analyzed. Microscopy and XPS completed the investigations to show the changes in topography and chemical composition of sample surfaces after plasma treatment.

Influence of frequency

The generator of the plasma-jet is able to work with frequency ranges between 19 and 23 kHz. To check the influence of frequency, the samples were treated with 19 kHz and in a second measurement series with 23 kHz, keeping all other parameters like speed, distance and PCT constant. Fig. 9 shows the results.

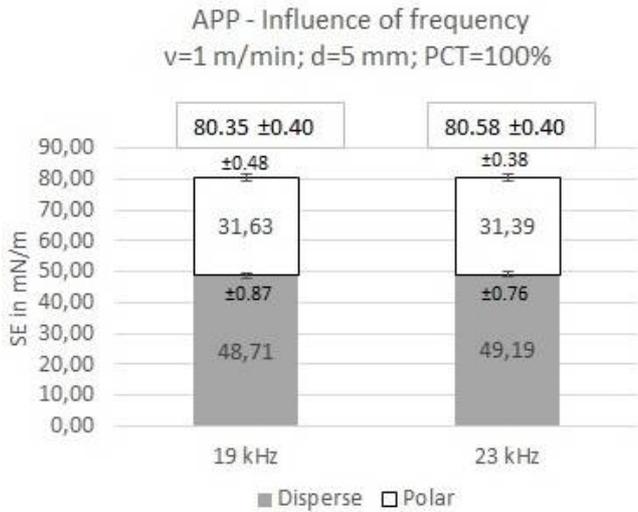


Figure 9: Influence of frequency on surface energy

The total surface energies for 19 kHz and 23 kHz are 80.35 mN/m and 80.58 mN/m, as shown above in the bar graphs. The difference between surface energies is nominal (< 1mN/m) and furthermore lies within the standard deviation, and therefore it is negligible. In this Figure, the total surface energies are divided into polar and disperse fractions. No great differences between the two frequencies are detectable. The polar fraction value for 19 kHz is 31.63 mN/m and for 23 kHz it is 0.76% less. Disperse parts show similar outcomes.

As a result, frequency has no significant influence on plasma treatment and frequency variation can be neglected for subsequent investigations. Therefore, 19 kHz as standard frequency for further researches was chosen.

Influence of plasma cycle time

To investigate the influence of plasma cycle time, specimens were activated with 50% and 100% PCT. Different settings were implemented to widen the investigation range. The distance 5mm and the frequency 10 kHz were set as fixed parameters. As variable parameters the speed and PCT were set. In Fig. 10, different speeds and surface energies for 50% and 100% PCT can be seen.

Consider that, the bars at different PCT are very similar in height. For example at 1 m/min the surface energy at 50% PCT

differs only 0.53% from the surface energy at 100% PCT. For other speeds the discrepancy varies from 0.62% (27 m/min) to 1.09% (60 m/min). PCT seems so have no influence on total surface energy. For closer examination we divided the surface energy in polar and disperse fractions. In Fig. 11 polar and disperse parts at 1 m/min speed, 5 mm distance and 19 kHz frequency are shown for 50% and 100% PCT. As expected, there is no huge influence neither on polar fractions nor on disperse fractions. The polar fraction at 50% PCT differs from 100% PCT by 0.48 mN/m, for the disperse fraction the difference with 0.07 mN/m is even less. This means no remarkable difference.

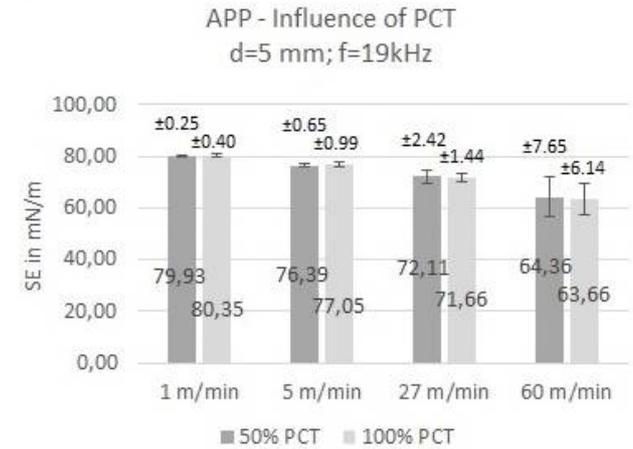


Figure 10: Influence of PCT on total surface energy

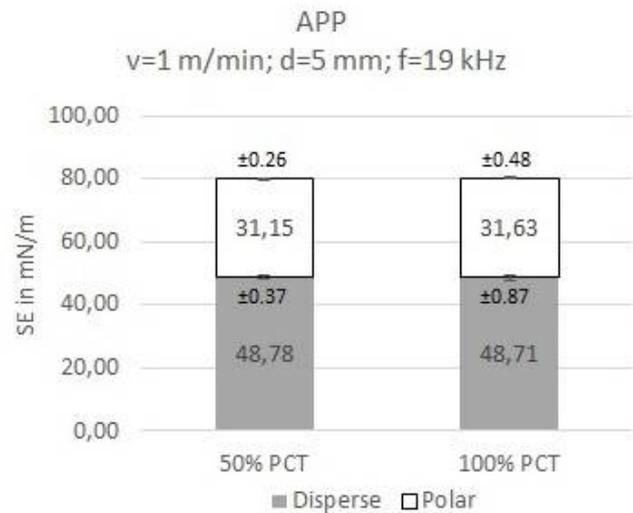


Figure 11: polar and disperse fractions at 1m/min

In summary, the plasma cycle time as well as the frequency has no crucial influence on surface energy. For this reason, plasma cycle time will be set at 100% for further investigations.

Influence of distance (plasma nozzle to sample)

For investigations concerning the influence of distance, the parameters distance and speed were set as variable parameters, whereas PCT (100%) and frequency (19 kHz) were fixed, respectively.

In Fig. 12 three distances (5mm, 10 mm and 18 mm) can be compared at four different speeds (1 m/min, 5 m/min, 27 m/min and 60 m/min). The first thing to notice is, that distance has an important influence on the plasma activation effect. The closer the plasma nozzle is set to specimens, the higher the surface energy becomes. This issue is very relevant at higher speeds, as it can be

seen at 27 m/in and 60 m/min. At such high speeds a small distance (5 mm) is necessary to produce high surface energy levels. An interesting insight one can gain by a closer look at the results, is that distance becomes less important the slower the specimens move through the plasma beam. The results at 1 m/min and 5 m/min with a distance of 5 mm and 10 mm are almost equal. At 1 m/min the difference between surface energy at 5 mm and 10 mm is about 0.29 mN/m and for a speed of 5 m/min it differs by 1.77 mN/m. These small differences can also be attributed to the standard deviations of surface energy.

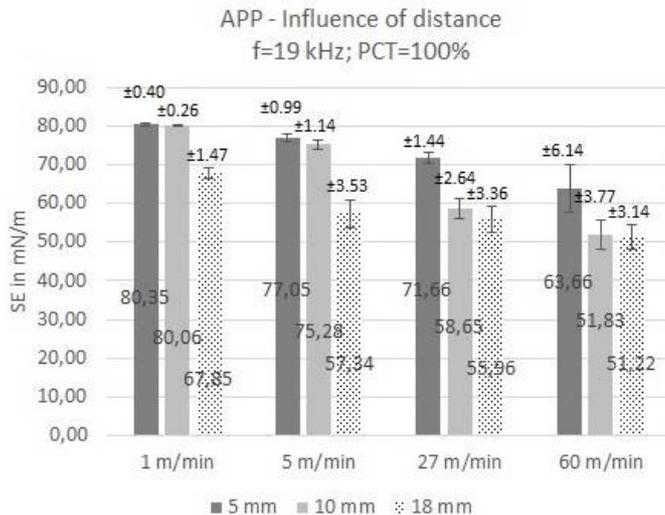


Figure 12: Influence of distance on total surface energy

The influence of distance on polar and dispersive fractions of surface energy is depicted in Fig. 13. The speed was set to 1 m/min. Regarding other speeds, the results show roughly the same behaviour and will therefore not be considered furthermore.

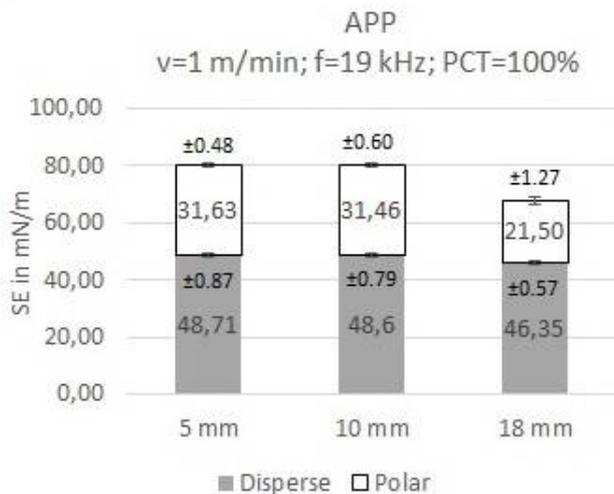


Figure 13: Influence of distance on polar and disperse parts

As might be expected, distance has a great influence on polar fractions whereas disperse fractions increase insignificantly visible. In Fig. 13 that polar fraction increases from 21.50 mN/m at a distance of 18 mm to 31.63 mN/m at distance of 5mm, which is a 47.11% increase. In comparison, disperse fractions increase 5.09% in total.

Recapitulating the insights, the distance has a huge influence on the effectiveness of plasma treatment. The nearer the plasma nozzle is set to specimens the higher the surface energy becomes.

Influence of activation speed

The last studied parameter is the influence of speed on surface energy. The parameters tried and tested are listed in chapter 3.3.3, for now, the focus was set on speed variation. Fig. 14 shows the total surface energy of specimens treated with four different speeds at three distances.

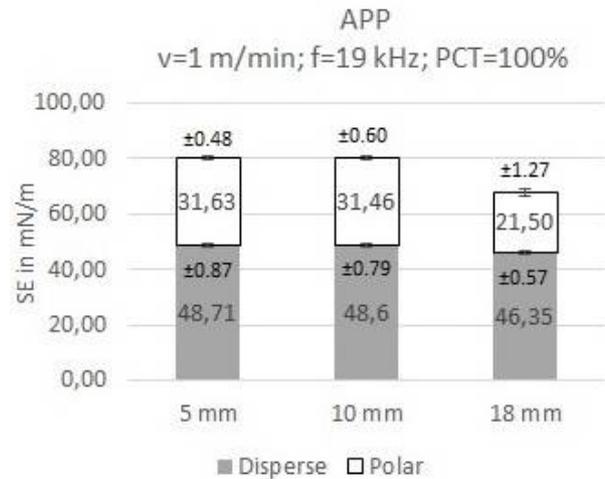


Figure 14: Influence of speed on total surface energy

As pictured above, the surface energy increases with decreasing speed at each distance. At a distance of 5 mm, the surface energy increased from 63.66 mN/m to 80.35 mN/m by reducing the speed from 60 m/min to 1 m/min. Another insight of these results is gained by looking at the standard deviations. Especially for 5 mm and 10 mm, the standard deviation reduces with decreasing speed. The rotation of the plasma nozzle could be responsible for this phenomenon, which will be discussed in chapter 3.4.

In this section, the polar and disperse parts of surface energy will be studied. Fig.15 presents the different parts of the four investigated speeds at a 5 mm distance. Outcomes of other analyzed distance variances show a similar behaviour and will not be further discussed.

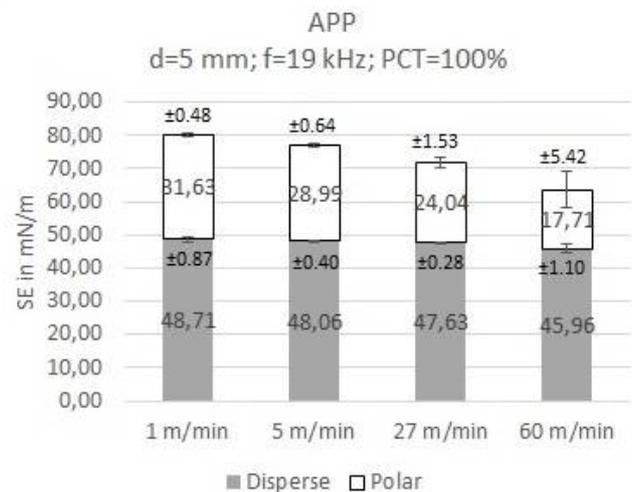


Figure 15: Speed influence on polar and disperse fractions

How visualized above the disperse fractions is increasing by 5.98% from 45.96 mN/m (60 m/min) to 48.71 mN/m (1 m/min). The polar part of surface energy, in comparison, increases significantly higher. Between polar fraction at 60 m/min and 1

m/min there is a difference of 13.92 mN/m, which is a rise of 78.6%.

It follows that the speed has also a crucial influence on surface energy. The slower the plasma activation speed the higher the surface energy with its polar fraction becomes.

Summary of parameter adjustment

All consequences of investigating the parameter adjustment for APP treatment are summed up in the next few lines. While frequency and plasma cycle time does not have a significant influence on the plasma treatment effectivity of surface energy, distance and speed are some decisive factors. The best results are achievable with small distance (5 mm) and low speed (1 m/min) plasma treatment. Analysed data of measurements are pictured by design of experiment (DOE), Design Expert 10 in Fig. 16.

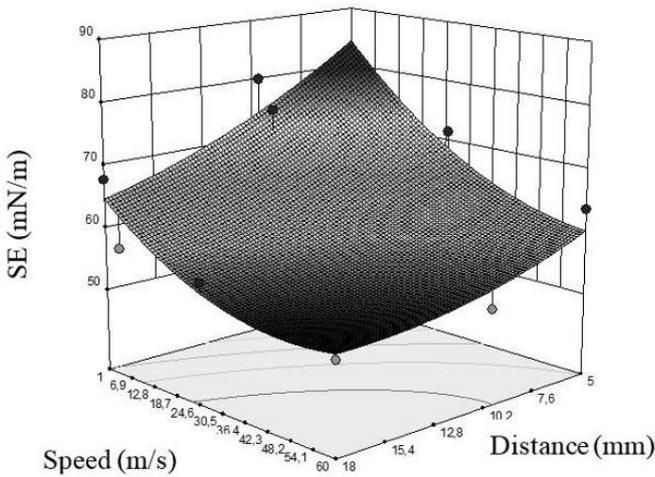


Figure 16: DOE graphical overview of APP results

The comparison of surface energies reached with APP treatment and the values of reference sample can be seen in Fig. 17/18.

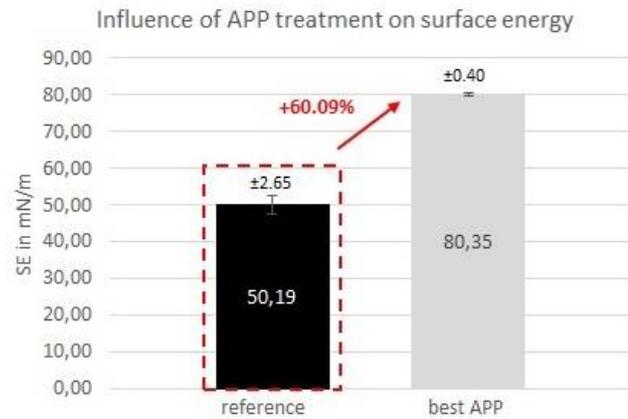


Figure 17: Influence of APP treatment on total surface energy

Fig. 17 shows an increase of total surface energy with APP treatment by 60.09% from 50.19 mN/m to 80.35 mN/m. As you can see in Fig. 18 this increase is attributed to the rise of the polar fraction from 3.46 mN/m to 31.63 mN/m. This is an increase of 814.16%, while the disperse part is increasing by 4.24% only.

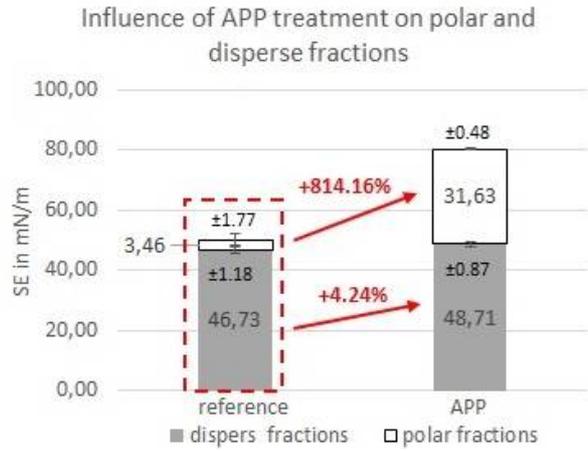


Figure 18: Influence of APP on polar and disperse parts

Investigations on temperature

In comparison to the low pressure plasma activation under room temperature up to max. 38°C, the APP activated specimens have to withstand higher temperatures. The gas temperature can vary between 150 and 300°C within the plasma beam. Therefore temperature on the sample surface can rise. To investigate temperatures on sample surfaces a specimen was prepared with a thermocouple. Fig. 19/20 illustrate the measured temperature profiles.

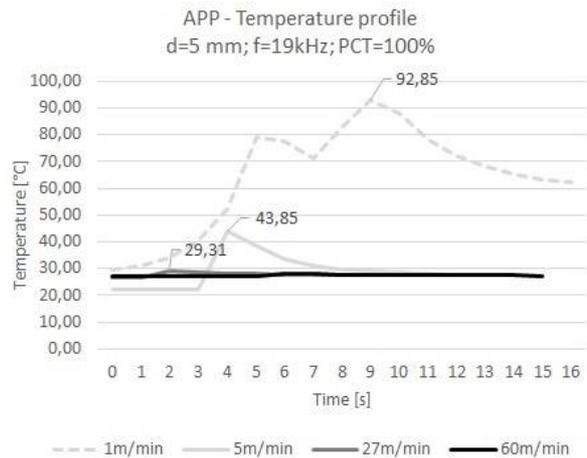


Figure 19: Temperature profiles at 5 mm distance

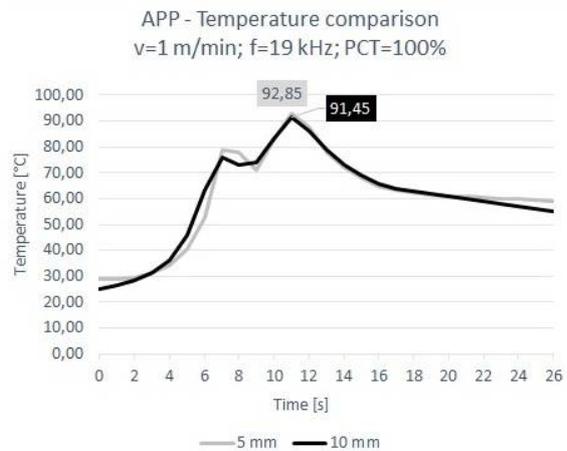


Figure 20: Temperature comparison at 1 m/min

To see in fig.19, the speed was varied at a constant distance of 5 mm. Here, the temperature depends on the speed. The lower the speed the higher the temperature level. While temperature increases over 90°C at lowest activation speed, samples were not affected with higher temperatures at higher speeds. Fig. 20 shows a temperature comparison of different distances (5 and 10 mm) at an activation speed of 1 m/min.

The influence of distance from sample to plasma nozzle is not as high as expected. The temperature maximum is nearly the same as can be seen above.

In summary, the effect of temperature upon the surface of the sample depends on activation speed. Resulting temperatures are below 100°C and do not cause damage to the sample surfaces.

Influence of double activation

For the APP investigations the specimens received a single activation. Zaldivar et al. [9] have done research on the effect of multiple activation. They measured the contact angle of epoxy based composites after several plasma treatments. The outcome was a reduction of the contact angle with a rising number of activations. However, the effect is not as strong as on other materials like polycyanurate composites. Consequently, we will not perform further investigations on multiple activations. Another point to discuss is the higher level of temperature when samples are treated several times. In Fig. 21 you can see the effect on temperature of an APP double activation at 1 m/min, 5 mm, 19 kHz and 100% PCT.

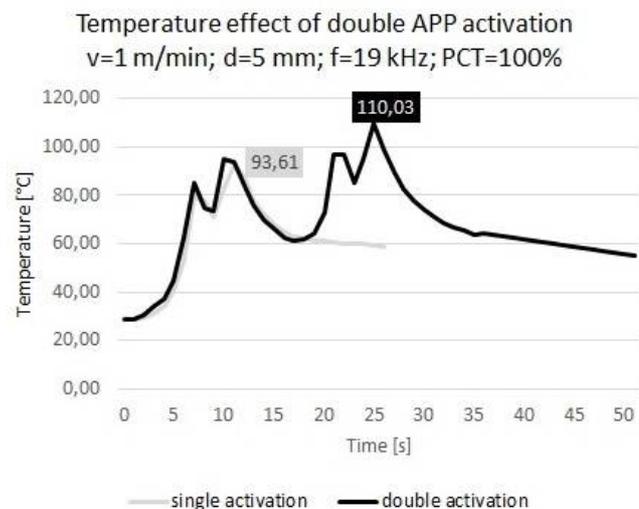


Figure 21: Temperature effect of double activation

The temperature upon the sample surface is almost seven degrees higher at a second activation. For RTM6-CFRP materials, this does not represent a problem because of its high decomposition temperature, but others materials could be damaged at higher temperatures.

Influence of aging

As is known, the effect of plasma activation declines over time. Many papers [6], [10] have investigated this topic. For this reason, we decided to investigate the decrease for two series of tests only after five weeks of storage at air.

Fig. 22 explains the decrease of surface energy by 24.41%, respectively 22.57% after a storage time of five weeks.

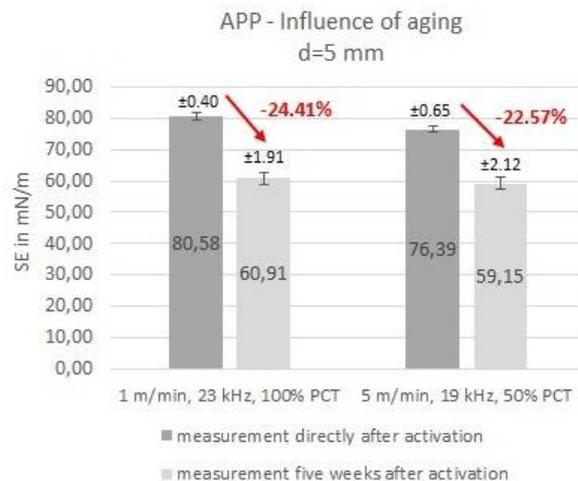


Figure 22: Influence of aging on total surface energy

As stated in Fig. 23, the polar part decreased by over 50% while the disperse part reduced by 6.10% only.

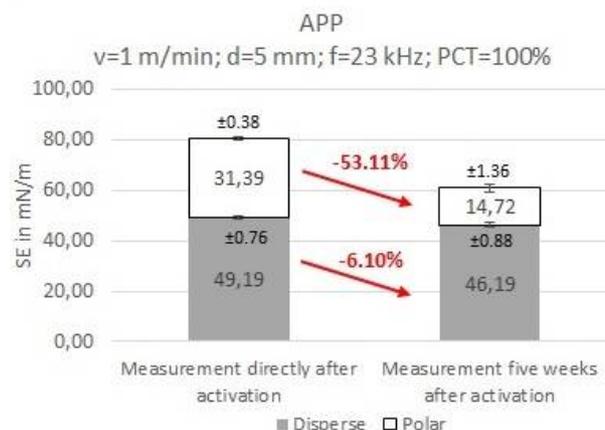


Figure 23: Influence of aging on polar/disperse parts

In summary, the plasma activation by APP has no long-term effect. Lahidjanian [10] describes that the effect of plasma activation on samples with different coatings is stable for 24 hours. After 120 h, the polar part shows a noticeable decrease and remains constant thereafter. Meer [6] investigated the storage life of APP activated CFRP-specimens and detected a reduction of plasma effect within 21 days without a drop back to initial values. That insight confirms our investigations. The reduced values are still higher than the surface energy of the reference samples after a storage of five weeks (total surface energy: 50.19 mN/m; polar part: 3.46 mN/m).

Discussion

Here, the results will be shortly reviewed and the benefits of the explored parameters will be described.

Considering LPP inquiries, we were able to gather the three following findings. Firstly, pressure and time lead to a saturation effect after a certain pressure/time of treatment. In our case, 200 sec plasma duration is sufficient (fig.7). This caused a value approximation, as it was mentioned in the section Influence of plasma cycle time. Because the surface is not able to absorb more particles after a specific time of plasma exposure, the saturation effect sets in. This is backed up with particle fluence that is described in detail by Wischmeier [11].

Gleich [3] explains in his investigation an asymptotic pathway determined by exposure time, polymer type and limiting value of surface energy that is not exceedable. Our second finding concerns the relationship between pressure and plasma intensity. Moderate or high pressure results in higher intensities, which correlate with a higher amount of particle collisions/ interactions and therefore corresponding higher levels of ionization degree. Besides, species are able to leave the vacuum chamber via electrodes at high pressure (0.8 mbar) that means higher degree of plasma-wall interactions. At last, our third insight on LPP investigation is related to the kind of working gas for plasma generation. Using compressed air from laboratory environment, the polar part of surface energy can be raised slightly, but for a maximum of polar parts the usage of oxygen gas is an essential condition.

For APP the following insights were made. They can be divided into different categories: distance, speed, multiple activation and aging.

Subject of section Influence of distance was the relationship between the distances from surface to nozzle. The smaller the distance the higher the increase in surface energy. Similar insights [10] regards in his research. Additionally, we verified that at low speed activation, a modification of distance between 5-10 mm does not yield any results. At higher speeds, like 27 m/min and 60 m/min, the distance becomes more important. Summarizing, the distance of nozzle to specimen surface has to be as near as possible for high-speed activation (around 5 mm).

The result of speed variation on APP investigations illustrates that the speed of the plasma-jet or sample holder needs to be adjusted in order not to damage the specimen through heat. On the other hand the activation speed needs to be fast enough to meet economic requirements. Best outputs were achieved with speeds of 1 m/min, but 5 m/min delivered good results, as well. This is because the rotation of the plasma nozzle depends on speed change. For tested samples with length of 75 mm at 60 m/min the nozzle rotates 3.125 times on sample surface. However, the nozzle rotates 187.5 times at a speed of 1 m/min. In consequence of the low number of rotations at 60 m/min, a homogeneous plasma distribution is not possible. Hence, the surface energies show a strong fluctuation which has an impact on the total surface energy of samples, as well as on the level of standard deviations. This insight is supported by [10] simulations, which illustrate the trajectory of the plasma nozzle for speeds from 20 m/min to 80 m/min. Considering this, positive activation effects at slower speeds can also be explained by theoretical multiple activations of some sample parts. "Multiple activation" means an overlapping in the trajectory of the plasma beam due to the slow forward movement.

Section Influence of aging reports the aging process of activated sample surfaces. Activation effects decline after a storage time of five weeks. Similar effects have been observed by Lommatzsch [12] for PA6. The effect of activation declined slightly within the first 30 days. According to [10] reasons for decreasing surface energy, particularly polar parts, are caused by the reorientation of functional groups or reactions with surface near elements. Meer [6] shows, by XPS-analysis, the reduction of oxygen and carboxyl concentration on sample surfaces over a 21-day period.

Comparison of APP and LPP

Surface energy

Both activation techniques enable significant increase of polar parts. The total surface energy is able to rise about 60%, the polar parts can rise up to around 782% (LPP) and 814% (APP). These results highlight the similar changes in surface transactions through both plasma technologies and disprove the claim of several studies,

which describe higher amounts of polar parts per LPP treatment [8].

Processing

In comparison with APP, LPP is a much more work intensive technique. Multiple factors need to be taken into consideration: the size of vacuum chamber, time for evacuation and cleaning, the maximum of sample quantity, costs of working gas and eventually, a risk of shadowing effects on sample surfaces during the activation process. Overall, LPP technology mainly operates discontinuously. LPP advantages are for example a reduced temperature load for specimens, lower probability of material damage and a more uniform plasma distribution on material surfaces. As another important aspect, elements and gaseous components of plasma can be diagnosed. APP enables continuous process management, which is suitable for large specimens with undercut forms. Thus, APP is applicable for inline production.

XPS

The following table lists the most important values of the XPS-analysis:

Table 1: XPS-analysis of activated specimens

	C [at%]	O [at%]	N [at%]	rest [at%]
CFRP untreated	79.7	21.1	2.2	*
CFRP LPP treated	46.8	28.6	1.1	23.5
CFRP APP treated	63.7	28.3	5.7	2.3

* smalltraces

In summary, as mentioned in [1] levels of carbon and oxygen are correlated. If carbon levels rise, the oxygen part decreases and vice versa. Oxygen levels increase for both plasma activation technologies from 21% to up to 28%, which is a rise of 33%. Other publications detected similar changes of oxygen levels through plasma treatment [8]. The level of nitrogen depends on ambient atmosphere. Untreated RTM6-CFRP contains 2.2% nitrogen while LPP specimens have lower quantities (1%) caused by vacuum atmosphere. In contrast, APP delivers a noticeable increase to 5.7%. As indicated by Wolf [13] some APP devices create nitrogen as byproduct. XPS analysis detects further elements in all specimens designated as "rest" in Tab. 1. This refers to elements like silicon, fluorine, sodium, calcium and magnesium. To explain the silicon content, [6] investigates the influence of release agents of peel ply and their detectable amount using a number of analytical methods. It illustrates the conversion of the peel ply component siloxane to silicate, which is responsible for silicone peaks in XPS-analysis. For RTM6-CFRP studies the content of silicone varies between small traces and 12% in LPP. Due to the higher bombardment of plasma species in APP and therefore resulting stronger cleansing effects, the silicone content is much lower than in a LPP treatment. Wolf [13] delivers detailed explanations on this. Besides, fluorine was measured in LPP activated specimens. Potential causes could be impurities of the vacuum chamber or defective equipment components. This fact was impossibly to eliminate. It is of interest to record that [8] detected fluorine in all CFRP-specimens after LPP and APP treatment, as well.

Topography

A few publications on this topic discuss the smoothing effect of an LPP activation. Therefore, the influence of both treatment methods to do change in surface topography will be inspected in the following section. First, the topography of all specimens was analyzed by digital microscope Keyence VHX-5000 with 250x and 2500x magnification and by ESEM XL30 with 1000x magnification. Whereas the LPP-treated samples do not show structural changes or smoothing effects through oxygen plasma,

the APP-treated material shows evenly distributed crater depressions as pictured in Fig.24. These craters affect the topography of the whole range of specimen length and width. The formation is caused by arc discharges, which create a form of tufted corona discharges. This kind of discharges are responsible for craters with homogeneous structure in size and depth. Fig. 24 shows the average crater geometry above and a smaller one beneath.

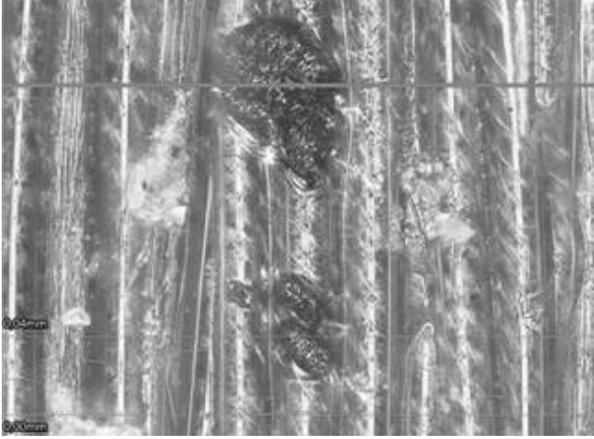


Figure 24: craters on APP-treated specimen

Dark areas indicate a matrix burning and a damage of NCF polyester thread. It is not ascertainable if carbon fiber damage occurs.

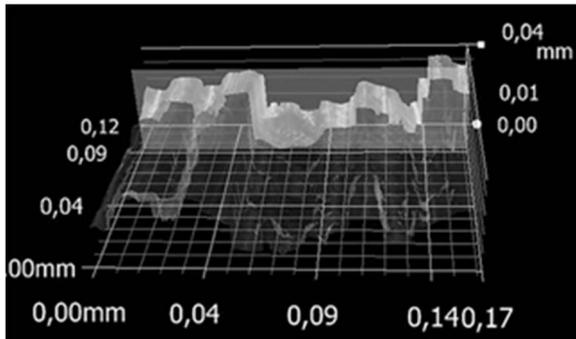


Figure 25: height profile of APP-treated specimen by Keyence microscope

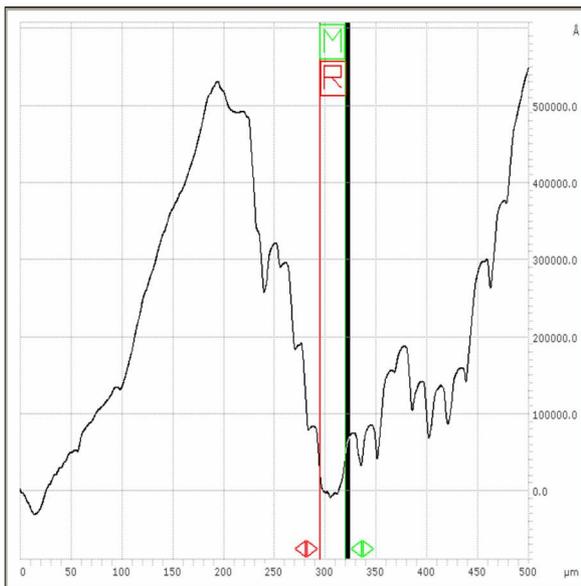


Figure 26: height profile of APP-treated specimen by Dektak

Fig. 25 and 26 present the height profile of investigated specimen. Dektak measurements seek to demonstrate the results of microscopy. For both, crater diameter vary from 30-40 μm , crater depth is about 8-10 μm . An atomic force microscope test was carried out to prove calculated values. Unfortunately, due to the high roughness of specimens (50+/-2 μm), measurements were not successful. For this, further investigations on the influence of APP on surface topography are strictly necessary. Trials on computer tomography are in preparation.

Summary

As the comparison shows similar outcomes of surface activation can be obtained with both plasma types. Of particular importance are the polar parts, which result in almost equivalent values. Considering the processing, APP is more cost-efficient, easier to handle and inline-capable. Therefore, our recommendation for activation of RTM6-CFRP in an industrial environment is APP processing. To verify the effectiveness of APP activation single-lap shear testes are performed with bonded samples.

Verification of the usability of plasma activation by single-lap shear test

Results of single-lap shear tests of the pre-treated samples are presented below. Sample geometry, overlap and testing speed, can be obtained from norm EN DIN 1465. The samples were bonded with DELO Duopox® AD895, a cold-curing, two component, epoxy system.

First, the untreated samples were joined and investigated after curing for reference. Subsequently, the APP-treated specimens were considered. The two sample configurations are compared in the graph beneath regarding shear stress. For each specimen ten tests were carried out.

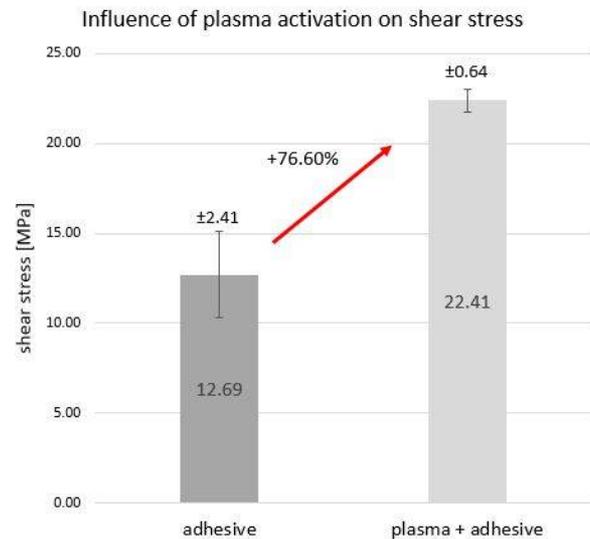


Figure 26: Influence of plasma activation on shear stress

Maximum shear stress of the untreated sample just with adhesive is 12.69 MPa with a standard deviation of 2.41 MPa. The untreated surface varies in its composition and its contaminations from production consequently. Standard deviation is higher than on the plasma treated surface. All untreated single-lap shear tests lead to adhesion failure. Plasma treated samples (5mm; 1m/min) could withstand shear stress up to 22.41 MPa. The smaller standard deviation of 0.64 MPa implies that surface properties are more homogenous. Whereas, untreated samples only failed because of deficient adhesive power (Fig. 28 a). Failure of plasma treated

samples consisted of a combination of cohesive failure of the adhesive and composite breakage of samples as seen in Fig. 28 b).

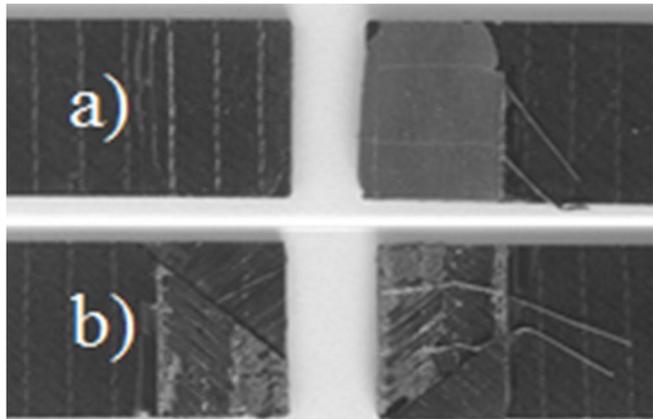


Figure 28: (a) adhesive failure; (b) cohesive failure and composite failure

Maximum shear stress endurance can be influenced by APP resulting in a 77% increase.

Conclusions

The results of this study demonstrate the effectiveness of surface activation even without a surface cleaning step before. With optimized adjustment of parameters, surface energy as well as polar parts of RTM6-CFRP can be raised to equal levels at APP and LPP. In either case, tested specimens are not affected by temperature even though higher temperatures are reached at APP treatment. Changes in topography of sample surfaces were documented for APP activation. However, they did not influence mechanical properties of the material as verified by single-lap shear tests. Summarizing, activation of RTM6-CFRP surfaces with plasma, generated a recognizable increase of lap shear strength for bonded samples. Consequently, fracture behaviour changed from adhesion failure to combinations of cohesion and component failures.

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