# Evaluation of hydronitrogen plasma treatment to improve the bonding process of PCM composite material in automotive: A case study

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**Abstract.** Atmospheric Pressure Plasma Treatment (APPT) technology, using hydronitrogen (95% N2 and 5% H2 composition) as the process gas, was used in this study to treat Prepreg Compression Molding (PCM) substrates to increase the lap shear strength of joints bonded with an epoxy adhesive. A crucial factor for plasma treatment is the torch working speed, which influences the treatment time of the substrate. In particular, it was found that the speed of 100 mm/s increased the lap shear strength by about three times compared to that of the untreated joints. Therefore, the mechanisms underlying the improvements in the lap shear strength of the bonded PCM joints were investigated. It was found that the surface roughness was not the main reason for the increase in the lap shear strength but the surface free energy (SFE). After plasma treatment, there is a significant increase in SFE which indicates a chemical change in the substrate surface. These functional groups introduced by APPT, especially those containing oxygen or amino groups, can covalently bind with the adhesive forming strong bonds and leading to the increase in the lap shear strength of the bonded joints.

## Introduction

Composites are increasingly used to replace conventional materials, such as metals, in automotive structural applications [1]. This substitution is due to better chemical resistance and mechanical properties of composites, in particular when referring to specific properties. In order to improve the efficiency and sustainability of components, in recent years there has been an attempt to replace more conventional assembly techniques, such as riveting and abrasion, with adhesive bonding in composites [2]. There are several reasons for this substitution. First of all, mechanical fastening requires drilling holes into the composite component and attaching each hole with metal objects, thus triggering a critical stress at a specific point. Adhesives, on the other hand, have the ability to act by working on a large surface area, rather than on multiple specific points, distributing the load across the entire bonding area. In addition, adhesives provide a virtually invisible fastening to keep surfaces smooth and clean without protruding screws, rivet heads, or nuts and bolts. Finally, incorporating adhesives into the manufacturing process can improve efficiency by eliminating some process steps, margins of error, and assembly times, thus increasing speed, reducing costs, and simplifying process operations. A typical problem with polymer matrix composites is that they have a low surface energy, and this causes the formation of weak adhesion bonds. To achieve a greater and more durable joint's strength, the surface of the composite material must therefore be cleaned and activated before joint fabrication [3]. To increase polarity and improve surface wettability, one of the safest and most versatile systems is surface treatment using plasma technology. Plasma is produced by applying a sufficiently intense electric field to a gas and is composed of a partially ionized gas containing an equal number of positive and negative charges, as well as some non-ionized gas particles [4]. Plasma treatment involves the interaction of free radicals and ions with the substrate surface [5,6], allowing the modification of the surface chemistry and morphology of polymeric materials depending on the specific gas and the conditions used for treatment [7]. In this study, the impact of atmospheric Pressure Plasma Treatment (APPT) using hydronitrogen gas to treat Prepreg Compression Molding (PCM) was investigated. Have been evaluated the effect on surface chemistry, morphology and mechanical properties of bonded joints.

## Material and methods

Material. The composite materials investigated in this study is SolvaLite 710 1, an epoxy resin prepreg matrix specifically for manufacture of components using compression moulding process. The PCM was cured in press at 150°C for 5 minutes at a pressure minimum of 6,2 Bar.

The PCM consisted of of 6 prepreg layers, alternating 400gsm with 12K fibres with 245 with 3K fibres, in 0/90 configuration

The adhesive used for bonding is 3M DP 490, a two-component epoxy structural adhesive. The 3M DP490 adhesive was cured at ambient temperature over 24 h, followed by an oven cure at 80°C for 1 h. The oven cure was used to ensure that the adhesive was fully

cured for all mechanical.

Plasma Treatment. Plasmatreat plasma technology was used to treat all analyzed samples. Hydronitrogen (95% Nitrogen and 5% Hydrogen) at a purity of 99.9% was used as process gas. Plasma parameters are shown in Table 1.

*Table 1 – table showing the parameters used for plasma treatment of PCM composite material.*

| Power [W] | Voltage [V] | PCT [%] | Frequency (kHz) | Process gas | Flow rate (L/min) |
|---|---|---|---|---|---|
| 780 | 260 | 100 | 24 | $N_2$(95%)<br>$H_2$ (5%) | 31 |

Plasma treatment was performed by placing the sample in a fixed position while the plasma head was connected to a six-axis robotic arm. The designated working distance was 12mm, the treatment width was 4mm, while three treatment speeds were investigated: 130mm/s, 100mm/s and 70mm/s.

Contact angle and Surface Free Energy measurements. SFE analyses were performed using a Biolin Scientific contact angle instrument. In this study, 3 samples were tested for each treatment rate by performing five measurements for each type of liquid (water and di-iodomethane) where the drop volume of the test liquid was 3 µL. The SFE of the PCM substrates was calculated using the Young equation that represents the relationship between the contact angle θ and the surface energy. The samples were obtained by manually cutting rectangles of size approximately 50x25mm with a diamond blade and cleaning them with isopropanol before plasma treatment. The plasma-treated samples were then compared with the values obtained from the untreated material.

Scanning Electron Microscopy – Energy dispersive X Ray analysis (SEM-EDX). The surface morphology was performed by scanning electron microscopy (SEM) analysis. Scanning electron microscopy allowed to analyze the surface microstructure of the composite material before and after plasma treatment. The analyses were performed in Electron BackScattered Diffraction (EBSD) mode with a voltage of 15kV.

Roughness measurements. To determine the surface roughness of the treated substrates, a roughness meter was used by carrying out tests on 50x25mm specimens. The roughness testing used for the analyses is the Mytutoyo SJ-210. The analyses were carried out in accordance with the ISO 4287 - ISO 4288 standards. The sampling length (lr) adopted is 0.8mm or 2.5mm depending on the average roughness values (Ra) and the maximum roughness height (Rz) of the specimens, as indicated by the ISO standard. The tests were carried out by performing three tests for each specimen and the sampling direction was parallel, perpendicular and oblique to the length of the specimen.

Mechanical test. The mechanical tests performed on the adhesive were single lap shear tests according to the ASTM D3165 standard (the geometry of the specimens is shown in Fig. 1, in order to determine the lap-shear strength (LSS).

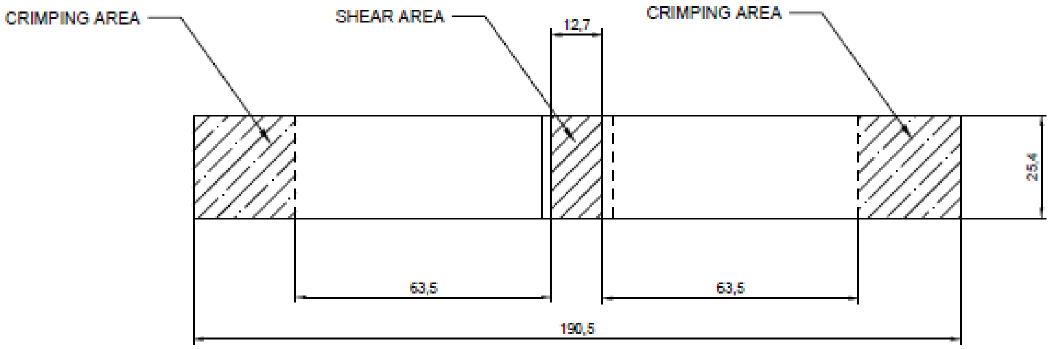


*Figure 1 – Configuration and dimensions of the lap-shear bonded specimens*

The adherends were obtained from a 500x500x2mm plate cut with a waterjet to obtain samples measuring 101.6x25.4x2mm. The specimens obtained were cleaned with isopropanol and plasma-treated using a path of four parallel passes to have a width of 4mm, as shown in Fig. 2.

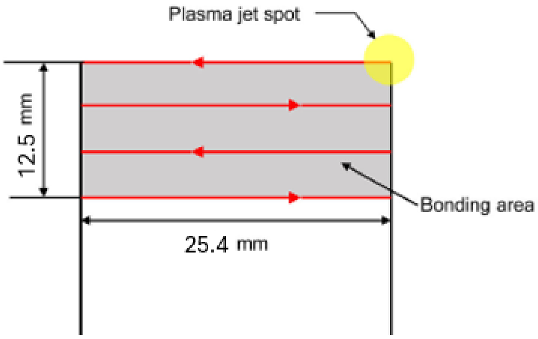


*Figure 2 – illustration of the plasma jet path on the substrate*

The plasma-treated specimens were bonded using 3M DP490 epoxy adhesive. Custom-designed bonding jigs were used to ensure adequate accuracy of adhesive thickness (bondline thickness 0.8mm) and correct alignment during specimen production. The lap shear specimens were cured for 24 hours at room temperature (23°C) and then placed in an oven at 80°C for one hour to ensure proper polymerisation of the adhesive, as suggested in the technical data sheet. A summary scheme of the bonding process is shown in Fig. 3.

The tests were performed using an LBG universal testing machine equipped with a 10kN load cell and using a crosshead displacement rate of 1 mm/min, in accordance with ASTM D3165.

## Results and Discussion

Lap Shear Strength. Fig. 3 shows the lap-shear strengths of the adhesive bonded PCM joints untreated and after APPT at various speeds.

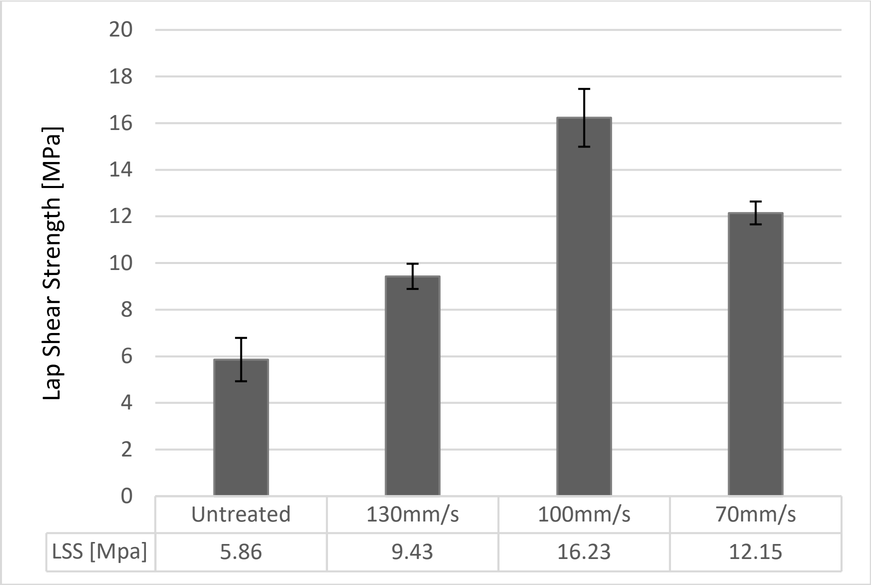


*Figure 3 – Lap-shear strengths of PCM joints in untreated condition and after APPT at various speeds*

The lap-shear strength of the untreated material joint is 5.86 MPa. With the plasma treatment the strength of the joints increased to 9,43MPa at a speed of 130mm/s; when the speed is 100mm/s the lap-shear strength reached its maximum of 16,23MPa (increase of 177% compared to untreated) and then decreases as the treatment speed decreases to 70 mm/s until reaching 12,15MPa.

The failure mode of the joint is another indicator that can be used to evaluate the adhesive bonding performance. The specimens failure mode is showed in Fig. 4. The failure mode of the untreated samples is adhesive (Fig. 4a), this indicates that the adhesion strength of the bonded joint is weaker than the cohesive forces of the adhesive. At a speed of 130mm/s the failure mode is always adhesive (Fig. 4b) which means that the surface treatment was not sufficient to achieve high adhesion. For speeds of 100mm/s (Fig. 4c) and 70mm/s (Fig. 4d) there is instead a delamination of the composite material. Since the failure mode of the joint is a delamination it is not possible to calculate exactly the value of interface strength between adhesive and substrate after the plasma treatment. However, it can certainly be stated that the resistance of the joint is increased after the plasma treatment and that it is higher than the delamination value of the material. Furthermore, it can be assumed that the decrease in lap shear strength for speed values of 70mm/s can be caused by an excessive treatment time which leads to an increase in temperature that can damage the PCM.

To better understand the reasons for the increase in joint strength after plasma treatment, further morphological and SFE analyses were performed on the plasma-treated PCM material and compared with the untreated one.

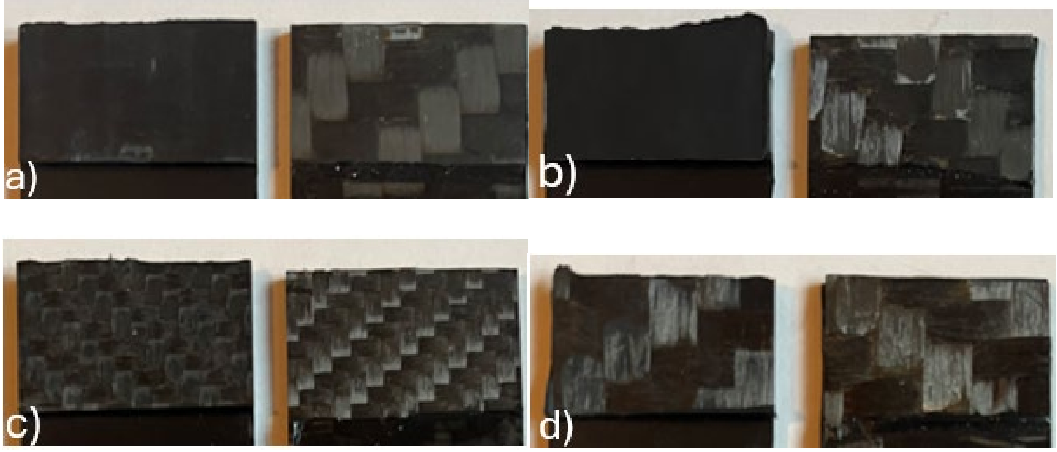
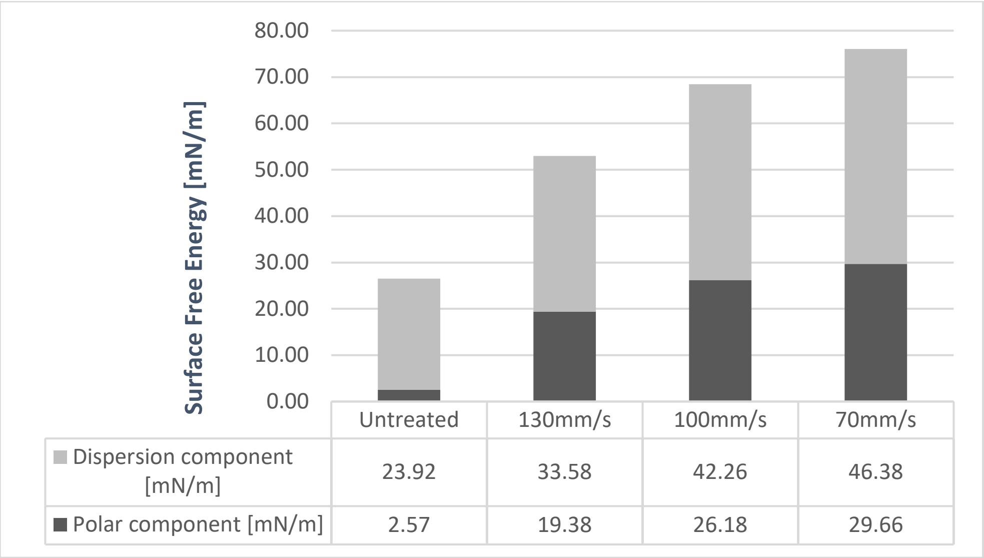


*Figure 4 – Failure modes of untreated specimens (a) and the plasma treated specimens at the speed of 130mm/s (b), 100mm/s (c) and 70mm/s (d).*

Contact Angle (CA) and Surface Free Energy (SFE). Contact angle analyses were performed to determine the SFE of the treated material and understand the mechanism behind the increase in lap shear strength. It is known that APPT causes a significant change in the contact angle and therefore in the surface free energy [8]. The contact angle measurements performed with two liquids (water and diodomethane) are shown in Table 2. Through the contact angle measurements, the polar component and the dispersion components of the SFE were then obtained using the Owens method, whose values are shown in the graph in Fig. 5.

*Table 2 – contact angle with the two liquids (water and diiodomethane) with relative standard deviations for the untreated and plasma-treated PCM material with different speeds*

| ***Sample*** | ***CA $H_2O$*** | ***S.D.*** | ***CA $CH_2I_2$*** | ***S.D.*** |
|---|---|---|---|---|
| *Untreated* | 93,38 | 0,98 | 68,16 | 1,1 |
| *130mm/s* | 52,66 | 1,26 | 51,27 | 0,91 |
| *100mm/s* | 33,12 | 1,52 | 34,51 | 0,85 |
| *70mm/s* | 19,61 | 1,62 | 24,37 | 1,96 |



| | Untreated | 130mm/s | 100mm/s | 70mm/s |
|---|---|---|---|---|
| ■ Dispersion component [mN/m] | 23.92 | 33.58 | 42.26 | 46.38 |
| ■ Polar component [mN/m] | 2.57 | 19.38 | 26.18 | 29.66 |

*Figure 5 – Calculated surface free energies of the different analyzed samples*

Before plasma treatment, the value of the polar component is 2.57 mN/m while that of the dispersive component is 23.92 mN/m, and therefore the surface free energy, given by the sum of the two components, is 26.49 mN/m. Plasma treatment causes a significant increase in both components, although the polar component increases slightly more. Comparing the three different treatment speeds, an increase in the SFE occurs as the speed decreases; in fact, the surface free energy is 52.95 mN/m for the speed of 130 mm/s, 68.44 mN/m for the speed of 130 mm/s and 76.05 mN/m for the speed of 70 mm/s. The increase in surface energy at 70mm/s compared to 100mm/s, despite the lower LSS, may be caused by an overtreatment that caused a partial degradation of the surface with consequences on the morphology. In fact Bascom et al. [9] have shown that surface inhomogeneities may promote wetting by capillary action.

Scanning Electron Microscopy and roughness analysis. Scanning Electron microscopy (SEM) was used to analyze the surface morphology of the PCM material. In Fig. 6 it is possible to see the images of the untreated substrate and the plasma treated samples at different speeds.

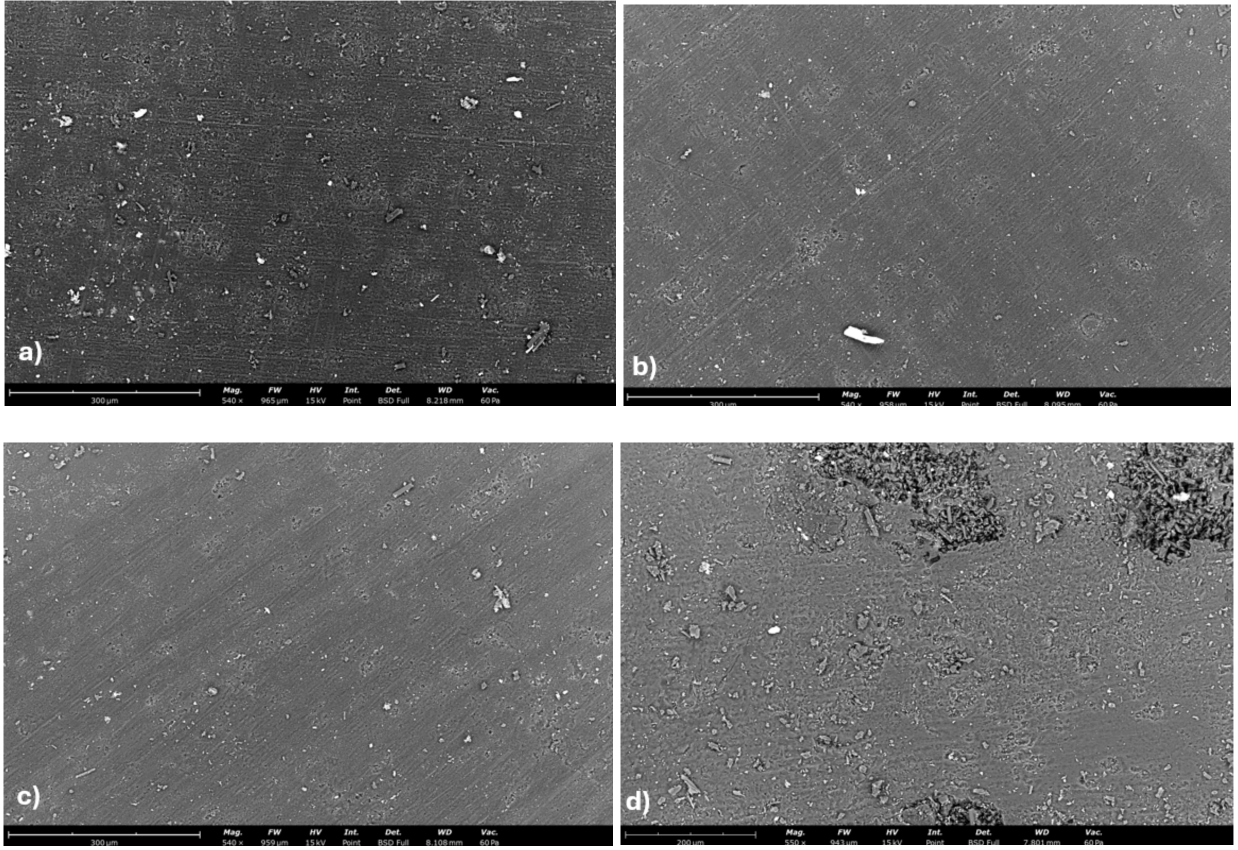


*Figure 6 – SEM immage of the surface of untreated specimens (a) and of the plasma treated specimens at the speed of 130mm/s (b), 100mm/s (c) and 70mm/s (d).*

Roughness testing was used to estimate the surface morphology modification of substrates induced by plasma treatment. The average roughness (Ra) values are shown in the graph in Fig. 7. The values show that there is no significant variation in the roughness of the samples between the untreated and the plasma-treated at 130mm/s and 100mm/s, with values around 0.500µm, while there is an increase in Ra for the samples treated at 70mm/s with the achievement of values of 0.882µm. As can also be seen in Fig. 6d, the surface of this sample shows some exposed fibres which are due to an overtreatment with consequent partial degradation/abrasion of the composite matrix. It can therefore be stated that the increase in LSS by the sample plasma-treated at 100mm/s is not due to an increase in the surface area.

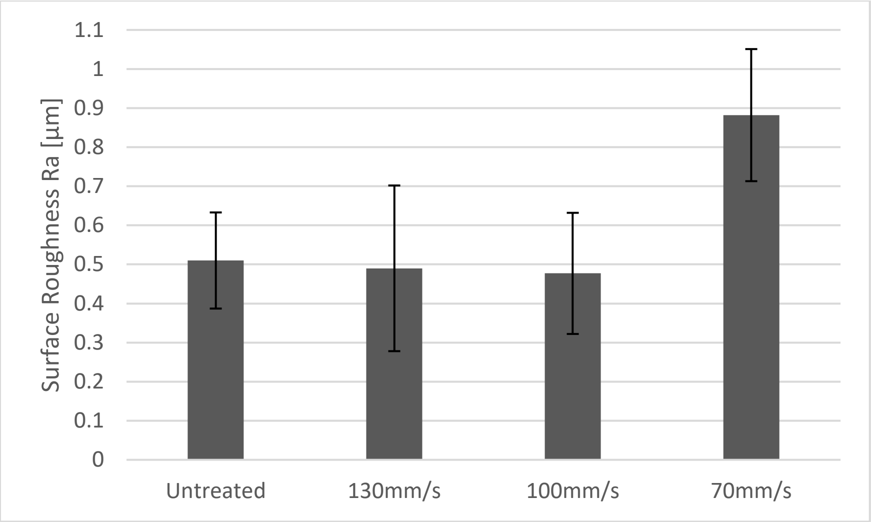


*Figure 7 – Surface roughness values of of the different analyzed samples*

## Conclusions

The results of this study showed an increase in the interface strength of the bonded joints after the plasma treatment. The maximum lap shear strength was obtained for the plasma treatment speed of 100 mm/s, with an increase of about 177% compared to the untreated samples. It can be concluded that the increase in LSS is not due to the increase in surface area (indeed the sample treated at 70 mm/s has lower LSS values than the one treated at 100 mm/s although a higher Ra) but by a change in the surface chemistry of the plasma treated samples which leads to an increase in the SFE of the samples. The increase in surface energy is in fact due to an increase in the quantity of functional groups on the surface such as carboxylic groups and above all, as hydronitrogen is used as the process gas, amine groups that can react with the epoxy adhesive leading to the formation of strong covalent bonds, as shown in Fig. 8. Furthermore, the plasma treatment can lead to a partial removal of pollutants, such as release agents, which have a low surface tension, allowing to further increase the wettability of the surface of the composite material.

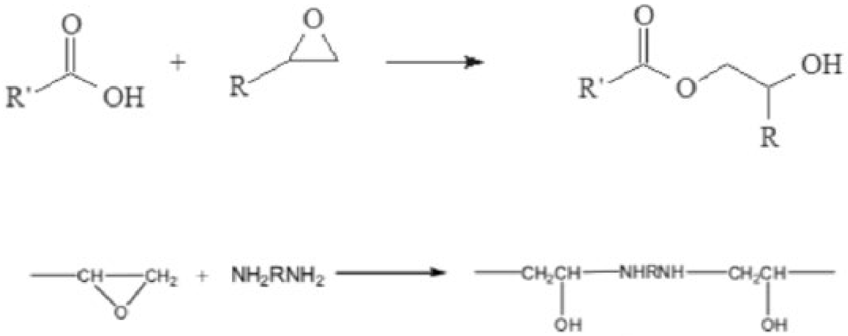


*Figure 8 – Chemical reactions of an epoxy group and a carboxyl group (above) and an epoxy group and an amino group (below)*

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