ATMOSPHERIC PRESSURE PLASMA SURFACE TREATMENT OF THERMOPLASTIC COMPOSITES FOR BONDED JOINTS

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ABSTRACT

Glass fiber reinforced polypropylene samples were treated by an atmospheric pressure plasma jet using a rotary nozzle, in order to improve adhesive properties of the material surface. Thereby, the influence of the most significant operational parameters of the plasma treatment was studied. These parameters are e.g. the distance between the nozzle and the treated substrate, and the total plasma exposure time, varied by the axial velocity of the plasma jet. Two different parameter sets were selected to be compared in the present study. The surface properties after the plasma treatment were investigated by atomic force microscopy in combination with the contact angle measurements followed by the surface free energy calculation according to the OWRK method. The results were compared with those of the untreated samples to evaluate the induced effects. The surface free energy and hence the wettability were found to be increased significantly by both treatments. The surface topography was changed also in both cases, whereas one of the used parameter sets resulted in a higher roughness comparing to the untreated reference sample, and another one reduced it. Moreover, the adhesion properties of the treated surfaces were evaluated by lap shear tests. All treated samples exhibit a significant increased bonding strength in comparison to the untreated substrates. This improvement can be related both to the changes of the surface topography, induced by the thermal component of the plasma, and the cleaning and activation effects caused by the reactive plasma species during the treatment. However, significant differences concerning the total bonding strength were found between the used process parameter sets. Thus, a higher intensity of the plasma treatment led to a lower resistance of the final bond. In this case, the polymer surface seems to be partly degraded, forming a weak boundary layer, which indicates an overtreatment of the material.

1 INTRODUCTION

The aerospace industry, in particular aircraft repair, is one example where the application of adhesive bonding is growing rapidly. Adhesive bonding distributes stresses over the whole bonded region and therefore stress concentrations occur less frequently than in conventional joining techniques, as welding or mechanical joining [1].

Polymeric based composites with thermoplastic matrix reinforced by continuous glass fibers are being used increasingly in engineering applications. Despite the many benefits from the use of these materials, the difficulty of manufacturing complex geometries leads to the need of employ joining techniques to manufacture complex structures. The use of structural adhesives, typically based upon epoxy resins, offers some advantages compared with other methods of joining, as induction or ultrasonic welding.

Many polymers and composite materials need a pretreatment step before adhesive bonding or painting. Matthews et al. [2], for example, have shown the importance of the correct surface treatment. Premature failure at low load is usually due to poor preparation prior to bonding. According to

Wingfield a good surface treatment involves several steps: elimination of contaminants; oxidized layers and low-molecular-weight species; improved wetting of low energy surfaces; chemical modifications and increase in surface roughness leading to an improved mechanical interlocking [1].

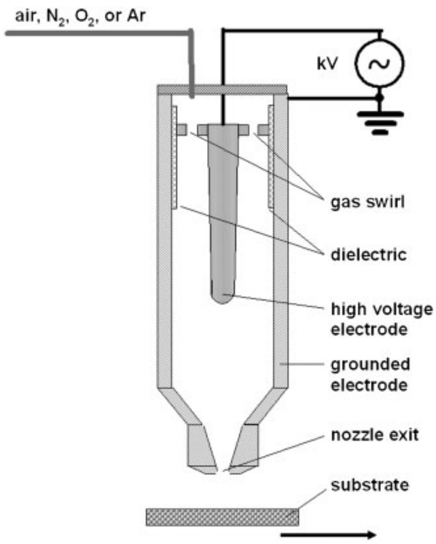

Figure 1. Components of an atmospheric pressure plasma torch

There are a wide variety of processes to increase adhesion properties of polymer substrates. These can be sorted into chemical, physical or combined processes [3]. For more conventional composites based on thermosetting polymeric matrices surface treatments prior to bonding are clearly established to ensure that failure along the adhesive and composite interface is avoided, that is, to achieve good bond strengths and cohesive failures of the joint. Light abrasion followed by solvent cleaning is usually enough as a surface treatment in this case, as long as the surface is not contaminated by release agents or by oil. However, in the case of fiber reinforced composites based on thermoplastic polymeric matrices, such as polypropylene (PP), a treatment employing abrasion followed by solvent cleaning is not enough to achieve desirable adhesive bonding resistances. Polypropylene is characterized by a hydrophobic behavior resulting from its non-polar nature, so previous surface treatment to promote the appropriate changes has to be carried out in order to increase surface activity thus enhancing anchorage processes of adhesives or coatings. Mainly chemical and surface topography changes are experimented on substrate surface. This is the reason why unconventional surface treatments are being investigated deeply during the last decades, to be employed with such materials. Nowadays, some technologies as atmospheric pressure plasmas are already installed in automated industrial processes [4]. In particular, atmospheric pressure plasma jets (APPJ), due to their facility to be integrated into existing production lines (it can be applied in a continuous way) and because they can treat specific parts of a substrate selectively, achieved a wide acceptance in the industry [5]. The pretreatment is employed to modify the surface properties of the substrate, so improving the adhesion strength and the durability of the adhesive joint.

Also, APPJs are not limited to flat and thin components to be treated but can also be used on large three-dimensional structures.

The operational process parameters of the treatment need to be determined for each application and each substrate individually, since the interaction between the plasma and the surface depends strongly on the material properties. In order to achieve adhesive joints as resistant as possible, the changes experimented by a polypropylene matrix reinforced composite pretreatment with a commercial APPJ system was studied. These modifications were analyzed by different techniques, as well as adhesive bonding strength was mechanically tested. The use of this APPJ for the pretreatment of polymers and metals has been reported before by several authors. [5] As an environmentally friendly solution to chemical wet processes, atmospheric pressure plasma treatment make possible to selectively increase surface wettability and consequently adhesion properties by physical processes [3].

Changes in surface topography can be produced by the action of the plasma gas promoting surface abrasion or etching due to removal of low molecular weight material. Furthermore, the highly unstable species present in the plasma gas promote free radical formation on the polymer surface by scission of polymeric chains [3].

The main aim of this work is to use atmospheric pressure plasma with dry air to increase surface wettability of polypropylene matrix reinforced composite substrates in order to improve mechanical performance of composite to composite adhesion joints. The work is focused on the quantification of the surface changes experimented by the material. The effect of different operational parameters (nozzle-to-sample distance and treatment rate) on overall performance of composite to composite adhesive joints with an epoxy adhesive has been studied. The mechanical response of the bonded joints has been tested by single lap shear standard tests according to DIN EN 1465.

2 EXPERIMENTAL DETAILS

2.1 Materials

The material studied is a glass fiber reinforced polypropylene matrix composite, manufactured by hot plate technique. For bonding to occur, melting temperatures of the materials must being reached, followed by the solidification that occurs during cooling, by applying pressure. Four woven balanced bidirectional layers of E-glass fibers and polypropylene matrix with a "wave twill 2/2" fabric reinforcing type of continuous layers were used. The total fiber fraction in the composite was 62'7%. The size of the samples was 100 mm x 25 mm x 3.2 mm. Polypropylene is a non-polar polymer and, consequently, presents poor adhesive properties to other materials. In this context Novak and Florian studied the free surface energy of iPP after surface modification by electric discharge at atmosphere pressure, generating hydrophilic functional groups, and subsequent grafting onto the polar groups [1]

2.2 Atmospheric plasma treatment

Polypropylene matrix composite samples were subjected to atmospheric plasma treatment with a plasma generator supplied by Plasmatreat (Plasmatreat GmbH, Steinhagen, Germany). This generator operates with a frequency of 19 kHz and an intermediate voltage of 300V. The plasma treatment was applied by using a rotating torch with a rotating nozzle (RD). It can treat a large area substrate in a single pass, with less intensity of treatment in comparison to static nozzles.
In order to evaluate the influence of the effective plasma treatment intensity, the key treatment parameters were varied in this study. Thus, the nozzle-to-sample distance was systematically varied in the range between 2 and 20 mm, whereas two values (h and 2h, see Table 1) were selected to present the results in this paper. On other hand, to analyze the influence of the exposure time, the axial velocity of the plasma jet moved over the substrate was fixed in two different values (v and 2v, see Table 1).

REF.	*Nozzle Type*	*Distance between the nozzle and the treated substrate*	*Speed of the plasma torch*
PS1	ROTARY	h	v
PS2		2h	2v

Table 1. Plasma treatment parameters

2.3 Contact angle measurements and surface energy calculation

Changes in wetting properties of the composite substrates were followed by contact angle measurements using a drop-shape-analysis goniometer model G2 supplied by KRÜSS (KRÜSS GmbH, Hamburg, Germany). This equipment is supplied with a video capture kit and analysis software. To obtain stable values, contact angle measurements were carried some minutes after the plasma treatment. Three different liquids were used as probe liquids for contact angle measurements: diiodomethane stabilized, ethylene glycol >99% purity and distilled water. Contact values for the three test references were used for contact angle measurements of the substrates. Surface free energy values were calculated using the approach of Owens–Wendt–Rabel and Kaelble which takes into account the dispersive (nonpolar) and polar contribution to the total surface free energy value. A drop volume of 6 µl was used, by a supplying rate of 11.76 µl/min.

2.4 Surface characterization

The sample topography was studied using an atomic force microscope AFM (Digital Instruments Nanoscope III multimode scanning probe microscope) operated in the ‘tapping mode’ in air. The maximum scan range of the scanner was 100 µm. The sensor or cantilever was a monolithic silicon symmetric tip (Tap190Al-G), with resonance frequencies around 250 kHz corresponding to force constants around 20 N/m. The sample area analyzed was 100µm x 100 µm in size. The maximum and minimum roughness obtained was 366 nm and 144 nm respectively, for the different operational process combinations.

2.4 Characterization of adhesive joints

A two-component epoxy adhesive (Araldite 2014-1, Huntsman) was used for composite to composite adhesive joint manufacturing. The thickness of the adhesive layer was 0.1 mm with an overlap of 12.5 mm between the samples (Figure 2).

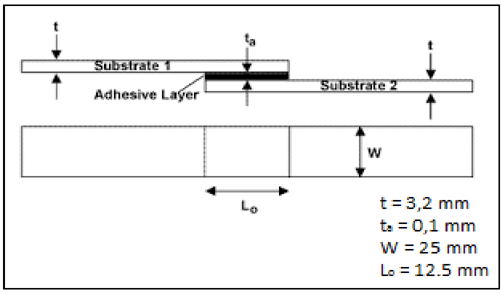

Figure 2. Geometry of specimens (mm)

Adhesive joints were subjected to constant pressure to avoid displacements. Samples were allowed to cure for, at least, seventy-two hours. After that waiting time, corresponding with the adhesive curing process, mechanical characterization was carried out by lap shear tests according to DIN EN 1465. At least five samples for each operational parameters combination (nozzle-to-sample distance, treatment rate/speed) were tested and average values of maximum shear strength were calculated.

4 RESULTS AND DISCUSSION

4.1 Influence of plasma treatment on substrate wettability

The plasma treatment alters the chemical and the surface roughness of the substrate. Improvements in adhesion result from the combination of these effects can be observed. After the plasma treatment the surface energy of the composite is strongly enhanced in both cases of different operational parameters compared to untreated samples and increased from 26 to 60 and 65 mN/m, respectively (Table 2). Small differences on total surface energy between the two treatments are observed. The major difference between both measurements is obtained in relation with the dispersive energy. While polar energy reached almost the same values, disperse energy obtained after the most intense treatment (PS1, h, v) is lower than the one obtained by the second treatment (PS2, 2h, 2v) where intensity of plasma is reduced. [6]

The importance of the surface energy or adhesion is usually related to the ability of the adhesive to wet the surface, which is the ability of the substrate surface to become wetted by the adhesive. A high surface energy leads to a better spreading of the adhesive and therefore to a more uniform contact with the substrate [1].

	Disperse part (mN/m)	Polar part (mN/m)	Total surface energy (mN/m)
Non-treated	16.06 (±0.18)	10.12 (±0.14)	26.17 (±0.32)
PS1	21.09 (±0.55)	38.93 (±0.50)	60.02 (±1.06)
PS2	28.30 (±0.18)	37.37 (±0.30)	65.67 (±0.52)

Table 2. Contact angle measurements and surface energy calculation

Thermodynamics adhesion mechanism defines adhesion process as a result of molecular interactions, so that the knowledge of the surface energy of the solid can be indicative of the quality of the adhesive bonding. To achieve a strong contact between a solid surface of a polymer and a liquid requires minimizing the surface tension of the liquid or increasing energy surface of the solid. Although there is a correlation between good wettability, high levels of surface energy and adhesion, adhesive bonding quality depends not only on these parameters but there are more factors affecting the final bond strength [7].

4.2. Influence of plasma treatment on the surface topography

Adhesion properties are also strongly influenced by the surface topology. Decisive factors are the size of the contact area and the size of unfilled volumes between the adherents. A microscopic roughness can also lead to a mechanical interlocking between the two partners of the adhesive joint. The relevance of topological changes on the adhesion properties were studied on PET and PVDF, which were treated as indicated in Table 1. AFM images of PET and PVDF before and after the plasma treatment are presented in Figs. 3 and 4, respectively. In the initial state both surfaces are largely different on a 10 or 30 mm scale. PVDF is characterized by a rather smooth surface, while PET has a much more distinct roughness. This difference in the initial state causes different surface modifications by the plasma. On the 30 mm scale the PET surface becomes much smoother after the plasma treatment. In contrast the surface roughness of PVDF remains nearly constant.

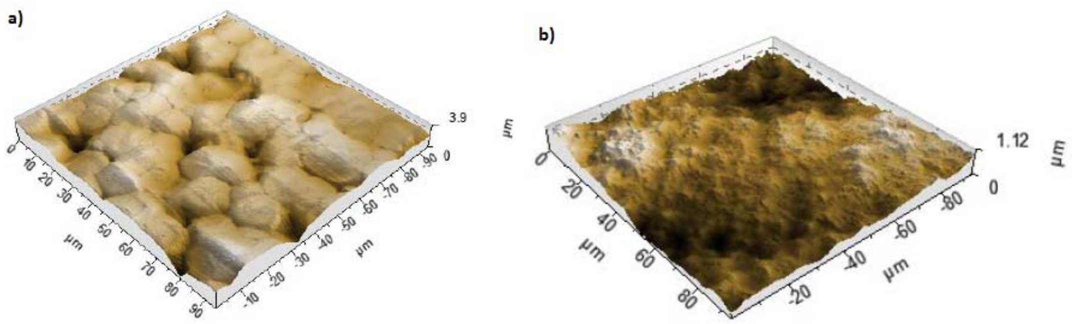

Figure 3. AFM 3D topographic images of polypropylene composite surface subjected to atmospheric plasma treatment with different operational parameter combinations (nozzle-to-sample distance/treatment rate), (a) plasma parameters reference PS1: h, v; (b) plasma parameters reference PS2: 2h, 2v

It is possible to evaluate and compare surface topographic changes produced by the different plasma treatments by using atomic force microscopy (AFM). The collisions produced by the unstable species of the plasma gas with the polymer surface chains promote chain scission and subsequent free radical formation. Chain scission can lead to formation low molecular weight species, which can be removed from surface thus promoting changes in the original composite surface topography. Etching effect, which can be observed with AFM, was studied by measuring area roughness parameters, as Sa and Sq (root mean square) roughness. Figure 3 shows surface topography of thermoplastic composite samples subjected to atmospheric plasma with different combination of operational parameters (treatment rate, nozzle-to-sample distance). It can be observed that surface topography changes with different treatment rate and nozzle-to-sample distances. For samples treated by PS1 treatment parameters the Sa value is about 366 nm which represents a percentage increase of 95.7% if compared to the Sa value of the untreated composite which is 187 nm. For samples referenced as PS2 treated with a higher speed of displacement of the nozzle (higher total time exposure to treatment) and a higher distance between substrate and nozzle Sa value is 144 nm. This fact indicates that surface abrasion has less effect as the treatment rate increases and distance between nozzle and substrate increases too because exposition of polymer surface to the action of plasma is restricted, so intensity of the treatment is lower [3].

4.3 Effect of dry pressured air plasma treatment on the thermo-mechanical behavior of the assemblies

To achieve high lap shear strengths in adhesive joints strong adhesion between the adhesive and the substrate is required. Usually the formation of new covalent bonds between the molecules of the adhesive and the substrate are needed to achieve this good adhesion. The main contribution of the atmospheric pressure plasma jet treatment is precisely this formation of additional functional groups at the surface, which could be greater by using different process gases from dry air. The advantages of the use of dry air as plasma process gas are the cost savings and the higher availability of this gas at the industry.

In order to evaluate the effectiveness of the plasma treatment for adhesion enhancement purposes, plasma-treated polypropylene-matrix composite samples have been bonded by using a two-component epoxy adhesive and finally, mechanical performance of the adhesion joints has been tested by shear standard tests. The results were compared with untreated bonded samples and high influence of the treatment on the stiffness and strength was observed. Figure 5 shows the lap shear strengths obtained for the adhesive bonds tested with and without plasma activation. The plasma treatment improves the adhesive bonding strength for all polymers, but greater results were achieved with a less intense plasma treatment (PS2). Noteworthy are the different failure obtained by the different treatments and the untreated samples. Only cohesive failure modes are observed for the activated samples with PS2 treatment, while a total adhesive failure is dominant for the non-treated and a mixed failure can be observed for the PS1 treated samples.

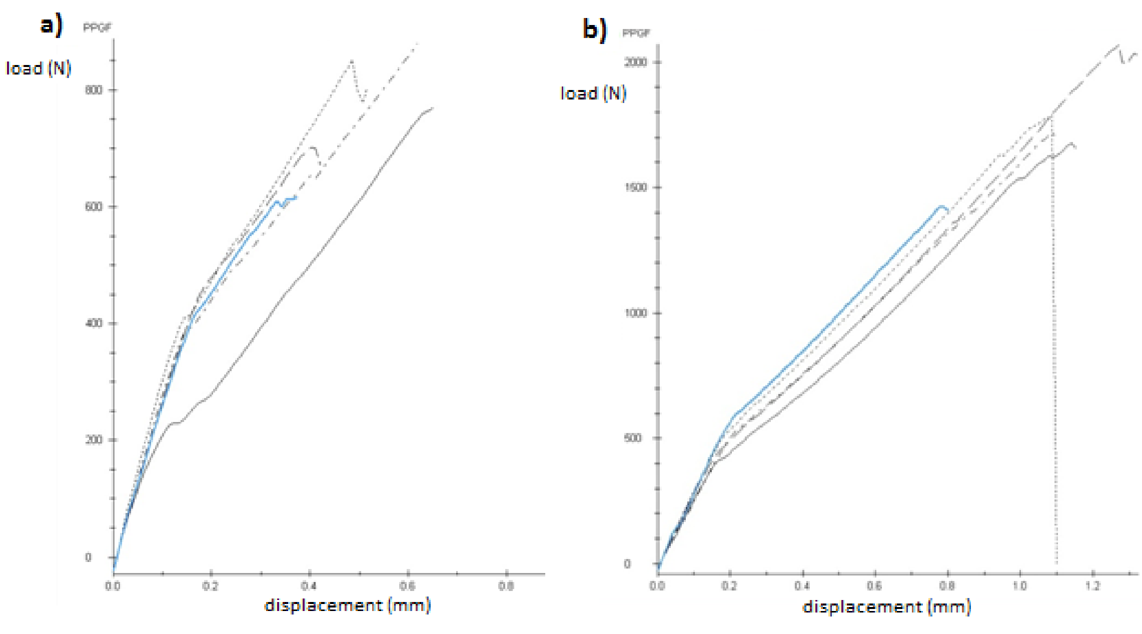

Figure 4. Lap shear test results of five specimens tested for both combinations of operational parameters; a) treatment referenced as PS1 (h, v), b) treatment referenced as PS2 (2h, 2v)

Figure 4 shows typical adhesive lap strength–displacement curves obtained from the single lap shear test of the adherents made of polypropylene reinforced glass fiber. Each of these graphics represents five tests corresponding with the five repetitions of each plasma treatment [1].
Figure 5 presents the average values of the ultimate shear strength, obtained considering five tests for each condition. The highest ultimate shear strength was obtained with the PS2 plasma treatment (2h, 2v) and presents a mean value of 4.7 MPa. The worst result was obtained with the untreated samples and is about 0.74 MPa. Higher strength values were obtained by PS1 treatment and the average is about 1.8 MPa. This treatment was not able to increase the surface energy of the polymer (PP) matrix as much as PS2 did, although PS1 is the most intense treatment and leads to the highest surface roughness. These results show a possible overtreatment effect. It consists on the formation of a weak boundary layer on the surface of the substrate, from a mechanical point of view, by using treatment intensities higher than those which the material can withstand. This experimented overexposure to plasma, due to the small distance from nozzle to substrate (h) and the low displacement speed of the torch (v), led to high surface energy values and the highest rough surfaces, but the mechanical resistance achieved by the joint was poorer than the expected. It can be said that overexposure to plasma treatments can lead to the formation of a thin surface layer that shows good surface properties from a chemical point. However, it leads to an insufficient mechanical strength too. This effect could delimit a process parameter window, which indicates the minimum distance from the nozzle to the substrate and the minimum velocity that should be used at atmospheric pressure plasma treatment of the polypropylene matrix composite. As can be seen by the results obtained the activation effects (lap shear strengths) are strongly dependent on the activation duration and the position of the substrate. This indicates that the thermal component of the plasma jet is very important for the mechanical strength of the bonded joints. The time to achieve a good activation of the surface, which is of the order of a few milliseconds, is much faster in comparison to other common plasma treatments.

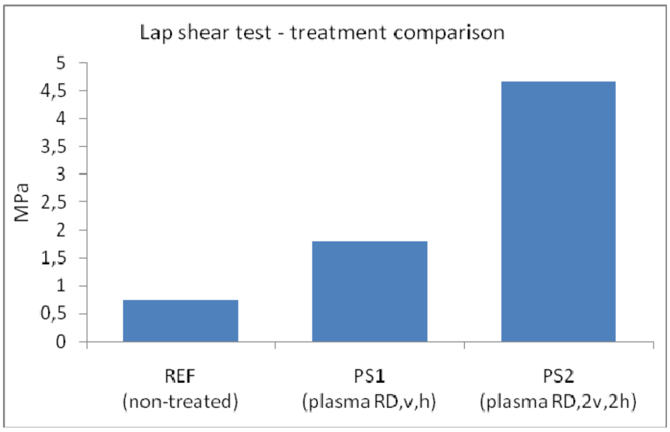

Figure 5. Lap shear test results

As evident from energy surface calculations (Table 2) and lap shear test results (Figure 5), as well as failure mode, there is no simple correlation between the absolute value of the surface energy and the resulting lap shear strength. Thus, a high surface energy after the treatment determines a high wettability of the substrate, but does not automatically guarantee a high adhesive bonding strength [6].

5 CONCLUSIONS

Atmospheric plasma treatment with compressed dry air as a process gas is an effective process to promote an increase in surface wetting properties of non-polar thermoplastic materials. The increase in surface wettability can be related to two main mechanisms: on the one hand, the action of the plasma gas promotes the formation of free radicals which act as interlock points for polar groups. On the other hand, the plasma action promotes material abrasion of low molecular weight materials, which produces changes in surface topography.

Treatment	*Total Surface Energy [mN/m]*	*AFM roughness (Sa, µm)*	*Adhesive bonding τ_{max} [MPa]*
Non Treated	26.17 (±0.32)	0.187 (±0.097)	0.74 (±0.17)
PS1	60.02 (±1.06)	0.366 (±0.048)	1.80 (±0.17)
PS2	65.67 (±0.52)	0.144 (±0.034)	4.67 (±0.61)

Table 3. Characterization results of plasma treated samples

AFM study has revealed a remarkable increase in surface roughness as the nozzle-to-sample distance and the treatment rate decrease. These two plasma-acting mechanisms occur simultaneously but depending on the operational process parameters, one can be predominant. The main plasma-acting mechanism for aggressive conditions (short nozzle-to-sample distance and low treatment rate) is abrasion while surface functionalization increases for less aggressive conditions.

The increase in wetting properties and surface free energy achieved by the atmospheric plasma treatment produces an increase in adhesion properties of polypropylene composite surface. Mechanical performance of composite to composite adhesion joints with a two-component epoxy adhesive is considerably increased for one of the process parameter combination tested. Differences are detected when using different plasma conditions. So that, in this study the use of les aggressive conditions leads to a mainly cohesive fracture type for shear lap tests and this represents a good interaction between the adhesive and the plasma treated surface. On other hand, more aggressive plasma conditions lead to a mainly adhesive fracture type. An overtreatment effect of the plasma can be detected in this last case, which leads to a poorer mechanical strength of the joints.

In conclusion, atmospheric plasma with compressed dry air is a useful technology to increase adhesion properties to polypropylene matrix glass fiber reinforced composites. In addition to this, atmospheric plasma is characterized by its high environmental efficiency and easy implementation at industry.

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