



OPTIMISING THE INTERFACIAL RESPONSE OF THE HIGH V_F GLASS FIBRE COMPOSITES USING FUNCTIONAL PLASMA POLYMER

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Abstract

The mechanical properties of high volume fraction (V_f) E-glass fiber composites were studied to explore the effect of plasma polymer surface modification of the fibres. Untreated and unsized E-glass fibre bundles were continuously coated with acrylic acid / 1, 7-octadiene or allylamine /1, 7-octadiene plasma copolymers in the plasma reactor to optimize the bond with matrix resin. The concentration of the functional group (-COOH), which can react with epoxide group from the matrix, in the coatings increased with the acrylic acid content in monomer gases. The similarly reactive amine ($-NH_2$) group exhibited the same trend with allylamine concentration in the monomer gases. The interlaminar shear strength of high volume fraction composites was used to measure the interfacial response in the presence of the plasma polymer coatings. The fracture surfaces of these glass fibre / epoxy composites were investigated by scanning electron microscopy (SEM) to confirm that shear failure had occurred. Interfacial adhesion within the composites containing fibre coated with high concentration of acrylic acid plasma copolymer was improved relative to the non-coated fibre. The effect of plasma polymer coating thickness.

1. Introduction

Over recent years we have demonstrated the value of plasma polymerisation as an environmentally friendly gas phase sizing technology for reinforcing

fibres. By using comonomers in a low power microwave reactor, the functionality of the fibre surface could be varied. In particular we have used amino and carboxylic acid groups to tailor the adhesion to epoxy resins. We have used the single filament fragmentation test to quantify the stress transfer between fibre and resin. The technique has been applied to carbon, PBO, aramid and glass fibres [1-5]. Surprisingly, we identified that the ineffective fibre length in the fragmentation test, which is an inverse measure of the fibre matrix interfacial bond strength, exhibited a minimum as the surface functional group concentration increased. This is difficult to fully comprehend using a chemical coupling mechanism. However, we had assumed that at a thickness of 15 nm, the stress transfer at a fibre-break was dominated by adhesion and ignored the effect of the plasma polymer thickness.

In this paper, we report interlaminar shear strengths of composites from fibres with conformal functional plasma polymer coatings of varying thickness.

2. Experimental

2.1 Materials

E-glass fibres were supplied by Owen Corning Ltd, whose diameter is $14.32 \pm 1.47 \mu\text{m}$, the density 2.60 g/cm^3 , and tensile modulus 76 GPa.

The monomers, acrylic acid, allylamine and 1, 7-octadiene utilized for plasma deposition were

obtained from Aldrich Chemical Company, UK with the purity of 99% or more. Acrylic acid and allylamine were selected to allow the introduction of functional groups (carboxylic acid or amine) into the plasma polymer. 1, 7–octadiene was used as a co-monomer to dilute the acrylic acid and allylamine and provide a crosslinked mechanically stable structure.

The matrix resin used for the experiment was a mixture of Epikote 828 which is a diglycidyl ether of bisphenol-A (Robnor Resins, UK), 90 phr (per hundred resin) 1-methyl-5-norbornene-2, 3-dicarboxylic anhydride (NMA), a curing agent (Huntsman Advanced Materials Ltd, UK), and 1 phr DY062, Benzyldimethylamine (BDMA), used as the accelerator (Huntsman Advanced Materials Ltd, UK). The resin was cured using the following schedule: at 80 °C for 2 h, 120 °C for 3 h, 150 °C for 4 h. Its mechanical properties are given in Table 1.

Table 1 Mechanical properties of the matrix resin

E modulus (GPa)	Yield stress (MPa)	Shear yield stress (MPa)	Failure Strain (%)
3.3 ±0.1	127.2±0.9	73.5*±0.6	4.5±0.2

* Calculated based on von Mises Yield Criterion

2.2 Plasma polymer fibre sizing

Uncoated unsized E-glass fiber tows were spread with an air jet and continuously coated with either a plasma copolymer of acrylic acid / 1, 7-octadiene or allylamine / 1, 7-octadiene. The plasma was induced in a tubular glass reactor at 3.56 Hz radiofrequency signal generator and matching network (Coaxial Power Systems (UK)) at a low power (1W) and at a flow rate $2 \text{ cm}^3_{\text{STP}} \text{ min}^{-1}$ (sccm). The low plasma power to flow rate confers high levels of functional group retention in the plasma polymer deposit as detected by XPS. Full details of the plasma polymer continuous coating and the plasma reactor have been described elsewhere [5].

2.3 Interlaminar Shear Strength Measurements

The plasma polymer coated E-glass tows were wound around a carbon fibre composite frame (2

mm × 5 mm × 7.5 mm) to form a panel of eight layers. To remove absorbed moisture, and prevent void formation, the wound frame was put into a mould and placed in a vacuum oven at 80 °C for 30 minutes. The catalysed epoxy resin was homogenised at 80 °C and gently poured into the mould, so that the liquid resin completely penetrated the array of fibres. This was placed into a vacuum oven to remove the bubbles entrapped in the resin. After ten minutes, the panel was removed from the mould and put onto the bottom plate of a pressclave, and covered with a steel platen. Then the panel was kept under a pressure of 8 tons for 2 hour at 80 °C to remove excess resin and to partially cure it. The partially cured panel was removed, vacuum bagged and replaced in the pressclave and cured at 120 °C for 3 h, followed by post curing at 150 °C for 4 h under a pressure of 5 psi. Short beam shear specimens (2 mm × 10 mm × 20 mm) were cut directly from the composite plate. Five specimens were prepared system from each. Polished cross-sections were examined in the optical microscope and shown to be essentially void free. The fibre weight fraction in the composite was obtained by ignition of the matrix resin in a furnace at 650 °C for 60 min. The corresponding volume fraction (V_f) was calculated from the densities of the fibre and resin. The V_f of the specimens prepared from acrylic acid / 1, 7-octadiene coated fibres was found to be $57.0 \pm 1.1\%$. For the allylamine / 1, 7-octadiene series, the average V_f was $57.7 \pm 1.3\%$. Using SEM at 15 kV, the distribution of the fibres was found to be good and compared favourably with prepreg based systems.

The interlaminar shear strength was measured using a short beam shear test using the CRAG standard [6] with a span to depth ratio (s/t) of 5. The diameter of the support and loading rollers was 6 mm.

The interlaminar shear strength was calculated from equation (1):

$$ILSS = 0.75P / wt \quad (1)$$

where w is the width and t the thickness of specimen and P the failure load. After each test the specimens were examined to ensure that failure had occurred through shear.

3. Results

3.1 Functionality of the Plasma Polymer sizing

E-glass fibres are coated with a range of plasma copolymers from 0-100% acrylic acid co – 1,7 octadiene and 0-100% allylamine co – 1,7 octadiene. Previous papers [4, 5] have reported a surface analysis study of the retention of the COOH and NH₂ groups within the coating. XPS has also been used to quantify their surface concentrations. The concentration of the functional monomer in the plasma feed determines the concentrations of functional reactive groups in the coating. The thickness of the coating was varied using the residence time of the fibres in the plasma. The short beam shear test was always accompanied by examination of the failure mechanism to ensure that the plasma coated specimens failed in shear. Therefore the test can be used to assess the influence of fibre functionalisation on the interfacial properties of high V_f composites.

Figure 1 shows the interlaminar shear strength (ILSS) of glass fibre / epoxy composites as a function of the acrylic acid concentration in the monomer feed. The plasma polymer coating time was 15 mins. The ILSS values tend to increase with the concentration of the functional monomer. With a plasma polymer from 100% acrylic acid, an ILSS of 72.3 ± 2.8 MPa was recorded. This is 48% higher than that of the non-functional coating from 0% acrylic acid (100% 1, 7-octadiene) plasma polymer samples, which had the lowest ILSS value of 48.8 ± 1.2 MPa. The shear strength (τ_y) of the matrix (Table 1) is estimated to be 73.5 ± 0.6 MPa, so that the interfacial bond strength of the former can be considered to exceed the shear strength of the resin while the latter system has a poor interfacial bond. Thus the fracture surfaces of these composites should be illustrative of cohesive failure within the interphasal matrix, of the former, and adhesive in the latter. Figure 2(a) shows that with the hydrocarbon plasma polymer coating, interfacial failure occurred. Figure 2(e) shows that with the functional acrylic acid, plasma polymer coating resin debris clearly indicates adhesive failure.

Figure 3 shows that the ILSS of composites from the allylamine plasma polymer coated fibres exhibited a similar trend with the concentration of amine group in the coating.

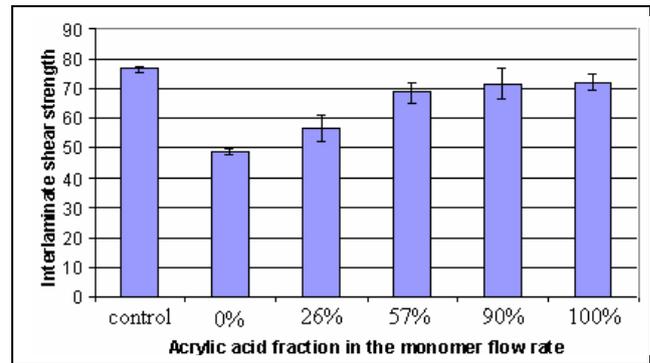


Figure 1 Interlaminar shear strength of 15 min plasma polymer coated glass fibre composites for different monomer ratios of acrylic acid and 1, 7-octadiene

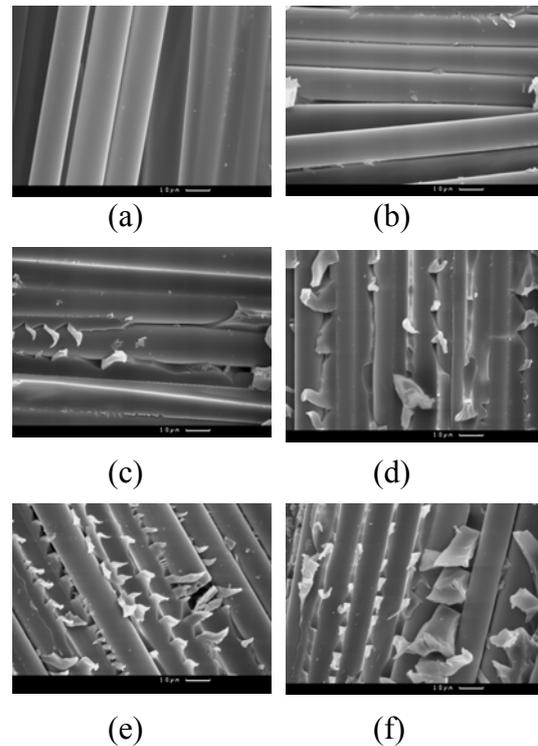


Figure 2 SEM micrographs of failure surface of acrylic acid / 1, 7-octadiene plasma copolymer coated fibre composite with 15 min deposition time: $\times 1000$ (a) 0%, (b) 26%, (c) 57%, (d) 90%, (e) 100% acrylic acid plasma polymer coated fibre composite, and (f) untreated, unsized fibre composite

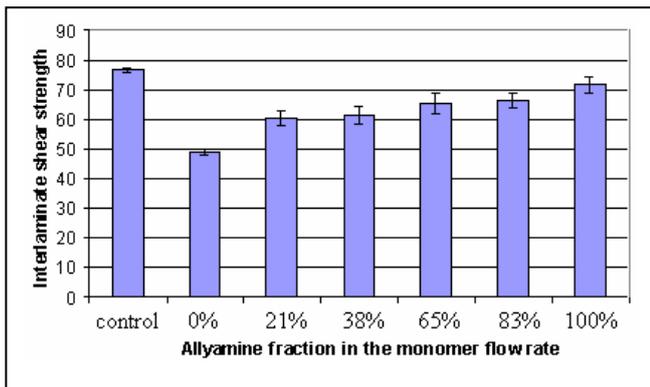


Figure 3 Interlaminar shear strength of 15 min plasma polymer coated glass fibre composites for different monomer ratios of allylamine and 1, 7-octadiene

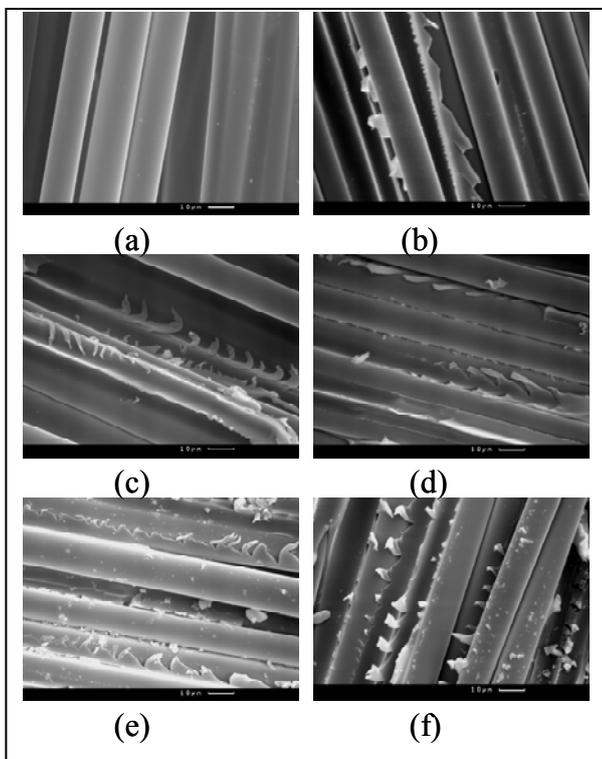


Figure 4 SEM micrographs of failure surface of allylamine coated fibre composite: $\times 1000$ (a) 0%, (b) 21%, (c) 38%, (d) 65%, (e) 83% (f) 100% allylamine plasma polymer coated fibre composite

Figures 2 and 4 show the fracture surfaces of the ILSS test specimens. It is clear that these are consistent with values of ILSS (Figures 1 and 3). Thus for the composite made with 0% acrylic acid coated fibres, failure in Figure 3(a) is clearly interfacial because of the lack of debris on the fibre surface. On the other hand, for the fracture surface

of the composite from the 100% acrylic acid coated fibres, shows significant quantities of residual matrix on the exposed fibres which arises from the stronger interfacial bond between fibres and matrix resin (Figure 3(e)). As the potential for interfacial chemical bonding between the fibre and matrix increases through the functionality of the plasma polymer coating, the extent of the residual resin on the fibres in the fracture surfaces also increases. Thus carboxylic acid groups are active in the formation of a chemical bonds at the fibre-matrix interface. A similar trend was observed with the allylamine concentration in the plasma polymer coatings used for the composites as shown in Figure 4.

The control composite from the uncoated fibres had an ILSS of 76.6 ± 1.0 MPa, which is higher than any from the coated fibres. This is slightly higher than the shear yield strength of the cast resin which was used as the matrix. This is a clear indication of matrix cohesive shear failure in the short beam shear test as shown in Figure 2(f). It is known that a strong interface forms with unsized glass fibres. This has been attributed to the thermal radial compressive stress which forms on cooling from the post cure temperature [5, 7, 8] and polar interactions between the resin and fibre surface.

3.2 Effect of plasma polymer sizing thickness

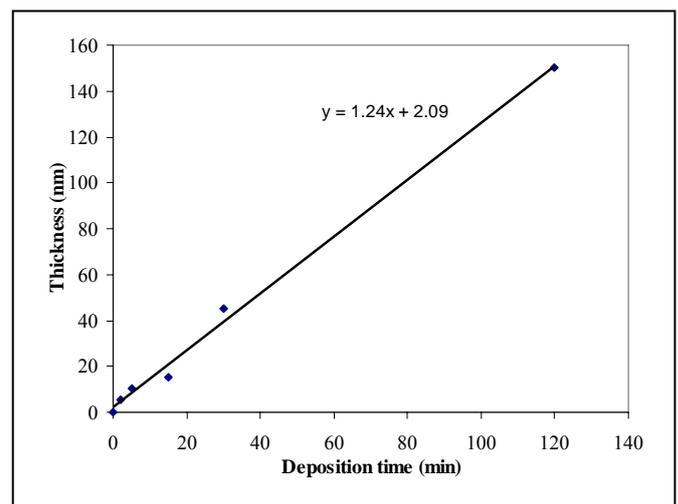


Figure 5 The thickness of the plasma copolymer deposited on to a silicon wafer at the power of 1 W as a function of deposition time.

Figure 5 shows how the thickness of the plasma polymer deposit varies linearly with the deposition time. The rate of deposition is 1.24 nm min^{-1} . The

ILSS data given in Figure 2 is therefore typical of composites containing fibres with an “interlayer” of plasma polymer of 15.32 nm. Figure 6 shows how the ILSS changes with a decrease in the thickness of the plasma polymer deposit. Of particular note in Figure 6 is that with a plasma polymer thickness of 15.32 nm, the ILSS is below that of the control and decreases with a reduction in the chemical functionality of the coating, as shown in Figure 1. However, at a thickness of 5 nm all of the values of ILSS are similar to that of the control even those with the reduced functionality coatings. For the least functional coating (26-30%) ILSS is at the lowest level for 10 and 15 nm interlayers. The only reasonable explanation is that an interphase is forming through penetration of the epoxy resin into the plasma polymer and that the penetration depth is less than 10 nm. By assuming that the mechanical properties of the interphase are similar to those of the matrix, we can conclude that the interphase has a thickness of approximately 5 nm, ie when the ILSS is similar to the other systems. Figure 7 gives a similar plot for allyl amine system. Here the ILSS values are lower across all of the systems and thicknesses. However, the most reactive coating with highest amine group concentration approaches the ILSS of the control. The implication of this data is therefore that the penetration depth of the epoxy resin into the plasma polymer of allylamine is lower.

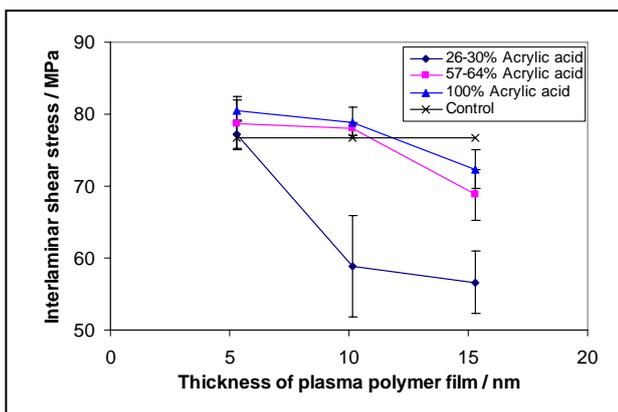


Figure 6 Interlaminar shear strength of high fibre volume composites as a function of plasma polymer thickness for different monomer ratios of acrylic acid and 1, 7-octadiene

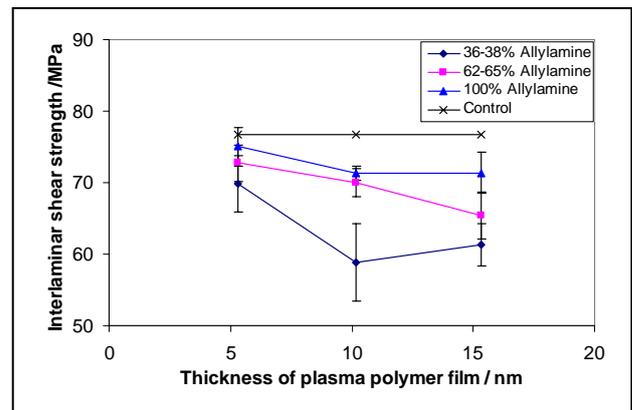


Figure 7 Figure 7 Interlaminar shear strength of high fibre volume composites as a function of plasma polymer deposition time for different monomer ratios of allylamine and 1, 7-octadiene

4. Discussion

Plasma polymers have the potential to be a modern size for reinforcing fibres used in composite manufacture. The process is an environmentally friendly gas phase polymerisation which deposits a conformal coating which protects the fibres from damage and whose chemistry can be adjusted to provide the functionality for reaction with the matrix polymers and resins. Furthermore, this study shows that the mechanical properties of the deposit can be used to control the micromechanics of failure and hence improve the durability and reliability of fibre composites.

Figures 6 and 7 show that the ILSS of these composites is a function of the plasma polymer thickness as well as the chemistry of the deposit. This is particularly interesting because it shows that even with a highly crosslinked plasma polymer interlayer, interphases form with the matrix resin. The variation in ILSS can be explained with reference to Figure 8 which describes the interaction between the plasma polymer coating on the fibre and the matrix resin.

Figure 8 shows how the diffusion or penetration of the epoxy resin into the plasma polymer coating occurs over a limited length scale (b in Figure 8). Thus, when the coating thickness exceeds this value, an interlayer of plasma polymer will exist (ii) in Figure 8. On the other hand, with a “thin” coating complete interaction between the matrix

and plasma polymer will occur giving rise to an “interphase” at the fibre-matrix interface (i) in Figure 8.

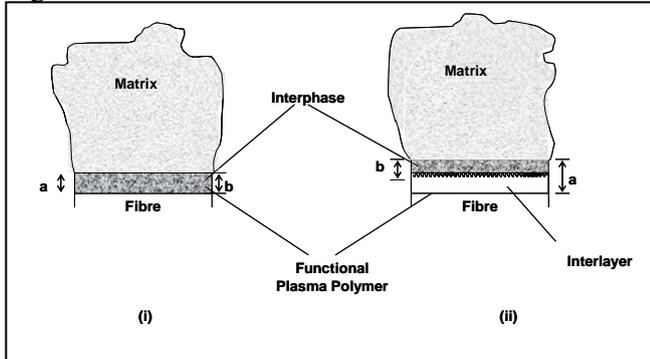


Figure 8 The formation of an interphase between a plasma polymer conformal coating (pp) and the matrix epoxy resin. (i) With a “thin” coating the penetration depth of the epoxy into pp exactly equals the thickness of the coating, a. (ii) With a “thick” coating an interlayer of pp remains on the fibre surface because the penetration depth, b is less than the thickness of the pp coating. For the acrylic acid pp, the interphase thickness, b, would appear to be ≈ 5 nm whereas for the allylamine pp ≈ 2 nm.

Thus the micromechanics of failure of a fibre composite will be dominated by the properties of this interphase region. In this work, we have measured ILSS in short beam shear tests. The shear stresses will be maximised at the fibre-matrix interface so that failure will occur within the region adjacent to the fibre surface. Thus, with the composites prepared from fibres with relatively thick plasma polymer coatings the mechanical properties of the interlayer of plasma polymer will determine the failure load. When the thickness of the coating is less than the penetration of length of the matrix, the interphase will be responsible.

Thus, the results given in Figures 6 and 7 can be explained by this hypothesis because the interphase region will have thermomechanical properties typical of a semi-interpenetrating network of the epoxy and plasma polymer. Since the density of the interphase can be expected to be higher than that of the plasma polymer, its modulus and yield strength will also be higher than both that of the plasma polymer interlayer and the matrix. As a result, the ILSS will rise when the thickness of the

coating equals that of the interphase. Figure 6 shows that this occurs at ≈ 5 nm. Thus, we can infer that an interphase region of 5 nm thickness forms in the acrylic acid pp system and that this controls the value of ILSS. Examination of Figure 7 for the ILSS of the allylamine pp system, shows that the situation defined in Figure 8 (i) has not been achieved. Therefore if we extrapolate the data in Figure 7 to lower plasma polymer coating thicknesses an interphase region of ≈ 2 nm would be predicted.

Evidence for this idea will be presented elsewhere. However, preliminary nanoindentation data shows that the reduced modulus of the plasma polymers from allylamine is significantly higher than that of those from acrylic acid [8, 9]. The latter has a reduced modulus which is very close to that of the cured matrix resin. Thus the different nanoindentation moduli for the two plasma polymer systems shows that the crosslink density of the allylamine plasma polymer is significantly larger than that of acrylic acid plasma polymer. This explains why the interphase dimension in these composites is smaller than that of the latter. Thus the diffusion of the epoxy resin into the allylamine plasma polymers will occur more slowly and over a shorter distance.

Similar observations were made using single embedded fragmentation tests on the same resins, where the stress transfer characteristics are also determined by the properties of the interphases [8, 9]. We are also examining the effect of these coatings on the tensile strength of these composites [10]. It is clear that there is an optimum functional group concentration in the coating as well as an optimum thickness as discussed here.

5. Conclusions

Plasma polymers with controlled chemical functionality have been deposited continuously onto unsized glass fibres with varying thickness ranging from 5 – 15 nm. Unidirectional composites with $V_f \approx 57\%$ have been prepared for the measurement of interlaminar shear strength (ILSS). The values of ILSS have been found to be a function of the coating thickness. Furthermore, the ILSS approaches and slightly exceeds the shear strength of the matrix when the thickness of the

plasma polymer is below ≈ 5 nm for the acrylic acid plasma polymers and ≈ 2 nm for the allylamine plasma polymers. These values represent the dimensions of the interphases which form in these epoxy resin composites prepared from plasma polymer coated glass fibres.

6. References

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7. Acknowledgements

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