OPTIMISTION OF INTERFACIAL PROPERTIES FOR TENSILE STRENGTH BY PLASMA POLMERISATION

T. J. Swait, C. Soutis, F. R. Jones

The University of Sheffield, Mappin Street, Sheffield S1 3JD, UK
Tel: +44 (0) 114 222 5941   Fax: +44 (0) 114 222 5943
Email: t.swait@sheffield.ac.uk

ABSTRACT

Plasma polymerisation was used to coat E glass fibres with an acrylic acid / 1, 7- octadiene copolymer at varying concentrations of acrylic acid. These fibres were then used to produce unidirectional composite panels. By so doing it was possible to produce composites with varying degrees of adhesion between fibre and matrix. The panels were then prepared into test pieces and tested to failure in tension.
It was found that stress, strain and energy absorbed to failure were higher in specimens produced from plasma polymer coated fibres than from uncoated controls. Tensile strength and energy absorbed in failure were dependent upon the concentration of acrylic acid in the monomer flow used to coat the fibres. The presence of a plasma polymer coating increased the longitudinal tensile strength by 25 %. By tailoring the composition of the coating to create the optimal degree of fibre – matrix bonding the tensile strength was increased by 35 % over uncoated controls. This optimal degree of bonding was obtained at an intermediate level of interfacial adhesion which was less than the maximum achievable. The fracture surfaces were examined by optical and electron microscopy and it was observed that the plasma polymer coating can change the failure mechanisms and fracture behaviour of the composite.

1. INTRODUCTION

The performance of most polymer composites has long been recognised to depend upon a good interface allowing optimal stress transfer between fibre and matrix [1]. To achieve this in the case of glass fibres water based sizes containing silanes [2] are common, wheras in the case of carbon fibres, oxidative treatments followed by a polymeric size [3] are used. More recently, plasma polymerisation has been proposed as a method of coating fibres to promote the formation of a good interphase between fibre and matrix [4-6].

Plasma polymerisation is a process which allows nanodimensional, conformal and pinhole free polymer coatings to be applied to a substrate of choice [7]. For this work a plasma polymer (PP) produced from co-polymerising acrylic acid and 1, 7- octadiene was applied to the surface of glass fibres prior to their incorporation into a high volume fraction (V_f) composite in order to control the degree of adhesion between the fibre and the matrix. It has been shown by Marks [6, 8] using the technique of X-ray photoelectron spectroscopy (XPS) with Trifluoroethanol derivatisation (TFE) that by varying the ratios of the above two monomers the concentration of carboxylic acid groups on the surface of the polymer coating can be varied. It has been shown by Marks[6] and by Kettle [4, 6] using the fragmentation test that the strength of the interfacial bond between a plasma polymer coated glass or carbon fibre and an epoxy resin can be controlled by the concentration of surface carboxylic acid groups.
Longitudinal tensile strength of a unidirectional glass fibre composite was chosen as the parameter to be measured against the strength of the interface. Longitudinal tensile strength is often considered to be less dependent upon the strength of the fibre / matrix interface than on factors such as the strength and volume fraction of the fibres [1]. However it is also well known that a bundle of fibres wetted with resin in the form of a composite will support substantially more load than a similar bundle of dry fibres. The

increase is not due to the load carrying capability of the resin itself, which is relatively weak, but due to its ability to redistribute load from broken to unbroken fibres [9]. The matrix can only redistribute the load if the interface (or the interphase region) is strong enough to transfer the stress. It is also known that in the case of a strong fibre matrix bond a failure of the fibre can lead to micro cracking of the matrix at the fibre-break [10, 11]. A crack in the matrix will lead to a higher stress concentration in the matrix than a debond [10], and it is thought that stress concentrations at fibre-breaks have an effect on the tensile failure of a composite [12]. A mechanism whereby an excessively strong fibre-matrix bond could reduce tensile strength therefore exists, making it likely that an optimal value of interfacial strength for maximum tensile strength will exist. Furthermore a ductile interphase can also redistribute the stored energy in a fibre which is released on fracture rather than debonding or fracturing the matrix.

2. EXPERIMENTAL
2.1 MATERIALS
E-glass fibres were supplied by Owens Corning Ltd of diameter 14.32 ± 1.47 μm, density 2.60 g/cm^3, and tensile modulus 76 GPa. The fibres were supplied as water sized; that is no silane or other coupling agents or lubricants had been applied but the fibres were sprayed with water during the manufacturing process.

The monomers, acrylic acid and 1, 7- octadiene utilised for plasma deposition were obtained from Aldrich Chemical Company, UK with a purity of 99% or more. Acrylic acid was used to introduce carboxylic acid functional groups into the plasma polymer and 1, 7–octadiene was used as a diluent.

The matrix resin used for the experiment was a mixture of 100 parts (by mass) Epikote 828 which is a diglycidyl ether of bisphenol-A (Robnor Resins, UK), 90 parts Aradur hardener HY906 (1-methyl-5-norbornene-2, 3-dicarboxylic anhydride), a curing agent (Robnor Resins, UK), and 1 part DY062, Benzyldimethylamine (BDMA), used as the accelerator (Huntsman Advanced Materials Ltd, UK). The resin was cured at 80 ^{o}C for 2 h, 120 ^{o}C for 3 h, 150 ^{o}C for 4 h, with ramp rates of 2 ^{o}C/min.

2.2 PLASMA POLYMER COATING
The fibre bundle was separated by a jet of blown air (to minimise shadowing effects), rolled onto spools and loaded into the plasma reactor. The fibres were then coated in a continuous process by being wound from spool to spool through the plasma chamber. The speed of the receiving spool was adjusted to maintain a constant deposition time of 10 minutes on the fibre bundle. The baseline pressure within the reactor without monomer flow was less than 3×10^{-3} mbar. The total flow rate of monomers was set to 2 sccm using needle valves. The ratio of acrylic acid : octadiene was varied from 100 % : 0 % to 0 % : 100 % in 20 % increments. A low power of 1W was used to maintain polymer functionality. Fibres used to create control specimens were produced in the same way, but without monomer flow or power.

2.3 SPECIMEN PREPARATION
The coated fibres were wound onto frames. These were placed in a resin bath and impregnated in a vacuum oven before being cured in a vacuum bag. The frames were then cut away to leave the composite panels, end-tabs were adhered with PTFE inserts to reduce the stress concentration at the end tab and the panel was cut into tensile test specimens.

2.4 TENSILE TESTING

The testing was carried out with a Hounsfield Universal Test Machine, a cross head speed of 1 mm/min, a 10 kN load cell and a clip on extensometer. Any specimens which showed evidence of the end tabs having debonded or which failed underneath the end tabs were discounted from the data set.

Due to the length of fibre bundle which could be coated by the plasma reactor it was not possible to produce panels large enough to prepare test pieces to ASTM or ISO standards. The variations in test piece geometry and methodology between the non standard test used and ISO 527 (parts 1 and 5) [15] are summarised in Table 1. However to validate the test piece geometry and methodology panels were prepared from a commercial pre-preg glass fibre material, MTM 28-1, supplied by Advanced Composites Group, and tested to both ISO 527 and to the non-standard geometry used in this work. Sufficiently close agreement was found between the samples prepared to the two different standards to validate the non standard test geometry.

Table 1: Differences in dimensions and methods between the standard (ISO 527) and non-standard test procedures

	ISO 527	Non Standard Test
Total Specimen Length /mm	250	95
End Tab length	50 mm	20 mm[*]
Gauge Length /mm	150	55
Width /mm	15	10
Thickness /mm	1	1.7
Minimum overlap of gripping jaws /mm	7	0
Minimum number of samples tested	5	8

Note: [*] A 2.5 mm PTFE insert was used to reduce stress concentration at tab.

Optical microscopy was used to examine the fracture surfaces by viewing through the thickness of the tested specimens in transmission mode. This was possible due to the transparent nature of GFRP.

Electron microscopy was carried out using a Jeol JSM6400 scanning electron microscope in secondary electron mode at 20kV accelerating voltage and 20mm working distance to image the surfaces of longitudinal splits in the fractured samples. The samples were prepared by sputtering a layer of gold onto the surface to prevent sample charging.

2.5 DETERMINATION OF VOLUME FRACTION

After testing and microscopic examination the volume fraction of the specimens was determined using the matrix burn off technique. Sections were cut from the undamaged part of the tested specimens, placed in ceramic crucibles of known mass and heated to 650 ^{o}C for two hours to remove the epoxy matrix by thermal decomposition. By weighing the crucibles before and after heating the mass fraction of fibre could be calculated. This could then be converted to a volume fraction using the relative densities of the glass and epoxy resin components.

3. RESULTS
3.1 TENSILE STRENGTHS

On testing, the specimens all displayed a roughly Hookean elastic increase in load up until the maximum stress was reached. A slight reduction in stiffness occurred at higher loads; this was especially pronounced in the 0% acrylic acid / 100 % 1, 7 – octadiene PP coated samples. Once the maximum stress had been reached the specimen would either fail abruptly or would continue to support a reduced load as strain increased in a manner similar to ductile extension in metals. The samples with intermediate levels of acrylic acid (40, 60 and 80 %), tended to mostly display this pseudo ductile type behaviour while those at lower and higher levels of acrylic acid displayed it less. All specimens composed of fibres coated with 0 % acrylic acid / 100% 1, 7 – octadiene PP failed abruptly at their maximum stress. The uncoated controls behaved in a similar manner and most, but not all, failed abruptly. There is variability in the maximum stress and modulus apparent in the data, in particular for the specimens prepared from uncoated control fibres and the 0 % acrylic acid PP coated fibres. The most likely explanation is variability in fibre volume fraction and alignment. Optical microscopy showed the fibre alignment to be good, but fibre volume fractions ranged from 24% to 41%, with a mean of 31 %. The effects of this variability can be minimised by normalising the stress data for each specimen to the fibre volume fraction of that individual specimen. Normalising in this way substantially reduced the scatter in the data as can be seen from the lower standard deviations for the normalised versus the raw parameters in Table 2. The results from the tensile testing are given in Table 2. Normalised stress/strain plots for samples produced from fibres coated with 0, 40 and 100 % acrylic acid are shown in Figure 1.

Table 2: Longitudinal tensile failure data for unidirectional specimens produced using plasma polymer coated and uncoated control glass fibres

Composition of monomer feed to apply plasma coating to glass fibre	Un-coated control	0% Acrylic Acid / 100% Octadiene	20% Acrylic Acid / 80% Octadiene	40% Acrylic Acid / 60% Octadiene	60% Acrylic Acid / 40% Octadiene	80% Acrylic Acid / 20% Octadiene	100% Acrylic Acid / 0% Octadiene
Average maximum stress /MPa	295 (45)	340 (46)	387 (42)	440 (54)	404 (51)	384 (64)	352 (53)
Average maximum normalised stress /MPa	310 (16)	348 (21)	364 (37)	415 (28)	415 (35)	379 (19)	385 (31)
Average energy absorbed to failure / J/mm^3	0.40 (0.29)	0.27 (0.04)	0.34 (0.13)	0.75 (0.51)	0.61 (0.44)	0.50 (0.36)	0.54 (0.46)
Average strain at maximum stress /%	1.36 (0.20)	1.48 (0.11)	1.48 (0.11)	1.55 (0.13)	1.55 (0.15)	1.56 (0.11)	1.57 (0.13)

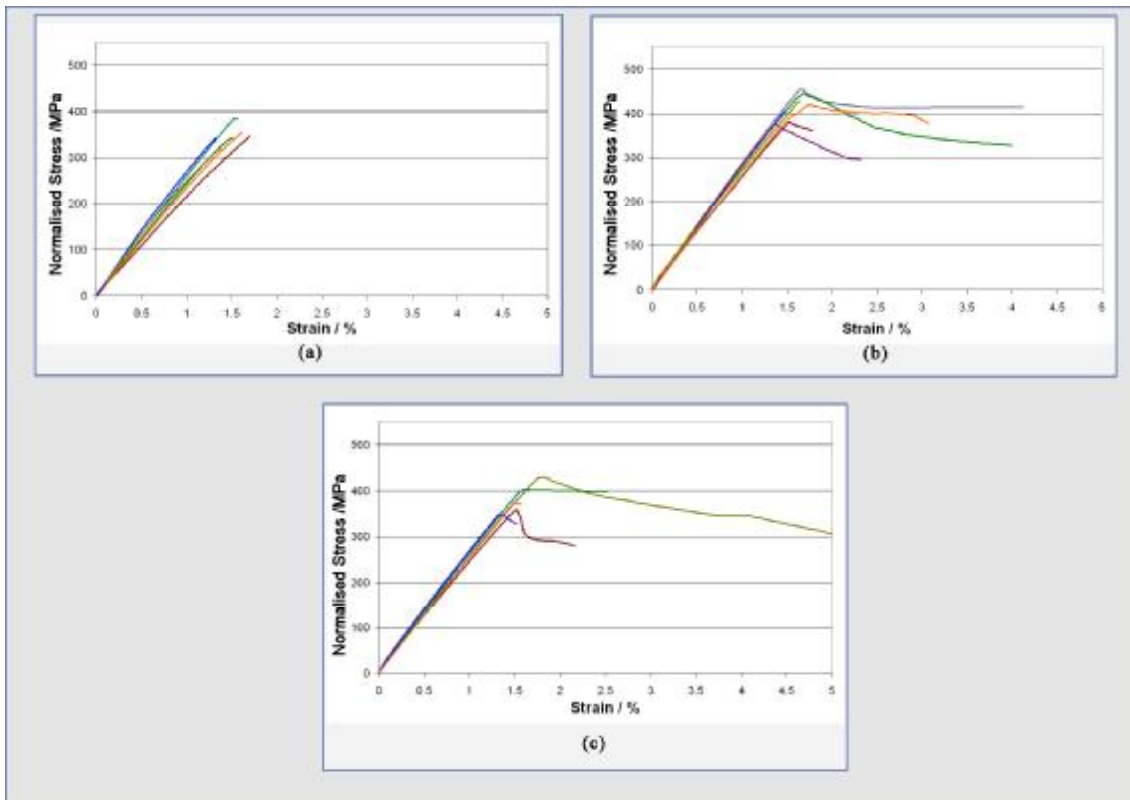|							
Elastic modulus /GPa	22.7 (3.3)	26.3 (5.9)	27.1 (3.6)	29.7 (2.7)	27.7 (2.6)	26.5 (3.6)	23.9 (3.2)
Normalised Elastic Modulus /GPa	24.5 (2.9)	25.4 (2.3)	26.0 (2.8)	28.1 (1.1)	28.5 (2.1)	26.5 (2.9)	26.6 (2.0)

( ) denotes standard deviation

Figure 1: Normalised stress/strain plots to tensile failure for unidirectional composite specimens produced from glass fibres coated with plasma polymer from polymerising (a) 0% acrylic acid/100% octadiene (b) 40% acrylic acid/60% octadiene (c) 100% acrylic acid/0% octadiene.

The specimens produced from 40 % acrylic acid PP coated fibres exhibited the highest maximum stress, with higher and lower concentrations of acrylic acid giving lower values of maximum stress. The specimens produced from PP coated fibres all reached a higher maximum stress than the specimens produced from uncoated control fibres. Modulus (calculated at 0.5 % strain) shows a similar trend to maximum stress, although more weakly. The energy absorbed to failure (in J mm^{-3}) was taken as the area under the stress / strain plot (calculated as a numerical integral of the stress / strain data $(= \int_0^e s\, de)$) to failure. The specimens produced with 40 % acrylic acid PP coated fibres exhibited the most energy absorbed before failure since most exhibited the pseudo ductile type of behaviour. Lower and higher concentrations of acrylic acid in the PP

feed were typified by less energy absorbed. The large amount of scatter in the data results from some specimens failing abruptly at maximum stress whereas others continued to support load up to much higher strains. The strain at which maximum stress is supported does not show a clear trend with concentration of acrylic acid, but the specimens produced with plasma polymer coated fibres generally show higher values than the uncoated controls. The normalised maximum stress, energy absorbed, elastic modulus and strain at maximum stress are shown in Figure 2.
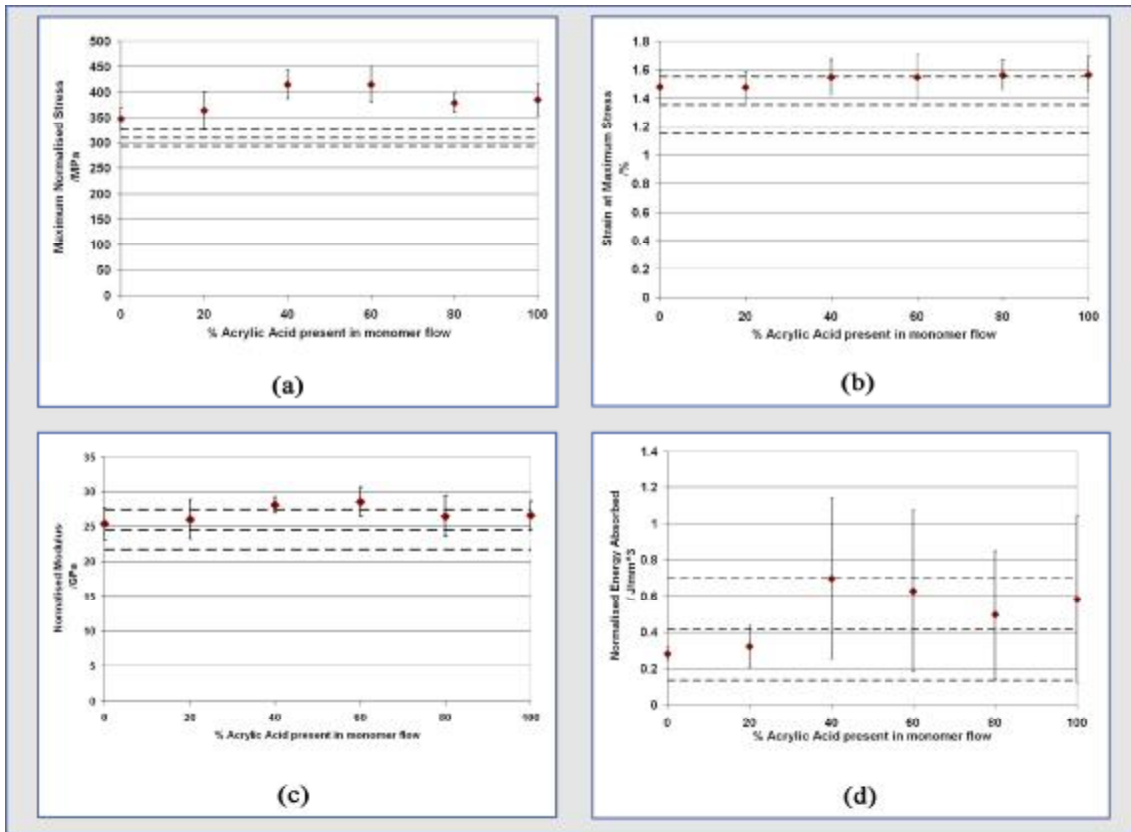

Figure 2: (a) Maximum normalised stress supported, (b) Strain at which maximum stress is supported, (c) Normalised modulus and (d) Normalised energy absorbed to failure versus concentration of acrylic acid in the monomer feed used to plasma polymer coat the glass fibres used to produce the specimen. Error bars represent plus and minus one standard deviation. Dashed horizontal lines represent results from uncoated control specimens, mean and mean plus and minus one standard deviation.

3.3 MICROSCOPY

Prior to testing all of the specimens were transparent. After testing it was noticed that the 0 % acrylic acid specimens had become opaque, while all other specimens remained transparent away from the actual fracture surface.

The through thickness optical micrographs of specimens containing 0, 40 and 100% acrylic acid PP coated glass fibres are shown in Figure 3. Electron micrographs obtained from specimens containing 0, 20, 40 and 100% acrylic acid PP coated glass fibres are shown in Figure 4.
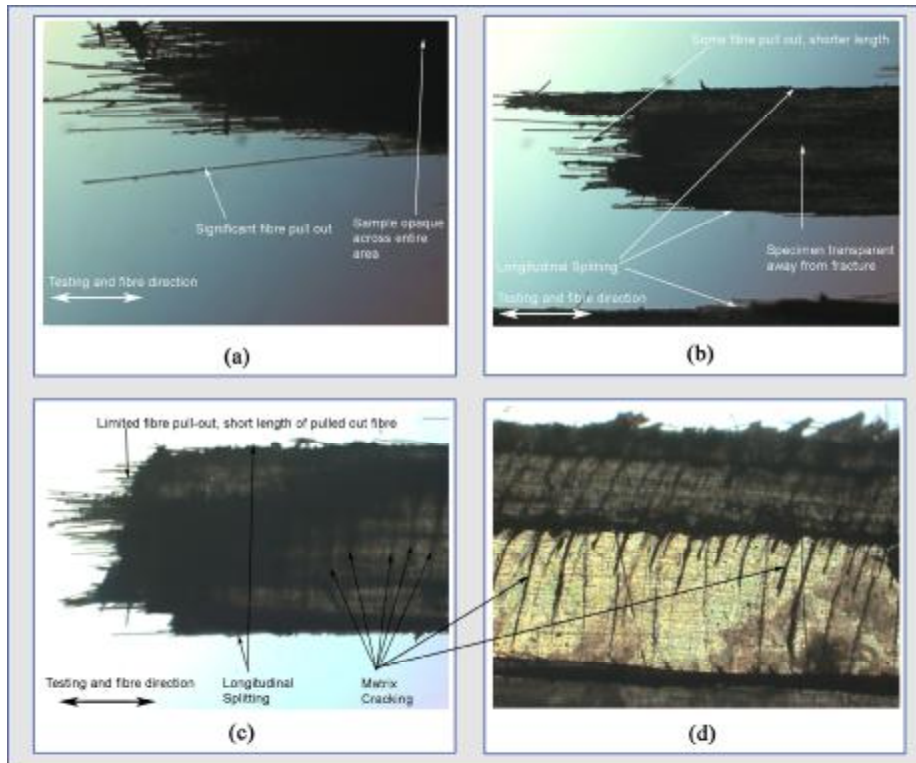
Figure 3: Through thickness optical micrographs of specimens produced from fibres coated with PP consisting of (a) 0% acrylic acid, (b) 40% acrylic acid, (c) and (d) 100% acrylic acid.
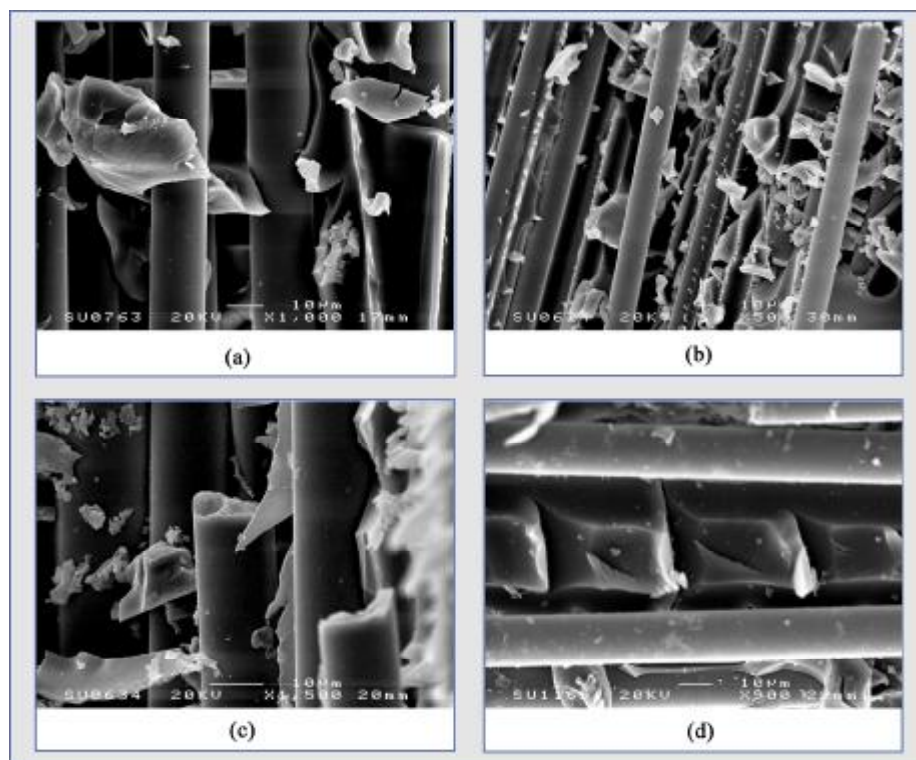

Figure 4: Electron micrographs of surface of longitudinal splits for specimens produced from fibres coated with PP consisting of (a) 0% acrylic acid, (b) 40% acrylic acid, (c) and (d) 100% acrylic acid.

4. DISCUSSION

The test pieces all failed by a mixture of longitudinal splitting, fibre fracture and transverse matrix cracking.

Without acrylic acid in the plasma polymer coating (100% 1, 7 – octadiene) there was very little splitting. However after testing these specimens they became opaque and white despite being transparent prior to testing. This may indicate widespread debonding resulting from the weak interfacial bond between the non-functional hydrocarbon polymer coating and the epoxy resin. It can be seen from Figure 3 (a) that substantial lengths of fibre have pulled out in the fracture of these specimens, again indicating a weaker fibre / matrix bond. The electron micrograph, figure 4 (a) also shows that the resin has pulled away from the fibre surface. There is also some surface roughness on the glass fibres visible, this may be plastically deformed plasma polymer remaining on the surface of the fibre after the resin has debonded. The stress / strain plot, Figure 1 (a), shows a gradual reduction in stiffness before an abrupt failure.

The stress/strain plots for specimens produced from fibres coated with a 20-100 % acrylic acid PP coating showed little reduction in stiffness prior to maximum stress being reached. Some specimens fail abruptly when maximum stress is reached but other specimens continue to support load up to unusually high strains (up to 3 – 5 %). This is higher than the failure strain of the fibre alone and an unusual result for a unidirectional GFRP. They showed considerable longitudinal splitting and remained transparent away from the fracture surface. The optical micrographs show reduced lengths of fibre pull out as the concentration of acrylic acid in the monomer feed is increased. At 80 % and particularly at 100% acrylic acid transverse cracks were visible as shadows in the samples. This is unusual for a GFRP where the strain to failure of the matrix would be expected to be higher than the strain to failure of the fibre. The electron micrographs of specimens produced from fibres coated with 40-100% acrylic acid PP showed increasingly plastically deformed hackles of resin adhered to the fibre surface and an increasing incidence of micro-cracks in areas of resin previously adhered to the fibres as the concentration of acrylic acid increased. The surface of the fibres where they have pulled away from the resin was smooth other than small flecks of debris. The electron micrograph of the specimen produced from 20 % acrylic acid PP fibres showed few hackles of plastically deformed resin and no micro–cracking. There are, however, fibres visible with a sheath of coating partially covering the fibre. The coating appears too thick to be the plasma polymer itself, but may be an interphase region consisting of plasma polymer coating and matrix coating. Where the sheath is not in place on the fibre the surface of the fibre is smooth like the specimens produced from fibres at higher concentrations of acrylic acid, not rough like for the specimens produced without acrylic acid in the coating.

It appears that for the non-functional hydrocarbon coating produced from 100 % octadiene the bonding between the coating and resin is poor so debonding occurs at this interface. When higher concentrations of acrylic acid are used to produce the coating the adhesion between the resin and coating is better so the debond instead occurs between the fibre and the coating. When a low concentration of acrylic acid is used (around 20%) then both mechanisms occur resulting in fibres being partially sheathed in resin.

The mechanical properties (maximum stress supported, modulus and energy absorbed – Figure 2) were found to be maximised at 40 to 60 % acrylic acid in the monomer feed used to coat the glass fibres. This is in good agreement with previous work on interlaminar shear strength (ILSS) by Liu [14], which also found ILSS to be maximised

at 60 % acrylic acid in the monomer flow used to coat the fibres. It is interesting to note that the specimens produced from PP coated glass fibres tended to out perform those produced from uncoated control fibres regardless of the composition of the coating. Even the specimens produced from fibres coated with a 100 % octadiene coating yielded a maximum normalised stress 12% higher than the uncoated control specimens. For the optimal (60% acrylic acid) coating the maximum normalised stress was 35 % higher than for the uncoated controls. The average maximum normalised stress of the specimens produced from PP coated fibres was 25 % higher than the uncoated controls. It is also interesting to note that for these studies the macroscopic properties are optimised at an intermediate level of functionality in the coating. However single fibre fragmentation test results from Kettle [4] using carbon fibres show the apparent interfacial shear strength between a single fibre and matrix is maximised with maximum functionality of the coating.

It was reported by Marks [6] that a plasma polymer coating did not increase the average strength of glass fibres, but that it did reduce their variability in strength. It was suggested that this could occur by the plasma polymer coating protecting the fibre from damage or by filling surface flaws which lead to failure. This reduction in variability of fibre strength may be responsible for the increase in performance of the plasma polymer coated fibre composites over the uncoated controls. An alternative explanation is that the mechanical properties of the plasma polymer (which has a modulus slightly higher than that of the matrix, but much lower than that of the fibre) improve the stress transfer between the fibre and the matrix.

The mechanism for the effect of coating composition on mechanical properties is likely to be due to the PP coating optimising the strength of the fibre matrix bond. In the case of low concentrations of acrylic acid in the coating, the specimens are weak due to ineffective stress transfer between the fibre and the matrix, as evidenced by long lengths of fibre pull out and little plastic deformation of resin visible in the electron micrographs. For high concentrations (80-100 %) of acrylic acid in the PP coating is likely that the matrix cracks observed by optical and electron microscopy are causing premature failure of the composite.

5. CONCLUSIONS

It was found that the longitudinal tensile strength of a composite is in part controlled by the strength of the bonding between the fibre and the matrix. The presence of a plasma polymer coating was found to increase the longitudinal tensile strength of a unidirectional composite by 25 % over one produced from uncoated control fibres, even when the coating contains no carboxylic acid functionality. By tailoring the composition of the coating to create the optimal degree of fibre – matrix bonding the tensile strength was increased by a further 10 %.

The presence and composition of a plasma polymer coating can also change the failure mechanisms and fracture surfaces of a composite. For example introducing phenomena not normally associated with a unidirectional GFRP composite, such as multiple matrix cracking and the ability to support load up to higher than expected strains, beyond the strain at which maximum stress is supported.

Plasma polymerisation is therefore a promising fibre coating technique for improving macroscopic composite properties by tailoring the properties of the fibre - matrix interphase. However scaling up to an industrial level would present challenges due to the need to apply the coating under high vacuum conditions. Also the deposition time of

10 minutes used in this study would need to be reduced to be industrially useful. The work of Liu [14] is promising in that it demonstrates similar effects in shorter (2-5 minute) deposition times.

ACKNOWLEDGMENTS

REFERENCES

1. G. Dorey, "*The Fibre-Matrix Interface and Composite Strength*", in "*Composite Materials in Aircraft Structures*", ed. D. H. Middleton, Longman Scientific and Technical: New York, 1990, pp. 50-68.
2. E. P. Plueddemann, "*Silanes and other coupling agents*", Plenum Press, New York, 1991.
3. G. Dorey, "*Review Article Carbon Fibres and Their Applications*", Journal of Applied Physics, 1987, 20: pp. 245-256.
4. A. P. Kettle, A. J. Beck, L. O'Toole, F. R. Jones & R. D. Short, "*Plasma Polymerisation for Molecular Engineering of Carbon Fibre Surfaces for Optimised Composites*", Comp. Sci. Tech, 1997, 57: pp. 1023-1032.
5. T.J. Swait, C. Soutis and F.R. Jones, "*Optimisation of interfacial properties for tensile strength by plasma polymerisation*" Composites Science and Technology, In Press, Corrected Proof, Available online 23 August 2007.
6. D. J. Marks & F. R. Jones, "*Plasma Polymerised Coatings for Engineered Interfaces for Enhanced Composite Performance*", Composites Part A, 2002, 33: pp. 1293-1302.
7. H. Yasuda, "*Plasma Polymerization*", Academic Press Inc., London, 1985.
8. D. J. Marks, "*Scale Up of Plasma Polymer Coating for Interfacial Control in Fibre Composites*", 2002, PhD Thesis, Engineering Materials, University of Sheffield.
9. B. W. Rosen, "*Tensile Failure of Fibrous Composites*", AIAA Journal, 1964, 2(11): pp. 1985.
10. F. M. Zhao, "*Phase Stepping Photoelasticity for Quantifying the Interfacial Response in Fibre Composites at Fibre Breaks*", Materials Science and Engineering A, 2005, 412: pp. 83-87.
11. D. Tripathi, F. Chen & F. R. Jones, "*The Effect of Matrix Plasticity on the Stress Fields in a Single Filament Composite and the Value of Interfacial Shear Strength Obtained from the Fragmentation Test*", Proc. R. Soc. Lond., 1996, 452: pp. 621-653.
12. C. Zweben, "*Tensile Failure of Fiber Composites*", AIAA Journal, 1968, 6(12): pp. 2325.
13. "*Plastics - Determination of tensile properties (Parts 1 and 5)*", British Standard, 1996, EN ISO 527-1 and EN ISO 527-5.
14. Z. Liu, F. M. Zhao & F. R. Jones, "*Optimising the interfacial response of the high volume fraction glass fibre composites using a functional plasma polymer*", Submitted to Composites Science and Technology, 2007.