

The influence of fibre surface treatment on the formation of an interphase in CFRP

P. W. M. PETERS, H. ALBERTSEN

DLR, Institut für Werkstoff-Forschung, Linder Höhe, 5000 Köln 90, Germany

In the scheme of a EURAM programme the influence of a wet oxidative surface treatment on the formation of an interphase, on the fibre–matrix bond strength and on the mechanical properties is investigated. The fibre CG 43–750 was supplied by Courtaulds treated to four different surface treatment levels (designated STL=0% or untreated, 10, 50 and 100%) sized (1% by weight) and impregnated with the resin HG 9106. This resin consists of di-, tri- and tetrafunctional epoxies with the hardener 3.3 DDS and also contains polyethersulphone. During the cure this resin separates in a continuous (thermoset-rich) phase which completely covers the fibres and a discontinuous (thermoplastic-rich) phase with a roughly globular structure. From water uptake experiments and matrix (interphase) sensitive composite properties (shear modulus G_{12} , transverse modulus E_{22}) it was concluded that the activated carbon fibre surface gives rise to a more fully crosslinked interphase, resulting in a reduction of the modulus of this interphase.

1. Introduction

The fibre–matrix interphase in composites has received much attention recently, as it is generally accepted that this region can influence composite properties strongly. In contrast with an interface the interphase has a certain thickness. In this range of thickness the properties of the matrix material change from a certain value at the fibre surface to the properties of the bulk matrix at the outer surface of the interphase. The thickness of this interphase is rather unknown. It certainly depends on the activity of the fibre surface and the matrix systems used. Recently it was shown on a single-fibre composite that the interphase can have a thickness of 400 nm and a modulus of 1/4 of the bulk matrix modulus [1].

As a result of the unknown interphase properties the stress field in the composite on the micro-level can vary considerably, as has been shown by parametric studies [2, 3]. In this investigation an attempt will be undertaken to prove the existence of an interphase and the influence of the degree of fibre surface treatment on this interphase.

2. Experimental procedure

The intermediate-modulus fibre CG43-750 was given four different levels of surface treatment designated STL 0% (untreated), 10, 50 and 100% and subsequently sized 1% by weight (size designated size A). The fibre producer Courtaulds supplied four batches of prepreg containing the above-mentioned differently treated fibre and the resin system HG 9106, a blend of di-, tri- and tetrafunctional epoxies with the hardener 3.3 DDS and the thermoplastic modifier polyethersulphone.

Laminates were produced according to the advised cure cycle (3.5 h at 120 °C and 3.5 h at 177 °C under a pressure of 700 kPa). On specimens cut from UD-Material and (0/90₄/0) laminates the following properties were determined:

- (i) water uptake at saturation (by immersion in distilled water at 70 °C),
- (ii) transverse modulus E_{22} .

Results on transverse cracking in (0/90₄/0) laminates from which a fibre–matrix bond strength was deduced are published elsewhere [4]. Further the longitudinal shear modulus G_{12} was determined with the aid of strains measured in three directions of the 10°-off-axis specimen.

Pure resin plates were produced from the hot melt under four different cure conditions: 18.5 h at 100 °C, 6.5 h at 130 °C, 4.5 h at 160 °C and 2.5 h at 190 °C. Three-point bending experiments were performed on these materials to determine the flexural modulus and flexural strength (fracture strain) distribution. The morphology of the pure resin and the composite materials was investigated by etching a polished surface making use of an etching solution similar to the one described in [5].

3. Results

3.1. Pure resin experiments

From the plates cured at the different temperatures specimens with the dimensions 50 mm × 3 mm (width) × 3 mm (thickness) were cut, making use of a diamond wheel. These specimens (≈20 per cure temperature) were loaded in three-point bending up to fracture (span to thickness ratio = 16). The displacement

under the centre of the specimen was measured as a function of the load. From these curves the flexural modulus was determined making use of [6]

$$E = \frac{L^3 m}{4bd^3} \quad (1)$$

where m is the slope of the load–deflection curve and L, b, d the span, width and thickness of the specimen, respectively. The maximum strain at fracture was calculated with the aid of [6]

$$\varepsilon_{nr} = 6 Dd/L^2 \quad (2)$$

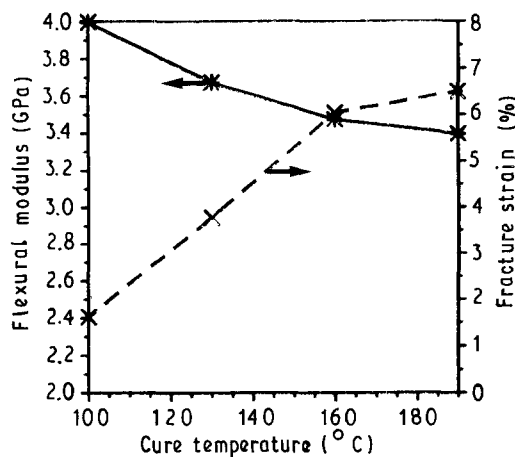


Figure 1 Flexural modulus and characteristic flexural fracture strain of the pure HG 9106 matrix as a function of the cure temperature.

where D is the deflection at fracture. The fracture strain data are described with the aid of a two-parameter Weibull distribution, where the probability of specimen failure F as a function of the maximum strain ε_m is expressed as

$$F = 1 - \exp[-(\varepsilon_m/\hat{\varepsilon}_m)^a] \quad (3)$$

with the two Weibull parameters the shape parameter a and the characteristic maximum strain $\hat{\varepsilon}_m$. These two parameters a and $\hat{\varepsilon}_m$ are determined from the experimental data, making use of linear regression and least-squares analysis.

The determined characteristic maximum strain $\hat{\varepsilon}_m$ and flexural modulus as a function of the cure temperature are indicated in Fig. 1. It clearly shows that the modulus decreases at increased cure temperature. Simultaneously the characteristic fracture strain increases. A similar behaviour was also found for other resin systems (Fiberite 934 and Fiberite 976 [7]). The morphology of the matrix was investigated by polishing and subsequently etching a pure resin specimen. Fig. 2 shows SEM-pictures of specimens cured at different temperatures. These pictures make clear that on curing the matrix separates into a continuous thermoset-rich phase and a discontinuous (approximately globular) thermoplastic-rich phase. The morphology of the matrix becomes visible since the thermoplastic-rich regions are etched more severely than the thermoset-rich regions. The cure temperature has a pronounced influence on the domain size of the second phase. An increased cure temperature leads to a larger domain size and thus to a coarser matrix morphology.

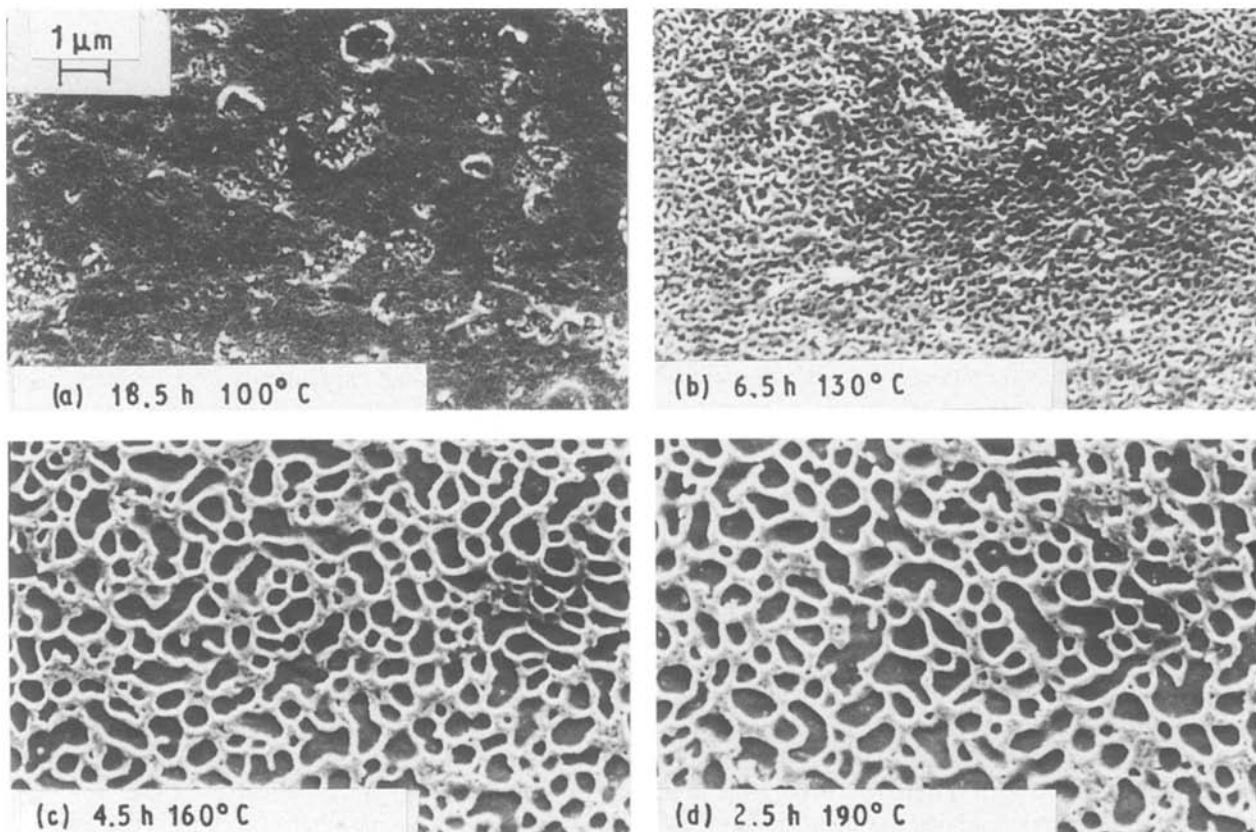


Figure 2 Morphology of the pure matrix (polished and etched subsequently) as influenced by the different cure temperatures.

3.2 Morphology of the matrix in the composite

The morphology of the matrix in the composite was also investigated by SEM observation of some specimens which were subsequently polished and etched. Fig. 3 makes it clear that the continuous phase completely surrounds the fibres, so that the interphase in this material in the first place consists of the continuous thermoset-rich phase. The influence of fibre surface treatment on the morphology was studied for two cure cycles:

- (i) 3.5 h at 120°C and 3.5 h at 177°C, and
- (ii) 2.5 h at 190°C.

The resulting morphology for the different materials is visible in Figs 4 and 5.

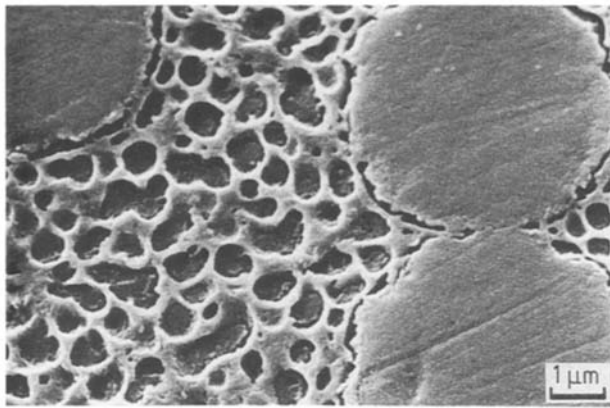


Figure 3 Morphology of the matrix in the composite (after polishing and etching, fibre STL = 50%, cure conditions: 3.5 h at 120°C and 3.5 h at 177°C).

Comparing Figs 4 and 5 with Fig. 2b (the 130°C cured pure resin) and Fig. 2d shows that the materials with 0 and 100% fibres tend towards a smaller domain size for the second phase (for the 190°C cure cycle), whereas the materials with 10 and 50% treated fibres tend towards a larger domain size for the second phase (for the 120°C/177°C cure cycle).

Transverse cracking was investigated in (0/90₄/0) laminates and unidirectional laminates produced from the different prepregs. Based on these experiments a transverse strain at interphase failure was found [4]. It has been shown (see Fig. 6) that the fibre surface treatment leads to an increase of the strain at interphase failure by a factor of five (comparing the 100% with the untreated material). The transverse fracture surfaces of the different materials were investigated by SEM. It was found that at increased level of fibre surface treatment the fracture path is gradually shifted from the fibre surface into the matrix. This is shown schematically in Fig. 7. Whereas in the material with the untreated fibres the fracture path predominantly follows the fibre surface, in the material with 10 and 50% treated fibres the fracture path partly follows the outer surface of the continuous phase surrounding the fibres. This leads to a (for these materials) typical honeycomb-like fracture surface as indicated in Fig. 8. This is caused by fracture of the cell walls radially grown from the continuous phase surrounding the fibres. The interface between this continuous phase and the second discontinuous phase in the fibre-matrix interphase is too weak. This property is improved for the material with the 100% treated fibres, so that fracture predominantly takes place in

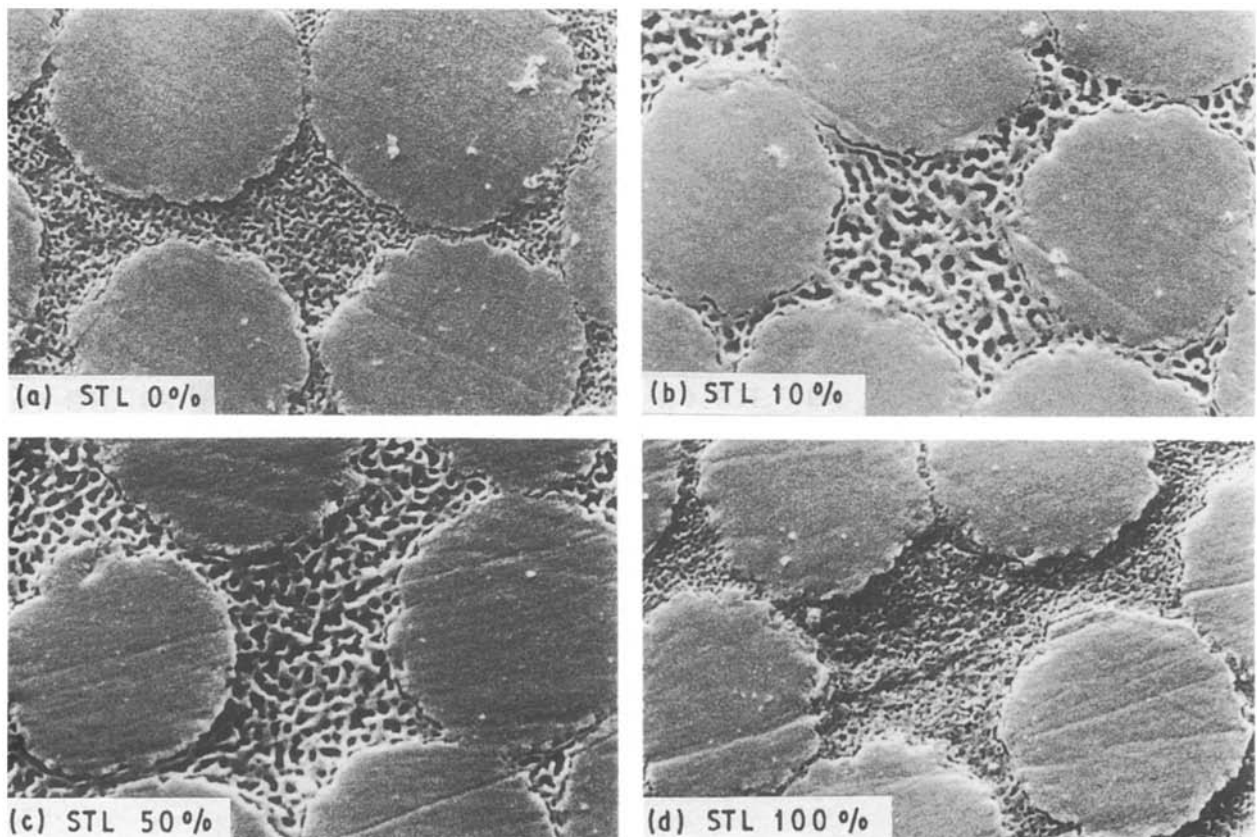


Figure 4 Morphology of the matrix as influenced by differently treated fibres in composite cured for 3.5 h at 120°C and 3.5 h at 177°C.

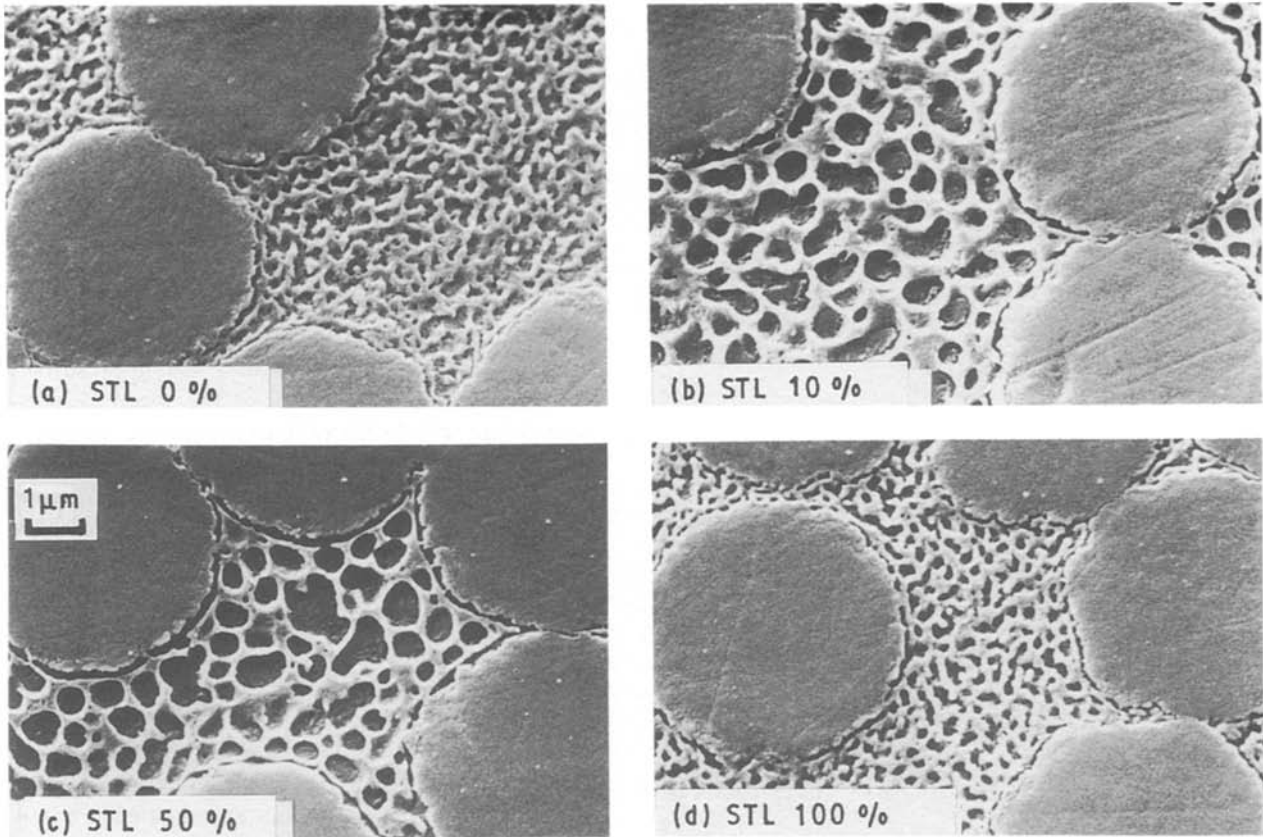


Figure 5 Morphology of the matrix as influenced by differently treated fibres in composites cured for 2.5 h at 190°C.

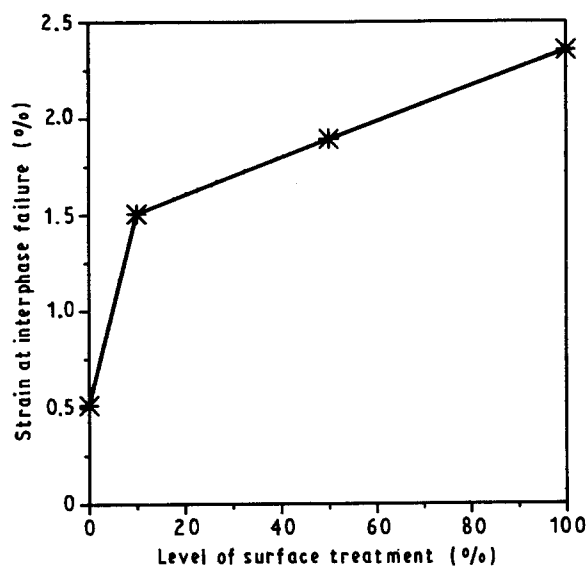


Figure 6 Strain at interphase failure as a function of the level of fibre surface treatment determined with the aid of a Weibull distribution for transverse cracking [4].

the matrix, although fracture sites at the fibre surface are also visible. (Fig. 9).

One aspect of interphase properties is the aforementioned strain at interphase failure. Another aspect of the interphase is the stiffness, which will certainly affect the strain at interphase failure. The effect of fibre surface treatment on the stiffness of the interphase can be determined with the aid of matrix-dominant composite elastic constants, as treated in the following sections.

3.3. The shear modulus G_{12}

Off-axis specimens (making an angle of 10° relative to the fibre direction) were cut from (0_8) laminates with the different treated fibres. First the engineering modulus in the longitudinal direction of the specimens was measured on five different specimens per surface treatment level. The mean modulus E_{10} was found to decrease from 88.3 GPa for specimens with untreated fibres to 68.4 GPa for specimens with 100% treated fibres. The shear modulus G_{12} is mainly responsible for the decrease in engineering modulus with increasing level of fibre surface treatment. In order to measure the actual modulus G_{12} a rosette strain gauge was glued on one or two specimens per material system. From the measured strains in three directions the shear modulus G_{12} was calculated, according to the theory presented by Chamis and Sinclair [8].

The resulting shear moduli as a function of level of fibre surface treatment are indicated in Fig. 10. The shear modulus clearly decreases at increasing level of surface treatment, reaching a value of 4.45 GPa for the material with 100% treated fibres, which is 18% less than the value of 5.41 GPa for the material with untreated fibres. The only relevant parameter which is being changed by the surface treatment is the property of the interphase. Thus the decrease in shear modulus of the composite has to be attributed to the change in modulus of the interphase.

3.4. The transverse modulus E_{22}

The transverse modulus E_{22} was measured on 16 mm wide specimens cut from (90_8) laminates with the

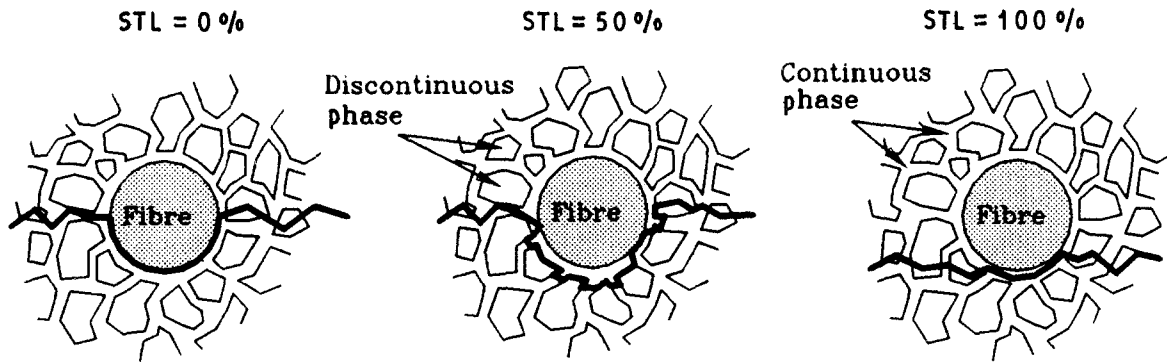


Figure 7 Schematic diagrams of crack propagation (in transverse ply) near the carbon fibre as influenced by the level of fibre surface treatment.

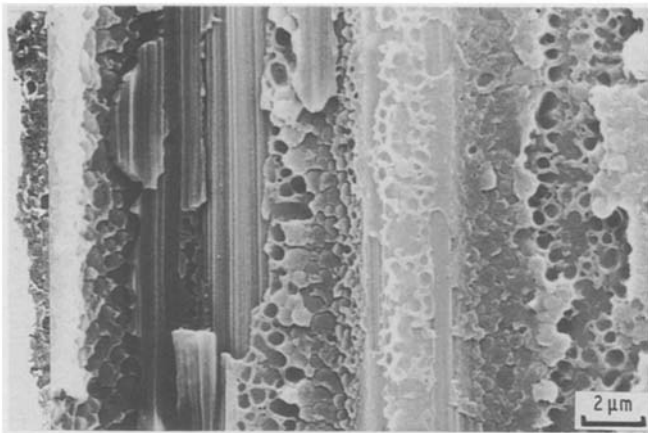


Figure 8 Transverse fracture surface of 10% treated material cured 2.5 h at 190 °C.

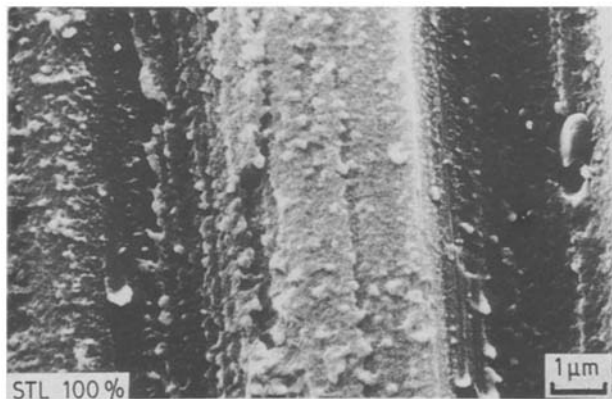


Figure 9 Transverse fracture surface of 100% treated material cured for 3.5 h at 120 °C and 3.5 h at 177 °C.

different treated fibres. The influence of two different cure cycles was investigated:

- (i) 3.5 h at 120 °C and 3.5 h at 177 °C, and
- (ii) 2.5 h at 190 °C.

The results for nine specimens per material are indicated in Fig. 11. The materials cured at 120 and 177 °C show a continuous decrease of the transverse modulus at increasing level of surface treatment. The decrease of the modulus, however, is small, only about 5%. The material cured at 190 °C only shows a modulus decrease from STL 50% to STL 100%, whereas the

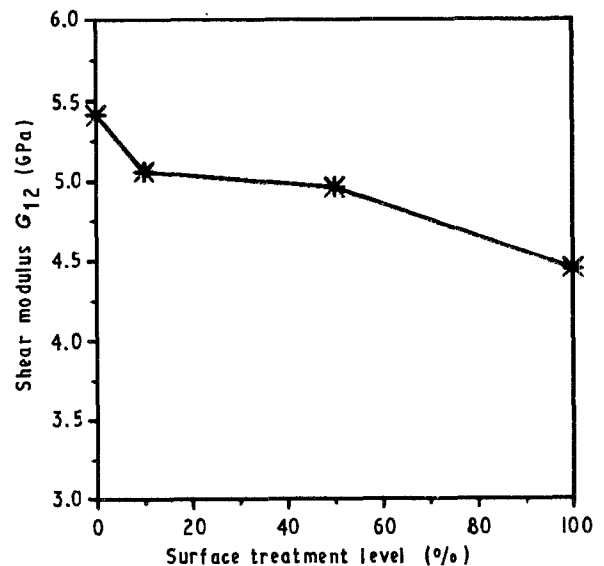


Figure 10 Shear modulus G_{12} as a function of the level of fibre surface treatment.

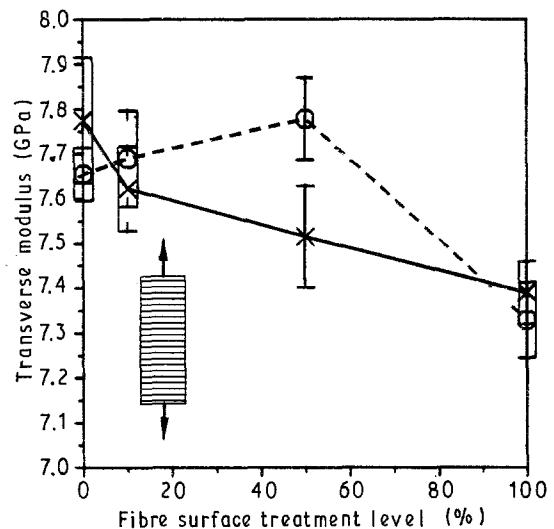


Figure 11 Transverse modulus E_{22} as a function of level of fibre surface treatment for material cured (x) 3.5 h at 120 °C and 3.5 h at 177 °C, (o) 2.5 h at 190 °C.

modulus increases from STL 0% to STL 50%. The thermal strain in this material (cured at 190 °C) is larger than in the material cured at 120 and 177 °C. At this stage of investigation, however, it is uncertain

whether there is a loss of transverse stiffness in the 0 and 10% treated material (cured at 190 °C) because of thermally induced microdamage.

3.5. Moisture uptake

Specimens cut from the laminate (0/90₄/0) with dimensions 200 mm × 16 mm × 0.95 mm were immersed in distilled water at 70 °C up to the saturation level of moisture uptake. Water uptake was investigated as a function of cure temperature for the cure cycles 6.5 h at 130 °C, 3.5 h at 120 °C followed by 3.5 h at 177 °C and 4.5 h at 160 °C. The results are indicated in Fig. 12. Results for the material with untreated fibres are not available. These specimens contained thermally induced cracks making them useless for water uptake experiments. From Fig. 12 two general phenomena can be seen. First moisture uptake is larger for the material cured at higher cure temperatures and further moisture uptake generally increases at increasing level of surface treatment. The pure resin (cured according to the standard cure cycle) takes up 4.7% moisture. An interesting aspect of comparing the composite material with the pure resin is the fact that the composite always takes up less moisture than the pure resin (weight increase measured relative to the polymer weight).

4. Discussion

At first glance (see Figs 4 and 5) the morphology of the matrix seems to be influenced by the level of surface treatment. Attempts were undertaken to reproduce the morphology found, but now making use of the hot melt resin and loose bundles of the differently treated fibres (sized and unsized). The bundles of fibres were attached in a mould and the fibres allowed to be impregnated by the hot melt resin at the temperature of 120 °C (applying the advised cure cycle of 3.5 h at 120 °C and 3.5 h at 177 °C). Inside the 10 and 50%

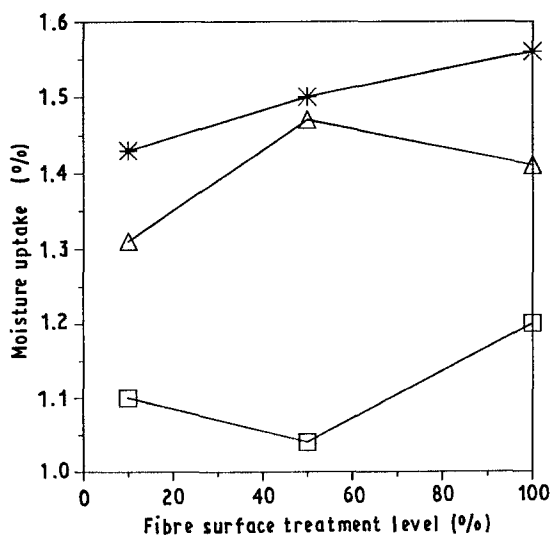


Figure 12 Moisture uptake at saturation (by immersion in distilled water at 70 °C) as a function of level of fibre surface treatment for differently cured materials: (□) 130 °C, (△) 3.5 h at 120 °C + 3.5 h at 177 °C, (*) 160 °C.

treated fibre bundles the morphology of the matrix was not significantly different from that of the 0 and 100% treated fibre bundles. For this reason it cannot be concluded that the fibre surface treatment influences the morphology of the matrix. The opposite, a firm denial of an influence of fibre surface treatment, can however also not be concluded because the processing conditions for prepregging are certainly different (e.g. in processing temperature) from those of the small-scale laboratory experiment performed.

Another reason for the difference in morphology of the resin could be small variations in the constituents of the matrix system in the different prepreg batches.

In the present case dealing with a phase-separating matrix system the interphase consists of two phases, the strengths of which depend on the level of fibre surface treatment. The strength of the interphase as a function of the distance to the fibre, representative of the 10 and 50% treated materials, is shown schematically in Fig. 13. The lowest strength occurs in the interface between the continuous (first) phase and the second phase, as can be deduced from the SEM pictures of transverse fracture surfaces. For the untreated fibres the lowest strength occurs in the interface between the fibre and the first (continuous phase), whereas for the 100% treated fibres the strength of the interphase reaches or exceeds the strength of the bulk matrix.

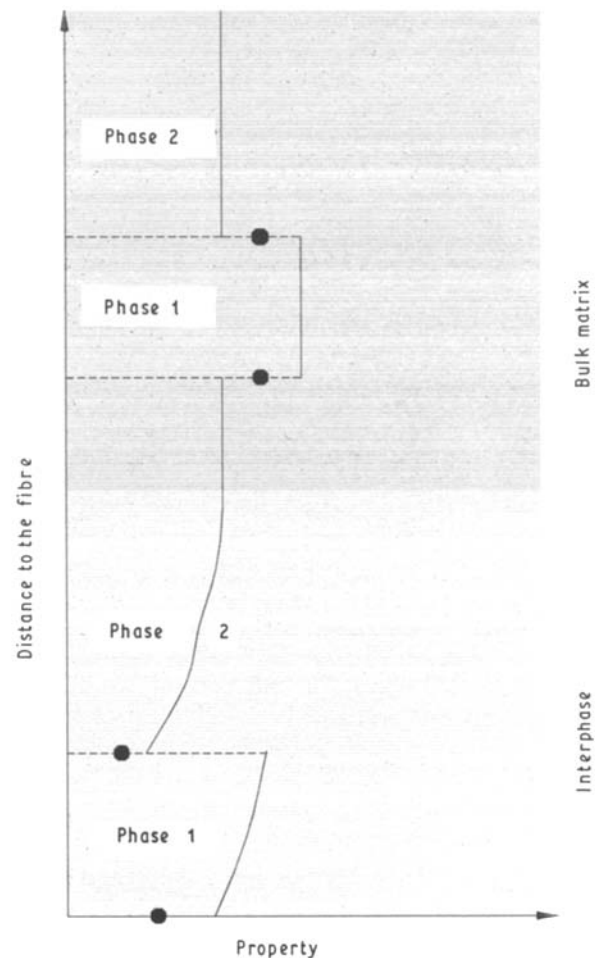


Figure 13 Schematic diagram of the strength of the interphase as a function of the distance (Y axis) to the fibre (representative for the behaviour of the 10 and 50% treated materials).

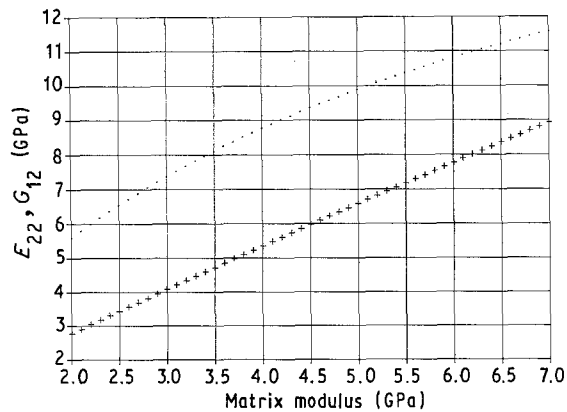


Figure 14 (●) transverse modulus E_{22} and (+) shear modulus G_{12} as a function of the matrix modulus (calculated according to Chamis [13]).

The present results not only give information about the strength of the interphase but also about the stiffness. From the decreasing shear modulus G_{12} (Fig. 10) and transverse stiffness E_{22} (Fig. 11) it can be concluded that the stiffness of the interphase decreases at increasing level of surface treatment. The reason for this decrease can be found with the aid of the relation between the degree of epoxy conversion and the properties of the polymer, to mention especially the modulus, the fracture strain and the specific weight. For HDPE at increasing mean molecular mass [9] and for several epoxy systems at increasing epoxy conversion [10] the modulus was found to decrease moderately, whereas the fracture strain or the flexural strength initially increases strongly. Also the specific weight decreases by the introduction of a larger free volume into the material. Moisture migrates into this free volume so that moisture uptake is generally larger if the mean molecular mass is larger. The pure resin (Fig. 1) shows the typical effects of increased epoxy conversion mass (at higher cure temperatures) on modulus and fracture strain. Further, the increased moisture uptake for the material cured at higher temperatures is also an indication of increased cross-linking. If we now consider the decrease of the modulus of the interphase and the increase in water uptake found at increased level of surface treatment, it can be concluded that the epoxy conversion of the interphase increases at increased level of surface treatment. The increased activity of the fibre surface, as described by our programme partners [11], thus interacts with the polymerization in the interfacial region.

Although generally the matrix (interphase)-dominated moduli decrease at increasing level of surface treatment there are a few exceptions. Unclear at this stage is why the transverse moduli measured on the 0 and 10% treated material cured at 190°C are lower than expected. Possibly they are reduced by thermally and through-cutting induced micro-damage. Specimen dimensions and the carefulness of the cutting procedure certainly play a role in this.

An interesting result of the present investigation is that the shear modulus G_{12} is obviously more influ-

enced by the interphase than the transverse modulus E_{22} . The reason for this is being studied with available models which describe the moduli G_{12} and E_{22} as a function of the modulus of the resin. Further, a parametric study is being performed by FEM techniques in which the modulus of the interphase is varied systematically [12]. Making use of the theory of Chamis [13], the shear modulus and transverse modulus vary with the matrix modulus as indicated in Fig. 14. The absolute variation of both moduli in the indicated range of matrix moduli is similar, but because of the lower values of G_{12} the relative degree of variation is larger for G_{12} (about twice as high). Experimentally the relative decrease for the shear modulus is found to be about four times the decrease measured for the transverse stiffness. Thus, the shear modulus G_{12} seems to be more influenced by fibre surface treatment than the transverse modulus, indicating that the interphase can have anisotropic properties. Madhukar *et al* [14] also found a strong decrease of the shear modulus (G_{12} measured with the aid of ± 45 -specimens) but no significant decrease for the transverse modulus E_{22} for CFRP with treated fibres in comparison with CFRP with untreated fibres. The authors, however, propose a different explanation for this effect.

5. Conclusions

Experiments have shown that matrix (interphase)-dominated properties (shear modulus G_{12} , transverse stiffness E_{22} , water uptake) are influenced by the surface treatment of the fibre. Materials with fibres treated at a higher level generally show a smaller shear modulus (up to $\approx 20\%$), a smaller transverse stiffness ($\approx 5\%$) and larger water uptake. The larger water uptake indicates that there is a larger free volume as a result of a more fully crosslinked polymer in the interphase. This more crosslinked structure leads to a reduced modulus of the interphase. The larger reduction of the shear modulus in comparison with the transverse modulus could indicate that the interphase is anisotropic.

Acknowledgements

The authors thank the European Commission for financial support and their partners in the EURAM-programme (Courtaulds Research, ICI Advanced Materials, Katholieke Universiteit Leuven, University of Lisbon, University of Surrey) for their participation in fruitful discussions.

References

1. J. G. WILLIAMS, M. E. DONNELAN, M. R. JAMES and W. J. MORRIS, *Mater. Sci. Engng. A* **126** (1990) 305.
2. K. JAYARAMAN and K. L. REIFSNIDER, *J. Compos. Mater.* **26** (1992) 770.
3. J. JAYARAMAN, Z. GAO and K. L. REIFSNIDER, in Proceedings of 6th Technical Conference of American Society for Composites (1991) pp. 759-768.
4. P. W. M. PETERS, *J. Compos. Mater.* to be published.
5. D. J. BLUNDELL, R. A. CRICK, B. FIFE, J. PEACOCK, A. KELLER and A. WADDON, *J. Mater. Sci.* **24** (1989) 2057.

6. Annual Book of ASTM standards, Part 35, ASTM Standard D 790-81 (1991).
7. P. W. M. PETERS and G. S. SPRINGER, *J. Compos. Mater.*, **21**, (1987) 157.
8. C. C. CHAMIS and J. H. SINCLAIR, *Exper. Mech.* **17** (1977) 339.
9. A. F. MARGOLIS, *SPE J.* **27**, (June 1971).
10. A. NOORDAM, J. J. M. H. WINTRAECKEN and G. WALTON, in Proc. 9th. Disc. Conf. Prague, July 14-17, 1986, 373-389.
11. V. da sa COSTA, R. ROBINSON, M. DESAEGER and B. CHARALAMBIDES, To be published.
12. H. ALBERTSEN and P. W. M. PETERS, to be published.
13. C. C. CHAMIS, *J. Comp. Techn. Res.*, **11** (1989) 3.
14. M. S. MADHUKAR and L. T. DRZAL, *J. Compos. Mater.*, **25** (1991) 932.

*Received 2 January
and accepted 30 June 1992*