DEFORMATION MICROMECHANICS OF GLASS FIBRE BASED AND HYBRID CELLULOSE-GLASS FIBRE COMPOSITES

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ABSTRACT

. In order to map the local deformation state of a glass fibre, it is necessary to dope the sample using lanthanide ions such as Sm^{3+} and follow shifts in luminescent peaks. This technique is presented and it is shown that one can follow fragmentation and derive interfacial shear stress values for epoxy matrix/E-glass model composites. Natural fibres offer a potential for replacing traditional materials such as glass in polymeric based composites. However, the mechanical properties of natural fibres vary considerably within a batch of material provided for this purpose. Therefore many people have invested time into hybrid composites, where the weight and monetary savings can be made by using some natural fibres to replace the glass component, whilst not compromising on mechanical properties. This talk discusses the use of a regenerated cellulose fibre (Bocell^{TM}), which does not vary in mechanical properties as much as a natural analogue, in a hybrid glass fibre model composite

1. INTRODUCTION

Glass fibre composites are a ubiquitous material and have been extensively studied. In order to characterise the interface between fibres and resin materials in polymeric-based composites a number of micromechanical tests have been developed; including pull-out [1, 2] and fragmentation. Both pull-out testing and fragmentation have been applied to the study of glass fibre composites, with mixed results. Theoretical approaches for understanding the interface between a fibre and a matrix material are well-established [2, 3]. It is known that in a fibre composite the stress transfers from the matrix to the fibre, manifested in a variation in the shear stress at the fibre ends. Axial stress is known to reach a maximum in the centre of the reinforcing fibre. The point-to-point variation in the fibre stress has been difficult to determine for glass fibre composites in order to verify this. With the advent of Raman spectroscopic and fluorescence techniques this has become possible for other types of reinforcement, wherein a large shift in a characteristic well-defined band has been shown to enable the determination of the local strain in a fibre [4-6]. Using these methods a large number of analyses of the stress transfer between fibres and matrices have been undertaken [7]. Theoretical analysis of the stress transfer at the interface between glass fibres and polymeric resins has also been undertaken [8, 9]. Since glass fibres have relatively broad and weak Raman bands it has not been possible to apply this particular technique to this material. Alumina fluorescence methods of stress determination [5, 6] rely on the presence of a chromium impurity (Cr^{3+}), which is not present in glass formulations. Attempts have been made to follow local stress transfer at a glass fibre interface using half-fringe photoelasticity [10] or by coating the fibre with a strain sensitive material such as a polydiacetylene-urethane copolymer [11]. In addition to these techniques it has also been possible to use carbon nanotubes dispersed in the resin to follow stresses around glass fibres [12].

In recent studies, samarium fluoride (SmF_3) has been used to enable the local stress state in glass to be followed using either electro or photoluminescence[13]. A similar study has also been reported where Er^{3+} doped material was used to measure residual stresses in optical fibres [14]. Our group have also recently reported that it is possible to determine the local stress state of a doped glass fibre embedded in an epoxy matrix [15]. In this study we report data showing the stress-transfer of a single doped E-glass fibre embedded in a model composite. We also show data for a hybrid model composite where a glass fibre is placed next to a regenerated cellulose fibre (Bocell™). Hybrid composites are of industrial interest as it may be possible to replace some glass fibres with plant based cellulose fibres. However, little is known about the interaction of these two types of fibre.

2. EXPERIMENTS

2.1. Materials and sample preparation

A typical E-glass formulation was used in order to generate these fibres; namely 54.9% SiO_2, 17.9% CaO, 12.9% Al_2O_3, 9.9% B_2O_3, 2.9% MgO, 0.5% Na_2O, Sm_2O_3, and 0.3% SO_3. A previous report of these types of fibres used SmF_3 in order to generate Sm^{3+} ions [15]. In this study we used Sm_2O_3 instead. This formulation was then heated in a platinum crucible using a standard furnace to 1300 °C. Glass rods were then extruded from this melt. Losses of these initial components occurred in the final composition. Nevertheless the Sm^{3+} ions were of a sufficient concentration for the detection of luminescence. Thinner fibres were then drawn by stretching the glass rods whilst holding them in a gas flame. This produced small filaments with an average diameter[†] of 56±4 μm. These filaments are larger than typical glass fibres, which typically have diameters of about 10 μm (for E-glass) [16]. Single filaments were then glued at each end to testing cards using a two-part cold-curing epoxy resin.

Short fibres were also embedded in an epoxy resin dumbbell composite specimen, according to a method described previously [15]. A number of the fibres were also treated using a silane coupling agent ((3-Aminopropyl) triethoxysilane or APS). Filaments were placed into a 2% aqueous solution of APS for 10 minutes and then dried in a furnace at 120°C for 3 hours. In order to form the composite materials, an epoxy resin matrix, cured at room temperature, was used; namely Araldite® LY/HY 5052 (Ciba-Geigy 5052). This resin comes in two parts; a butan-1,4,-diol diglycidyl ether resin (LY5052) and a isophorone diamine hardener (HY5052) which are mixed in the ratio 50:19. A small strain gauge was fitted to the cured dumbbell specimens to record the local strain value of the specimen in proximity to the fibre. In order to investigate hybrid composites, a single Bocell™ regenerated cellulose fibre was placed at a small distance from a glass fibre within a model dumbbell composite. The local deformation of the Bocell fibre was mapped using Raman spectroscopy. This technique has been used before for this type of fibre [17].

2.2. Mechanical Properties of Fibres

Single fibre samples (about 40) were deformed in tension (gauge length – 50 mm, cross-head speed of 0.5 mm/min) using an Instron (model 1122) tensile testing machine to determine their mechanical properties. Prior to each test the sides of the cards, onto which fibres were secured, were burnt away using an artists pyrography machine.

[†] Value determined using Scanning Electron Microscopy

2.3. Luminescence Spectroscopy Methods

The technique relies on the detection of photon excited luminescence from a material. A laser was used to excite the luminescence, and the detector of a Raman spectrometer was used to capture the spectra. It is worth pointing out that this *is not Raman spectroscopy*, and the luminescence effect is quite different from this technique.

A Renishaw system 1000 spectrometer was used to record luminescence spectra excited using a 514 nm Ar^+ laser. A ×50 lens and an Olympus microscope system was used to focus the laser to a spot size of about 2 μm. All spectra were recorded using an exposure time of 10 s and then fitted using a mixed Gaussian/Lorentzian function to find the peak position.

For the calibration of the fibre strain in a dumbbell composite, single filaments were first deformed in tension. Each sample was deformed in tension using increments of 0.1 %. At each deformation step a luminescence spectrum was taken using an exposure time of 10 s.

The dumbbell specimens were deformed mechanically in tension using a Miniature Materials straining rig (MINIMAT^{TM}, Polymer Laboratories Ltd., UK) which was placed onto the microscope stage of the Raman spectrometer. The surface strain of the composite was determined by using a strain gauge attached to the matrix, adjacent to the fibre. Luminescence spectra were recorded along the fibre within the composite at a range of matrix strains up to the specimen failure (~ 1 %) using an exposure time of 10 s.

3. EXPERIMENTAL RESULTS

3.1. Mechanical Properties of Fibres

The mean Young's modulus, stress at failure and strain at failure values obtained for the fibres were found to be 73.62 ± 3.81 GPa, 0.92 ± 0.13 GPa and 1.26 ± 0.16 % respectively. These values are typical for E-glass fibres [16].

3.2. Single Fibre Calibration

The calibration of the luminescent band located at ~ 647nm with respect to glass fibre filament strain is shown in Figure 1. It is clear that there is a good correlation between these two parameters, and as such the position of this band can be used to act as a calibrant of local fibre strain for the model composites.

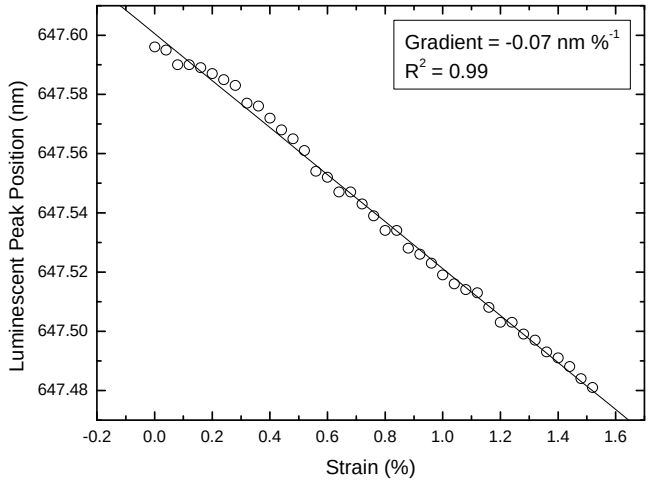
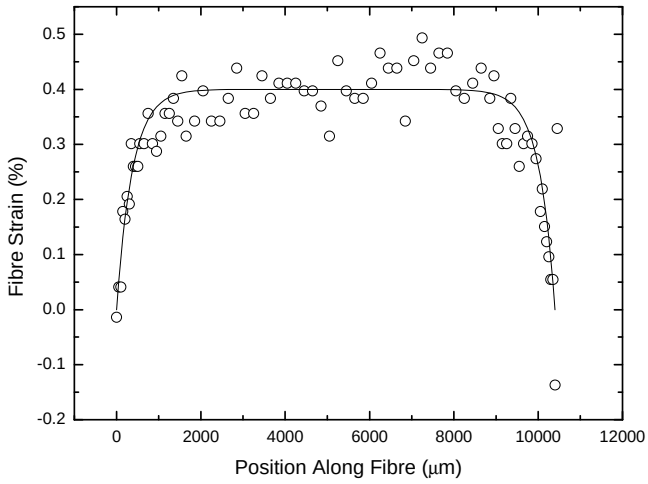


Figure 1: Calibration of the position of the 647 nm luminescence band with respect to glass fibre filament strain.

3.3. Stress-Transfer in Model Composites

The data obtained for point-to-point fibre strain, as obtained by the calibration procedure described in section 3.2 and the mapping of model composites in section 2.1, are shown in Figure 2 (for a sized E-glass fibre). These data are for two levels of strain applied to the same model composite. These data show quite clearly how the strain in the fibres increases over the fibre ends, indicative of the stress transfer process, to the same level as the matrix strain in the centres of each fibre. The form of these data is analogous to a large number of other studies of polymeric fibre based composites, such as Kevlar [18]. At lower strains (Fig. 2a – 0.4 %) the glass fibre remains in one-piece but later fragments into two sections at elevated levels of matrix strain (Fig. 2b – 1.4 %). Each of these fragments then acts as a reinforcing phase within the composite.

(a)



(b)

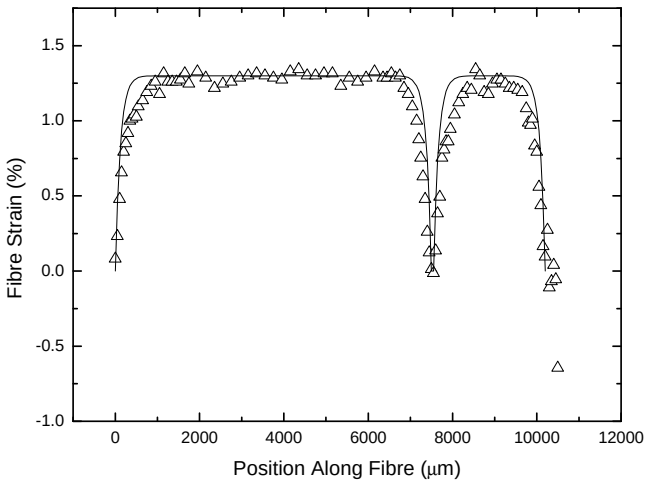


Figure 2: Fibre strain as a function of distance along a short silane treated glass fibre at (a) 0.4 % and (b) 1.4 % matrix strain. Solid lines are a fit of equation 1 to the data.

By fitting the following equation

$$\varepsilon_{\mathrm{f}} = \varepsilon_{m}\left(1-\cosh\left(nx/r\right)/\cosh\left(ns\right)\right) \quad (1)$$

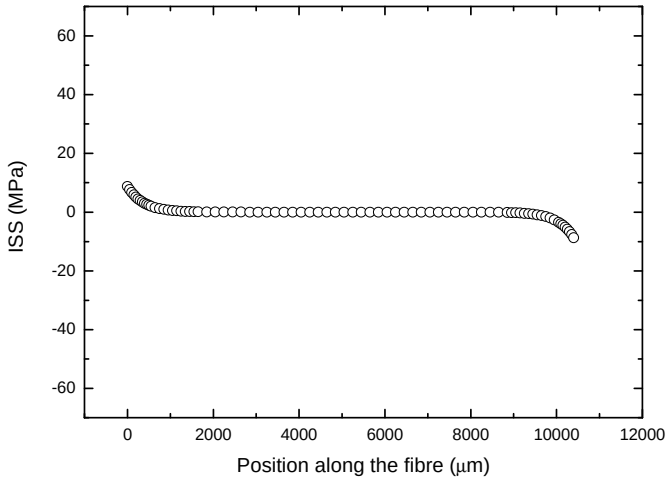
where ε_{f} is the fibre strain, ε_{m} is the matrix strain, x is the distance along the fibre or fragment, s is defined as the length of the fibre divided by its radius r and n is a fitting parameter, to these data (solid lines in Figure 2) it is possible to derive the interfacial shear stress (ISS) between the glass fibre and epoxy matrix. These ISS (τ) data are found from the equation

$$\frac{\mathrm{d}\varepsilon_{\mathrm{f}}}{\mathrm{d}x} = -\frac{2\tau}{E_{\mathrm{f}}r} \quad (2)$$

where E_{f} is the fibre modulus obtained from Section 3.1, and are reported in Figure 3.

As can be seen the ISS is at a maximum value at the fibre ends, reducing to zero in the centre of the fibre. This is further indication that the stress transfers, *via* shear, across the fibre ends, and is in agreement with other polymer fibre model composite data [18]. At low matrix strain (0.4 %) the maximum ISS value is low (~ 10 MPa). However, when the matrix strain is increased, by deforming the sample in tension, the ISS increases to a maximum value of > 60 MPa. This value is much higher than the shear yield stress of the resin (40-50 GPa) [19], which clearly cannot be the case. These interfacial shear stresses are close to theoretical values reported by Feilard and co-workers [20]. Shioya and Takaku [21] have also reported large ISS values (~ 80 MPa) for glass fibre-epoxy model composites. It may be that these high ISS values are associated with cracks in the fibres, and not debonding of the filaments. This is borne out to some extent by the fact that the fragments (Figure 2b) are fully bonded to the matrix. In order to see the effect of a fragmentation of the fibre and cracking of the glass fibre and matrix on a cellulose fibre, hybrid composites were also investigated.

(a)



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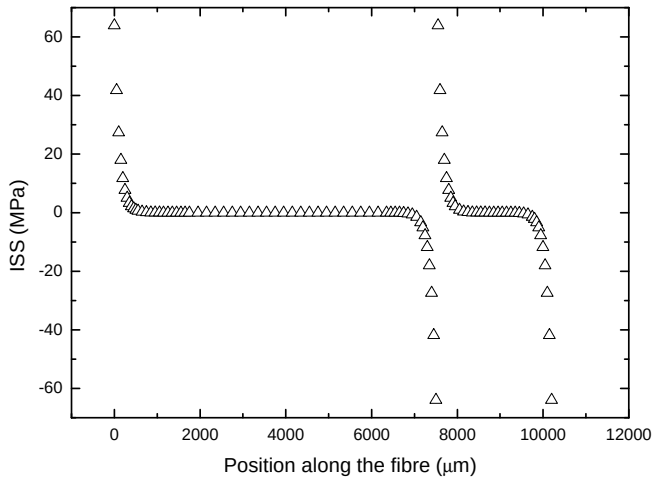

Figure 3: The interfacial shear stress (ISS) as a function of distance along a short silane treated glass fibre filament embedded in a model epoxy dumbbell specimen at (a) 0.4 % and (b) 1.4 % strain.

3.4. Hybrid Model Composites and the Influence of Cracks

A transmitted light image of a glass fibre proximal to a Bocell^{TM} fibre is shown in Figure 4. The image also shows the presence of a 'penny-shaped' crack that has formed in the glass fibre, which has also propagated into the matrix and subsequently the regenerated cellulose fibre

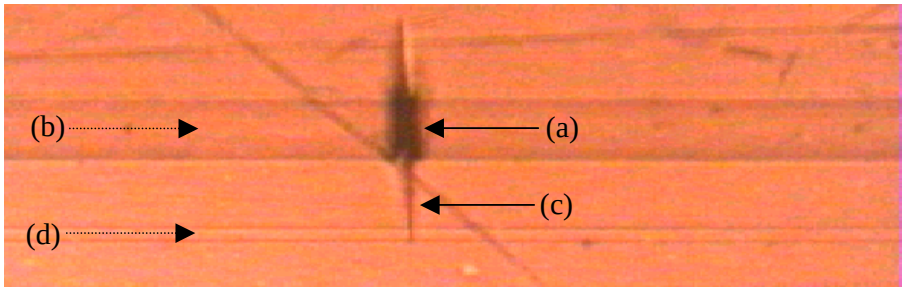

Figure 4: A light microscope image of a 'penny-shaped' crack (a) in a glass fibre (b) propagating (c) into a Bocell^{TM} regenerated cellulose fibre.

The local strain state around this crack within the glass fibre and the subsequent profile around the Bocell fibre are shown in Figure 5a. First of all it is noted that at the ends of the fibre it appears that the glass fibre is under compression (Figure 5a). At elevated matrix strains this compression is reduced. More importantly it is noted that the crack extends beyond the glass fibre (see Figure 4) into the matrix material and subsequently influences the regenerated cellulose fibre. The strain field around this regenerated cellulose fibre can be seen in Figure 5b, where the calibration of the Raman band with strain for this fibre type was taken from previously published data [17]. The break is thought to only occur at elevated strains, when the strain clearly exceeds that of the breaking strain for this particular fibre [17].

4. CONCLUSIONS

It is clear that luminescence spectroscopy is a powerful technique for elucidating the strain profiles around glass fibres embedded in model composites. Raman spectroscopy is not able to obtain such data. From these local strain data, the interfacial shear stress around a fragmenting E-glass fibre in a model composite has shown that a good interface is obtained between fibre and epoxy resin. Furthermore, it has been shown that a crack that develops in a glass fibre, and subsequently the matrix material surrounding it, and propagates into a regenerated cellulose fibre. The combined techniques of luminescence and Raman spectroscopy can then be used to map local strain distribution around these phenomena. This offers a powerful technique for following the local micromechanics of hybrid composite materials.

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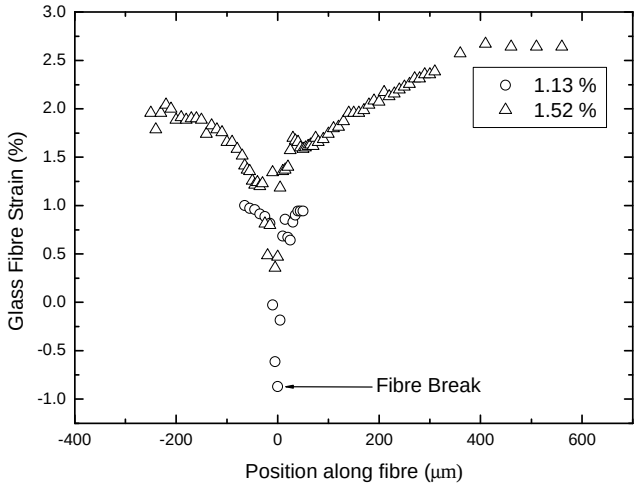
(a)



(b)

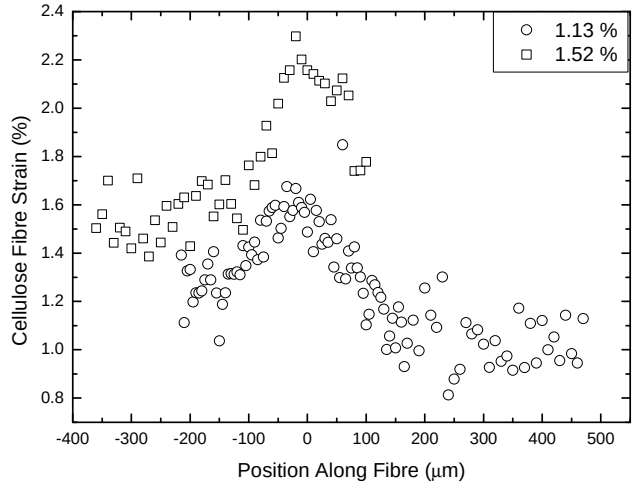


Figure 5: Strain distributions around cracks and breaks in (a) a glass fibre and (b) a Bocell regenerated cellulose fibre in a model composite as a function of the position along the fibre at two different matrix strain levels.

REFERENCES

[1] B. Miller, P. Muri, L. Rebenfeld, A microbond method for determination of the shear-strength of a fiber resin interface, Composites Science and Technology 28 (1987) 17-32.

[2] A. Kelly, W.R. Tyson, Tensile properties of fibre-reinforced metals - Copper/Tungsten and Copper/Molybdenum, Journal of the Mechanics and Physics of Solids 13 (1965) 329-&.

[3] H.L. Cox, The elasticity and strength of paper and other fibrous materials, British Journal of Applied Physics 3 (1952) 72-79.

[4] C. Galiotis, R.J. Young, P.H.J. Yeung, D.N. Batchelder, The Study Of Model Polydiacetylene Epoxy Composites .1. The Axial Strain In The Fiber, Journal Of Materials Science 19 (1984) 3640-3648.

[5] J. He, D.R. Clarke, Determination of the piezospectroscopic coefficients for chromium-doped sapphire, Journal Of The American Ceramic Society 78 (1995) 1347-1353.
[6] R. Sinclair, R.J. Young, R.D.S. Martin, Determination of the axial and radial fibre stress distributions for the Broutman test, Composites Science And Technology 64 (2004) 181-189.
[7] R.J. Young, Evaluation of composite interfaces using Raman spectroscopy, Interfacial Effects in Particulate, Fibrous and Layered Composite Materials, 1996, pp. 173-192.
[8] P.S. Chua, M.R. Piggott, The glass-fiber polymer interface .1. theoretical consideration for single fiber pull-out tests, Composites Science and Technology 22 (1985) 33-42.
[9] P.S. Chua, M.R. Piggott, The glass-fiber polymer interface .2. work of fracture and shear stresses, Composites Science and Technology 22 (1985) 107-119.
[10] F.M. Zhao, S.A. Hayes, E.A. Patteson, F.R. Jones, Phase-stepping photoelasticity for the measurement of interfacial shear stress in single fibre composites, Composites Part a-Applied Science and Manufacturing 37 (2006) 216-221.
[11] R.J. Young, C. Thongpin, J.L. Stanford, P.A. Lovell, Fragmentation analysis of glass fibres in model composites through the use of Raman spectroscopy, Composites Part A-Applied Science And Manufacturing 32 (2001) 253-269.
[12] Q. Zhao, M.D. Frogley, H.D. Wagner, The use of carbon nanotubes to sense matrix stresses around a single glass fiber, Composites Science and Technology 61 (2001) 2139-2143.
[13] G. Pezzotti, Probing nanoscopic stresses in glass using luminescent atoms, Microscopy and Analysis 13 (2003).
[14] A. Leto, G. Pezzotti, Probing nanoscale stress fields in Er3+-doped optical fibres using their native luminescence, Journal of Physics-Condensed Matter 16 (2004) 4907-4920.
[15] M. Hejda, K. Kong, R.J. Young, S.J. Eichhorn, Deformation micromechanics of model glass fibre composites, Composites Science and Technology 68 (2008) 848-853.
[16] B. Harris, Engineering composite materials, IOM Communications Ltd., London, 1999.
[17] B. Mottershead, S.J. Eichhorn, Deformation micromechanics of model regenerated cellulose fibre-epoxy/polyester composites, Composites Science and Technology 67 (2007) 2150-2159.
[18] M.C. Andrews, R.J. Young, Fragmentation Of Aramid Fibers In Single-Fiber Model Composites, Journal Of Materials Science 30 (1995) 5607-5616.
[19] M.C. Andrews, Stress transfer in aramid/epoxy model composites, Manchester Materials Science Centre, UMIST, 1994.
[20] P. Feillard, G. Desarmot, J.P. Favre, A critical-assessment of the fragmentation test for glass epoxy systems, Composites Science and Technology 49 (1993) 109-119.
[21] M. Shioya, A. Takaku, Estimation of fiber and interfacial shear-strength by using a single-fiber composite, Composites Science and Technology 55 (1995) 33-39.