Mechanical and Morphological Properties of Carbon Fiber Reinforced–Modified Epoxy Composites

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ABSTRACT: Epoxy, prepared through aminomethyl 3,5,5-trimethylcyclohexylamine hardening of diglycidylether of bisphenol-A (DGEBA) prepolymer, toughened with polycarbonate (PC) in different proportions, and reinforced with carbon fiber, was investigated by differential scanning calorimetry, tensile and interlaminar shear strength testing, and scanning electron microscopy (SEM). A single glass transition temperature was found in all compositions of the epoxy/PC blend system. The tensile properties of the blend were found to be better than that of the pure epoxy matrix. They increased with PC content up to 10%, beyond which they decreased. The influence of carbon fiber orientation on the mechanical properties of the composites was studied, where the fiber content was kept constant at 68 wt %. Composites with 45° fiber orientation were found to have very weak mechanical properties, and the mechanical properties of the blend matrix composites were found to be better than those of the pure epoxy matrix composites. The fracture and surface morphologies of the composite samples were characterized by SEM. Good bonding was observed between the fiber and matrix for the blend matrix composites. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3529–3536, 2006

Key words: epoxy resin; polycarbonate; carbon fiber; composite; tensile properties; differential scanning calorimetry; interlaminar shear strength; morphology

INTRODUCTION

Polymeric composites are a combination of two or more materials in different phases that should give rise to better performance than what each material has individually.[1,2] Carbon fiber/polymeric matrix composites is a class of advanced materials that have been developed for a variety of applications in areas of high technology, such as aerospace, automobile, air craft, defense industry, and sporting goods. To take advantage of the excellent mechanical properties of carbon fibers in a composite, an optimized interfacial adhesion between the fiber and matrix is necessary.

In view of the fact that stress is transferred from one fiber to another through the matrix, the interface between the matrix and fiber plays a major role in the overall mechanical performance of composite materials. The composite materials and prepreg used for primary structures should have high specific tensile strength and modulus. Toughened polymer composites have attracted much interest, because of their low production costs and good processability. As is well known, epoxy resin is one of the most widely used matrices for carbon fiber-reinforced composite materials, by virtue of its good impregnation and adhesion to carbon fiber.[3–7] One of the most promising approaches for achieving these often opposing material properties is through thermoplastic/thermoset blends. Toughening of crosslinked epoxy resin by blending with various thermoplastics has been investigated extensively. Polycarbonate (PC) has attracted special attention due to its high toughness. It has been well recognized that reactions between PC and epoxy can occur in the following situations:[1] during the preparation of the PC-epoxy mixture and[2] during the curing of the PC-epoxy blend. Transesterification between PC and epoxy has been reported when the PC-epoxy was cured by tertiary amine,[8,9] anhydride,[10–13] quaternary ammonium salt,[10,14] and aromatic amine.[10,15–19] The PC could transamidate with amine when the PC-epoxy was cured with aliphatic amine.[10,20] Chen et al.[21] studied the miscibility and fracture behavior of an epoxy resin-PC blend. They reported that the blend was miscible and had better mechanical properties. With the recent development of high-temperature, high-performance thermoplastics, examples being polyetherimide, poly(1,6-dimethyl-1–1,4-phenylene ether or oxide), and poly(ether ether ketone), the blending of thermosets with these high glass transition thermoplastics is a potentially novel way to improve their processability.[22–29]

The advantage of blending a thermoset precursor with a thermoplastic is that the softening temperature is decreased significantly. But this advantage creates additional complexity and the potential for variability during processing. First, the processing time is now controlled by the themoset precursor reactivity. As it reacts, its molecular weight increases, and the entropy of mixing decreases. The entropy term ΔS^m usually dominates in the calculation of the free energy of mixing ($\Delta G^m = \Delta H^m - T\Delta S^m$). As the molecular weight increases, an average molecular weight is reached where a homogeneous mixture is no longer favored, and the thermoplastic-reacting thermoset system separates into two phases. One phase is called the α-phase, which is rich in the thermoset. The other is called the β-phase and is rich in the thermoplastic. For most thermoplastic-epoxy resin ratios with 25% or more by weight thermoplastic, the new phase-separated system is a continuous β-phase with occluded α-phase spheres. At this point, as a result of both phase separation and advancement of the epoxy–amine reaction, the viscosity increases rapidly. It has been shown that the viscosity at the cloud point, and the conditions of phase separation, can have a strong effect on the final morphology and mechanical properties.[29]

The objective of the present work is to investigate the mechanical performance of epoxy blended with PC, and their composites with carbon fiber at different orientations. The study focuses mainly on the mechanical properties of the blend composites, and on the surface and facture morphology of the composites. For this work, a DGEBA-type of epoxy resin and a bisphenol-A type of PC was used as the matrix material, and a polyacrylonitrile-based carbon fiber was used as the reinforcement. The article focuses on the effect of fiber orientation on the mechanical properties of the composites.

MATERIALS AND METHODS

All materials used throughout this work were from commercial sources and were used as received. The low molecular weight liquid DGEBA (LR-20), with a molecular weight of 384, epoxide equivalent weight of 186–192, viscosity 800–1100 mPa s, density 1.13 g cm^{-3}, flash point 130°C, and glass transition temperature of cured epoxy resin 70°C, was supplied by Laboratory Consumables and Chemical Supplies, Durban, South Africa. The aminomethyl 3,5,5-trimethylcyclohexylamine used as a hardener (LH 281), with a molecular weight of 170, viscosity 650 mPa s, density 1.01 g cm^{-3}, flash point 105°C, was also supplied by Laboratory Consumables and Chemical Supplies. The PC (L-12225Y), supplied by Plastamid (Elsies River, South Africa), has a molecular weight of 23,000, tensile strength of 62 MPa, flexural modulus of 2350 MPa,

density of 1.2 g cm^{-3}, and melt flow rate of 11 g/10 min (300°C, 1.2 kg). A carbon fiber with a nominal value of 195 g m^{-2}, supplied by Laboratory Consumables and Chemical Supplies was used as the reinforcement.

Preparation of the blend matrix and composites

To make the blend, the epoxy resin was added to PC dissolved in dichloromethane. The solvent was removed by degassing under vacuum for about 1 h. To this the hardener was added in a stoichiometric ratio. Thoroughly mixed mixtures with varying PC contents were used as the matrix. The blend mixture was poured into a glass mold (20 × 20 cm^2), kept in a vacuum oven at 120°C for 3 h to remove the solvent, and bubbled from the blend matrix. For the preparation of the composites, the carbon fabric was cut into squares measuring 20 × 20 cm^2. Each laminate sample was composed of six layers of fabric. Angle ply specimens were fabricated using unidirectional fabrics. These were laid-up as 15°, 30°, 45°, 60°, and 75°. The unidirectional fabrics were also used to construct laminates with a cross ply of 0 and 90° configuration. The epoxy/PC (90/10 w/w) blend matrix was coated onto the carbon fabrics using a brush. Composites of thickness 2 mm were prepared by compression molding at 120°C at a pressure of 100 bar for 3 h.

Differential scanning calorimetry

The glass transition temperatures of the epoxy/PC systems were determined with differential scanning calorimetry (DSC) using a Perkin–Elmer DSC-7 thermal analyzer in a flowing nitrogen atmosphere, at a heating rate of 5°C min^{-1}.

Solvent extraction

The soluble portion of the reacted samples was extracted with methylene chloride, and the percentage of curing was calculated.

% curing = (mass before extraction − mass after extraction)/(mass before extraction) × 100

Mechanical measurements

A Hounsfield (H5KS) universal testing machine was used to investigate the tensile, flexural, and interlaminar shear strength properties of the composite. Samples, with dimensions 150 mm × 15 mm × 2 mm, were cut as per ASTM D 3039–76 for tensile testing, and 40 mm × 6 mm × 2 mm were cut as per ASTM D 2344–84 for the interlaminar shear strength. The specimens were analyzed at a crosshead speed rate of 5 mm min^{-1}. A continuous load–deflection curve was
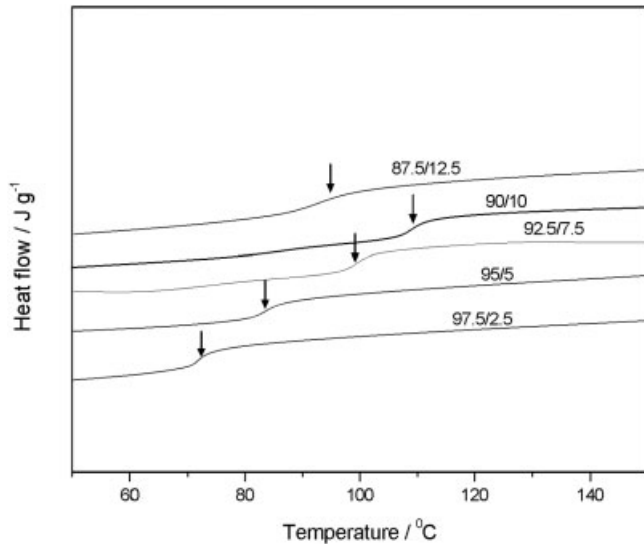
Figure 1 DSC specific heat curves showing glass transition temperatures of different epoxy/PC blends.

Figure 2 Glass transition temperatures of epoxy/PC blends as a function of PC content.

obtained. In each case, 10 samples were used and the average was taken.

Scanning electron microscopy

To study the bonding between the matrix and the reinforcement, scanning electron micrographs (SEM) of fractured samples were recorded using a Hitachi S530 electron microscope. The composite specimens were cryofractured in liquid nitrogen. The fractured surfaces were coated with gold by an electrodeposition method, to impart electrical conduction, before recording the SEM micrographs.
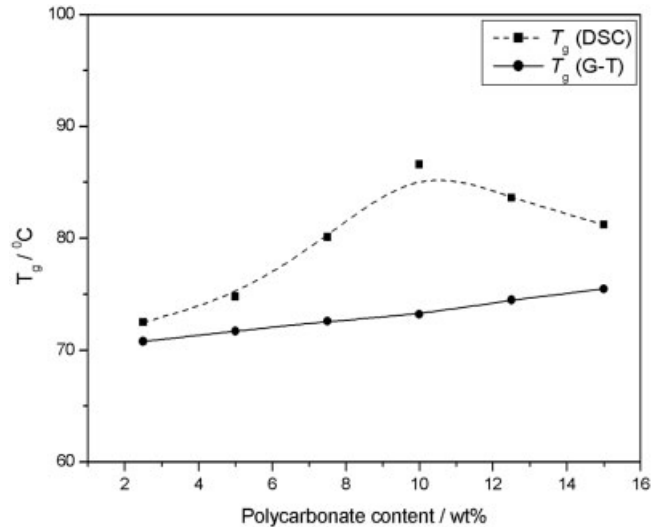
RESULTS AND DISCUSSION

Glass transition temperature

The DSC curves are shown in Figure 1. It can be seen that only a single glass transition is observed in each of the blends, within the whole composition range. This indicates the miscibility of the epoxy/PC blend. The composition dependence of blend T_g values are presented in Table I. Figure 2 shows that the glass transition temperatures of the epoxy/PC blends of various compositions do not agree with those calculated using the Gordon–Taylor equation:[30]

$$T_g = (T_{gA}w_A + KT_{gB}w_B)/(w_A + Kw_B)$$

where, w_A and w_B are the weight fractions, and T_{gA} and T_{gB} are the glass transition temperatures of the respective homopolymers, and K is defined as the ratio of the differences in expansion coefficient ($\Delta\alpha$) at T_gs of the epoxy and PC. However, when weight

fractions are used instead of volume fractions, and when it is assumed that $\Delta\alpha T_g$ = constant (Gordon and Taylor), K becomes

$$K = {}_{\rho A}T_{gA}/{}_{\rho B}T_{gB}$$

where ρ represents the density of the epoxy (ρ_A) and PC (ρ_B).

The Gordon–Taylor equation was proposed to predict T_g of a binary compatible blend, assuming volume additivity. It is clear that the experimental values are higher than the predicted ones (Fig. 2 and Table I). These higher values are the result of reactions taking place between the two components, which led to the formation of a network structure. The T_g(DSC) versus composition graph of the blend system exhibits a slightly sigmoidal shape. This reflects the fact that the extent of chemical links and network structure vary with the PC content in the blend. Su et al.[31] observed a similar behavior for a PC/tetraglycidyl 4,4'-diaminodiphenylmethane system. The T_g of the 90/10 blend

TABLE I
The Glass Transition Temperatures
(from DSC and G-T Equation)

Polycarbonate (%)	T_g (from DSC)	T_g (from G-T)	% curing
0	—	—	82.5
2.5	72.6	70.8	86.1
5.0	74.1	71.7	88.8
7.5	80.9	72.6	90.2
10.0	86.2	73.2	91.5
12.5	83.0	74.5	89.0
15.0	81.4	75.5	88.1

k-values and % curing of epoxy/polycarbonate blends.
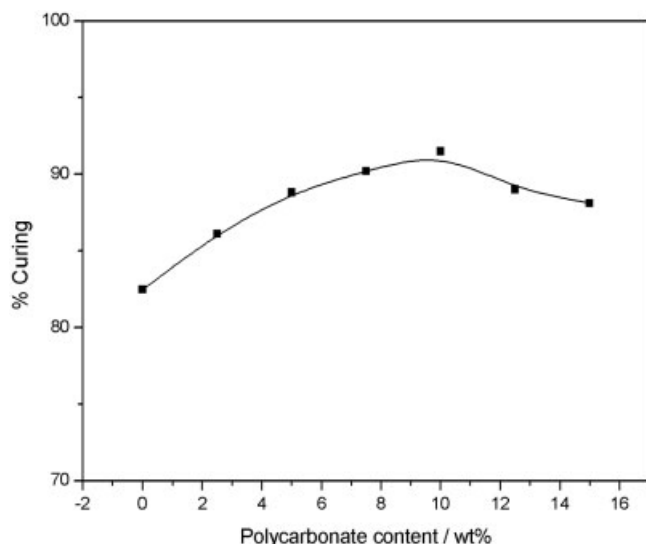
Figure 3 % curing of epoxy/PC blends as function of PC content in the blend.

is the highest, because this blend has the most extensive crosslinked network.

% curing

The % curing values of the pure epoxy resin and the epoxy/PC blends are presented in Table I. From the Table, it is clear that the blends have higher % of curing than does the pure epoxy resin. In Figure 3, it can be seen that the % curing linearly increases with an increase in PC content up to 10%, whereafter it decreases (see also Table I). This indicates the reactions between the epoxy and PC, which leads to curing. The % curing reaches an optimum value for 10% PC in the blend, explaining the trends observed for the T_g.

Mechanical properties

The tensile strength and modulus values of the epoxy and epoxy-PC blends with different PC concentrations are presented in Table II. It is evident that the tensile properties of the pure epoxy are lower than that of the blend matrix. However, as the PC content increases, the tensile properties of the blend matrix linearly increases up to 10% of PC in the blend, after which it decreases (Figs. 4 and 5). The reason for this is the fracture toughness, which is the result of an enhanced capacity for plastic deformation of the matrix because of the formation of an epoxy/PC-crosslinked network structure.

Su and Woo[19] reported that a PC/DGEBA prepolymer, without curing agent, and heated at 190°C for 6–12 h, could form a crosslinked structure. They explained that the DGEBA oligomers have multiple hy-

TABLE II
Tensile Strength and Modulus Values of Pure Epoxy and Epoxy/Polycarbonate Blend Matrices

Polycarbonate (%) in the epoxy/PC blend	Tensile properties (MPa)	
	Strength	Modulus
0	24	268
2.5	29	351
5.0	36	384
7.5	40	438
10.0	45	501
12.5	38	484
15.0	31	437

droxyl sites per molecule that can cause the exchange reactions between the PC and epoxy. The reaction that occurs has a natural tendency to form a network structure in the absence of any curing agent. The difference between the noncrosslinked and crosslinked structures of the PC/epoxy blend may come from the complicated oxidations involved. Whether the heated, precured PC/epoxy mixture forms a crosslinked structure or not depends on the type of epoxy monomer selected and the environmental conditions during mixing. In the hot-melt process of dissolving the PC into the epoxy, a transesterification reaction will replace the alcoholic hydroxyl of epoxy with a phenolic hydroxyl at the PC chain end. In the curing process of the PC/epoxy blends, the hydroxyl groups formed from the reaction between epoxy and amine will transesterify with carbonate groups to generate a phenol-chain end.[22] This is the reason for the improved mechanical properties of the PC/epoxy blend system.
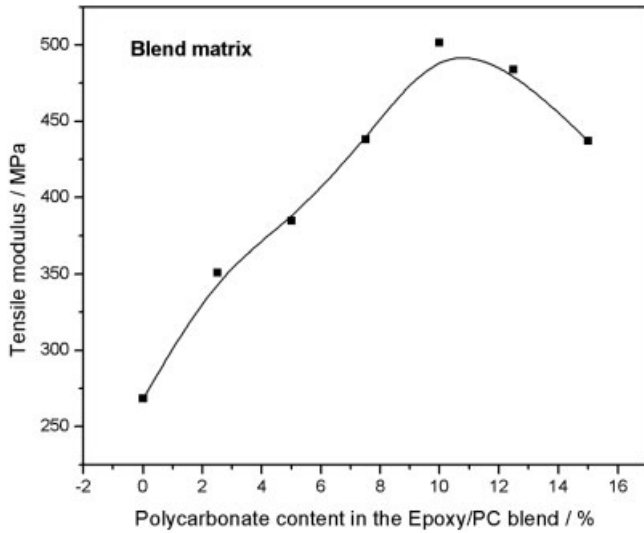
Properties of the composite

The tensile strength, modulus, and interlaminar shear strength values for different fiber orientations in car-
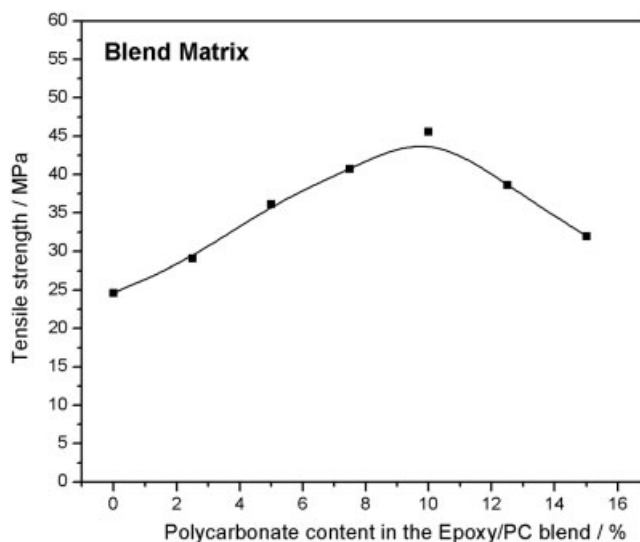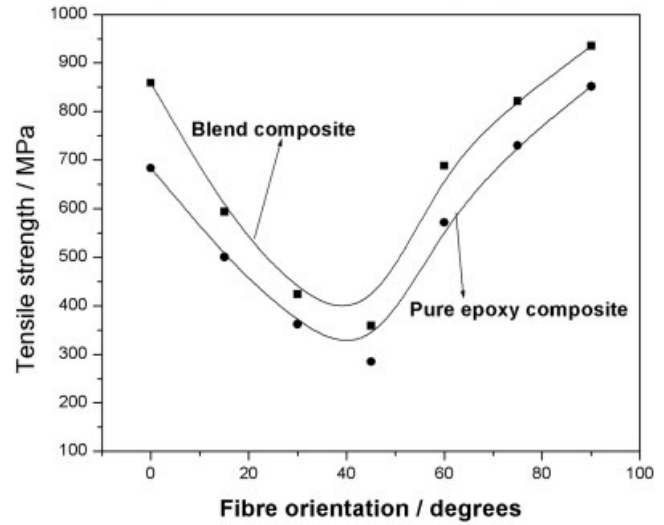

Figure 4 Tensile strength as a function of PC content of the epoxy/PC blend matrix.

Figure 5 Tensile modulus as a function of PC content of the epoxy/PC blend matrix.

Figure 6 Tensile strength as a function of fiber orientation of fiber composites with pure epoxy and an epoxy/PC blend.

bon fiber-modified epoxy composites are presented in Table III and Figures 6–8. For all orientations, the fiber content (68 wt %) was kept constant. The tensile and interlaminar shear properties of the pure epoxy-carbon fiber composites are lower than those of the blend matrix (epoxy/PC)-carbon fiber composites. It is clearly evident that the maximum strength is at orientation angles (θ) 0 and 90°, and the minimum at θ = 45° to the stress direction. The values for the other angles are intermediate between the maximum and the minimum. This behavior is expected as the orientation function is a cosine of the orientation angle.

Axial tensile strength is directly dependent on the ultimate strength of the fiber, the fiber volume or weight fraction, the matrix modulus, and the ultimate strain or matrix ductility. For a given matrix, the ultimate strain and the composite tensile strength will increase linearly with the matrix modulus. However, the interfacial bond between the fiber and the matrix

must be optimal. Too low an interfacial shear strength leads to premature debonding, while too high an interfacial strength can result in a brittle longitudinal or axial splitting failure mode. Axial tensile strength is also extremely sensitive to fiber alignment. Fiber misalignment, as little as ¼–½ a degree off-axis, can reduce the apparent composite tensile strength by 25–50%. In general, to achieve a high composite axial tensile strength with fixed interfacial shear strength, it is desirable to have a very strong fiber and a ductile, high ultimate strain matrix resin. The strengths of unidirectional composites are highly anisotropic. Perpendicular to the fibers, they are weak, and the failure is controlled by rupture of the plastic flow of the matrix, or by fiber-matrix debonding. In low-fiber volume or weight-fraction composites, the constraint imposed by the relatively undeformable fibers causes triaxial strain concentrations in the matrix, which may

TABLE III
Tensile and Interlaminar Shear Strength Values of Pure Epoxy and Epoxy/Polycarbonate Blend Composites with Carbon Fiber
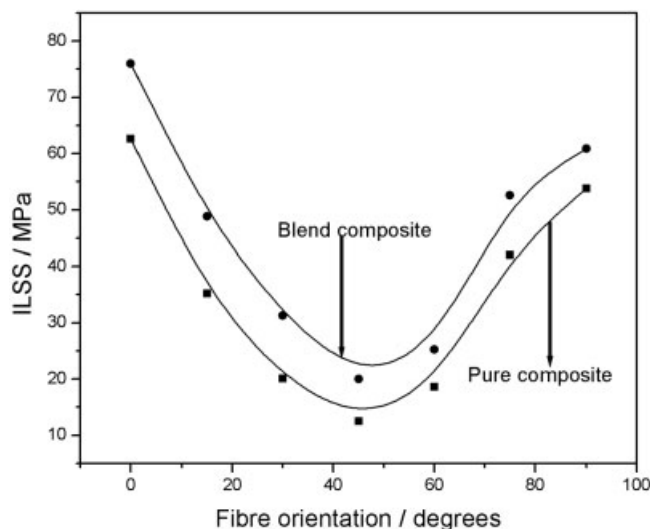
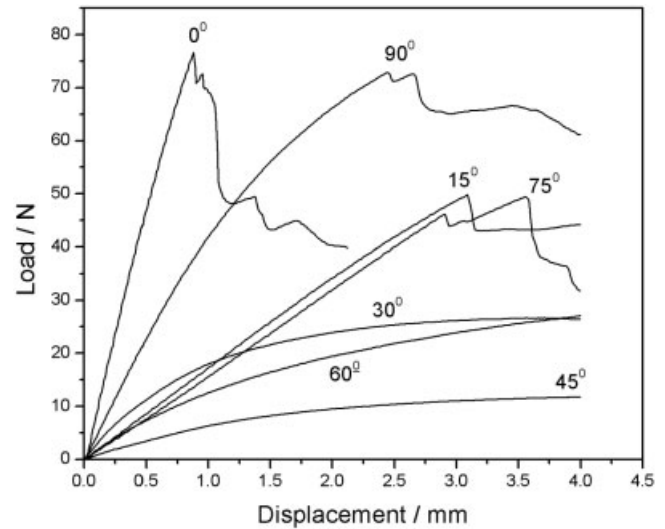| Fiber orientation (degrees)	Tensile properties (MPa)				Interlaminar shear strength (MPa)	
	Pure epoxy composite		Blend composite		Pure epoxy composite	Blend composite
	Strength	Modulus	Strength	Modulus		
0	683	11,547	852	13,569	62	76
15	501	8026	593	9714	35	48
30	362	3853	424	4142	20	31
45	285	2178	359	2564	12	20
60	571	3999	688	4279	18	25
75	730	10,675	821	12,530	42	52
90	852	12,718	935	13,229	53	60
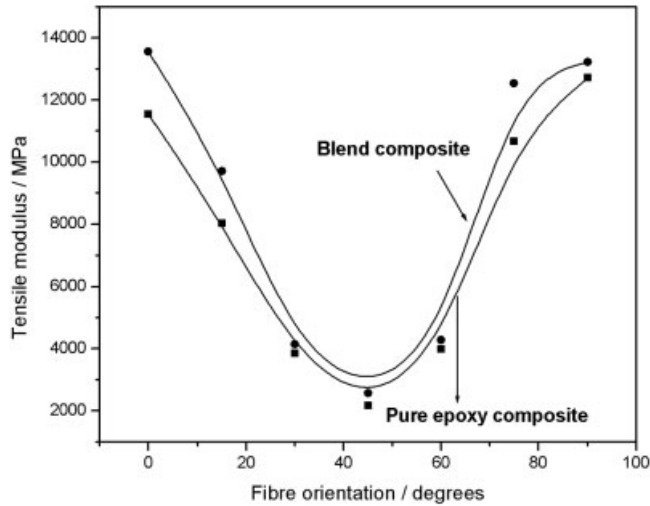
Figure 7 Tensile modulus as a function of fiber orientation of fiber composites with pure epoxy and an epoxy/PC blend.
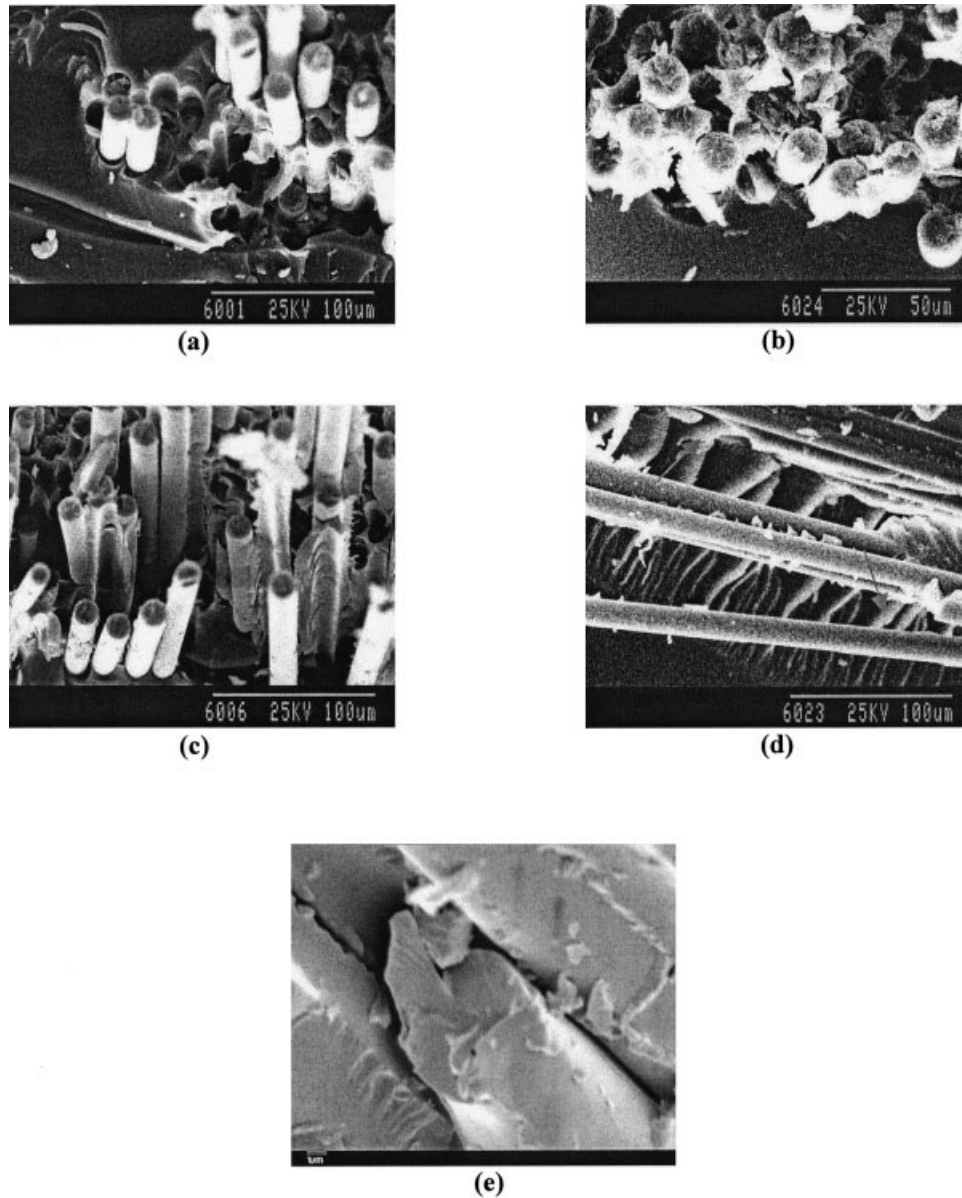

Figure 9 Load versus displacement curves for ILSS determinations of epoxy-PC blend/carbon fiber composites with different fiber orientation.

lead to brittle failure at low strains, even in otherwise ductile matrix materials.

Figure 8 shows a significant decrease in interlaminar shear strength with increasing fiber orientation up to 45°, after which the shear strength of the composite increases. From the figure, it is clearly evident that the interlaminar shear strength of the composite is a minimum at 45° and a maximum at 0 and 90° of the fiber orientation (Fig. 9). An examination of the failed specimens indicates that the mode of failure is predominantly interlaminar delamination and in-plane fiber separation for smaller fiber angles, and shifts to an in-plane matrix dominated crack mode for larger angles. These observations are in agreement with numer-

ical results reported,[32] which indicated that the mode of failure was predominantly interlaminar shear for small fiber angles, and primarily transverse tension for large fiber angles.

Morphology of the composites

The improvement in the mechanical properties of the modified epoxy-carbon fiber composites could be attributed to the enhancement of the interfacial strength between the fiber and the matrix. There are several mechanisms for the fiber-matrix bonding, which involve mechanical interlocking, adsorption interaction, electrostatic interaction, and diffusion of polymer chain segments.[33] The morphology of some ILSS fractured samples are presented in Figure 10, where the SEM micrograms of the epoxy matrix are compared to those of the blend matrix composites. From these micrographs, it is evident that the bonding between the blend matrix and the carbon fiber is better than that of the pure epoxy-carbon fiber composite. For our system, where carbon fiber was used as received, mechanical interlocking seems to play the most important role in the interfacial adhesion between the matrix and the fiber. This can also be seen in the SEM micrographs (Fig. 10) of the fractured samples after three-point bending tests. It can be seen in Figure 10(a) that the carbon fiber shows very poor interfacial bonding with the epoxy resin; the micrograph shows some of the carbon fibers pulled out from the pure epoxy. The epoxy/PC blends show good bonding between the carbon fiber and the blend matrix [Fig. 10(b)]. This micrograph shows that some of the fibers broke instead of being pulled from the matrix. The reason is that the bonding between the blend matrix and the

Figure 8 Interlaminar shear strength as function of fiber orientation of fiber composites with pure epoxy and an epoxy/PC blend.

Figure 10 SEMs of ILSS-fractured modified epoxy/carbon fiber composites. (a) Pure epoxy-carbon fiber composite; (b–d) Epoxy/PC-carbon fiber composite; (e) Pure epoxy-carbon fiber composite (high magnification).

carbon fiber is very strong. Strong interlocking of fiber-matrix interface can also be observed, as marked by arrows in Figure 10(d), which was termed a "mechanical anchor" by Kalantar and Drzal.[33] From Figure 10(e), it is clearly evident that the bonding is very poor between the fiber and the pure matrix. We can see a long crack in the micrograph, indicating that the pure epoxy is very brittle in nature, and the composite sample easily breaks when bended. Mechanical interlocking provides a strong interface bonding, even though other effects are weak.[34] These observations suggest the need for surface modification of the carbon fiber, probably by the use of different coupling agents, heat and plasma treatments. Further work in this direction is in progress.

CONCLUSIONS

The DSC results show a single glass transition temperature (T_g) for all the epoxy/PC blend compositions, indicating full miscibility. The glass transition temperatures increase with increasing PC content in the blends up to 10% PC, after which they decrease. This observation correlates well with the % curing determined through solvent extraction. The mechanical properties of the blend matrix composites are better than those of the pure epoxy composites. The 45° fiber orientation was found to have very low mechanical properties. The tensile and interlaminar shear properties of the epoxy-carbon fiber composites can be greatly improved by modification of the epoxy with

PC. The tensile properties of the blend matrix increased with PC content up to 10%, beyond which it decreased. The bonding between the matrix and carbon fiber is better when an epoxy/PC blend matrix was used.

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