Enhanced Glass Fiber-Reinforced Phenolphthalein Poly(ether ketone) Composites by Blending Poly(phenylene sulfide)

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SYNOPSIS

The mechanical properties of glass fiber-reinforced phenolphthalein poly(ether ketone)/poly(phenylene sulfide) (PEK-C/PPS) composites have been studied. The morphologies of fracture surfaces were observed by scanning electron microscope. Blending a semicrystalline component, PPS, can improve markedly the mechanical properties of glass fiber-reinforced PEK-C composites. These results can be attributed to the improvement of fiber/matrix interfacial adhesion and higher fiber aspect ratio. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

High-performance composites with thermoplastic matrices are of increasing interest in both industry and research. For a certain matrix, the mechanical properties of a fiber-reinforced composite depend on the fiber/matrix interface, fiber aspect ratio, and fiber content. Since the stress acting on the matrix is transmitted to the fiber across the interface, improvement of the interfacial adhesion for those composites with poor adhesion has great significance.

The fiber/matrix adhesion can be improved by use of appropriate chemical treatments of the fibers, but the treatments do not always yield a sufficient improvement of the mechanical properties to warrant the industrial use of such a costly and time-consuming pretreatment of the fibers.[1] Carbon or glass or Kevlar fibers have been found to act as a nucleating agent for semicrystalline polymers. In certain cases, some semicrystalline matrices, such as poly(ether ether ketone),[2] nylon,[3] and polyethylene,[4] can crystallize in the form of a sheath surrounding the fibers; thus, a strong interfacial adhesion and, as a result, improvement of mechanical properties of the composites can be obtained. This phenomenon is known as transcrystallinity.[5]

The aim of this study was to improve the poor fiber/matrix interfacial adhesion of unmodified glass fiber-reinforced phenolphthalein poly(ether ketone) (PEK-C) composites to obtain high reinforcing efficiency to meet its application need. Since the processing temperature of PEK-C is very high (about 330°C), chemical treatments of glass fibers seems to be of no use. The reinforcing efficiency of semicrystalline polymers by short glass fiber is more than 100%,[6] whereas it is only about 35% for PEK-C. Poly(phenylene sulfide) (PPS) is a semicrystalline high-performance thermoplastic with high-temperature resistance and high modulus. Its melting temperature is about 280°C. At the processing temperature of PEK-C/GF composites, its melt viscosity is much lower. It was hoped to gain a better fiber/matrix adhesion through blending a semicrystalline polymer, PPS, with the PEK-C/GF composites.

EXPERIMENTAL

The PEK-C matrix used in this study was offered by Xuzhou Engineering Plastic Co., China. Its reduced viscosity in chloroform at a temperature of 25°C is 0.37 dL/g. The PPS matrix was offered by Zigong Chemical Reagent Factory, China.

Powders of PEK-C and PPS were mechanically mixed with compositions ranging from 5 to 30 wt % of PPS in the PEK-C matrix. In all cases, a 30%

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Table I   Mechanical Properties of High-performance Thermoplastics and Their Glass Fiber-reinforced Composites

	σ_y MPa	σ_b MPa	ε %	E_f GPa	σ_f MPa
PEK-C	100		15.0	3.4	150
30% GF		135	6.7	7.4	190
PEK-C/PPS					
30% GF		152	7.1	8.6	230
PSF	70		50–100	2.7	106
20% GF		100	1.5	7.2	138
PES	84		30–80	2.6	128
20% GF		120–124	2–3.5	5.9	169
PEI	105		60	3.3	145
30% GF	169	172–197	3–5	8.3–8.6	228–255
PPS		65	1–2	3.8	97
40% GF		135–159	1–4	11.7–12.4	200–221
PEEK	91	70	50–150	3.9	
30% GF		162	3.0	8.7	237

GF concentration was used. The blends and un-modified glass fiber were then extruded at about 310–330°C in a SHJ-30 twin-screw extruder and pellet-ized. Test specimens were injection-molded on a JSW-17SA injection-molding machine (Japan) with barrel temperatures of 315–340°C.

Mechanical Testing

The tensile and flexural properties were measured with a WD-100E tester (China) according to ASTM D638 and D790, respectively. Reported values were the average of five measurements for each sample at room temperature. The crosshead speeds were 5 and 20 mm/min, respectively.

Observation of Morphology

The fractured surface morphologies were observed using a scanning electron microscope (SEM) (Model JAX-840). The samples were sputter-coated with gold before viewing under the microscope. The polarizing optical microscope was used to observe the crystallizing behavior of the PEK-C/PPS ma-trix around the glass fibers in the composites.

Determination of Fiber Aspect Ratio

After heating at 550–600°C for over 1 h, glass fibers were resolved from each injection-molded sample. The fiber aspect ratio is the average value of over 400 fibers for each sample determined by a traveling microscope.

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties of PEK-C and some other high-performance thermoplastics and their short glass fiber (SGF)-reinforced composites are shown in Table I. The strength and modulus of all composites are enhanced markedly. However, the elongation at break of the composites decreases. This is due to the fact that with introducing high mod-ulus-reinforced fibers into a flexible matrix it im-proves its modulus and strength, but interrupts the continuity of the matrix, which is responsible for the decrease of the elongation at break of the matrix. As can be seen from Table I, the reinforcing effi-ciency of these semicrystalline polymers (PEEK and PPS) by SGF is more than 100%, whereas it is around 50% for these amorphous polymers. For SGF-reinforced PEK-C, the reinforcing efficiency is only 35%. This may be due to the fact that the in-terfacial adhesion between the PEK-C matrix and SGF is very poor [Fig. 2(a)].

The results shown in Table I imply that the me-chanical properties of SGF-reinforced composites are largely dependent on that of the matrix. It is supposed that with introducing a semicrystalline component into the PEK-C matrix the reinforcing efficiency could be

improved. The mechanical properties of PEK-C/GF composites are enhanced pronouncedly by blending a third component, PPS, into the composites. The tensile strength of the PEK-C/PPS/GF composites (the 30% GF concentration remains unchanged) are shown in Figure 1. With increasing PPS content in the PEK-C matrix, the tensile strength of the composites increases markedly. The maximum value is 151.8 MPa for the composite with 20% PPS content. But there is no improvement when the PPS content exceeds 30%. For a better understanding of the mechanical properties of the composites, a study of fracture morphology is necessary.

Morphological Study

Morphological studies on PEK-C/PPS/GF composites were undertaken to correlate the mechanical properties. The SEM photographs of the composites, resulting from tensile tests as shown in Figure 2, reveal that the morphology of the broken section of the PEK-C/PPS/GF composites are quite different from that of the PEK-C/GF. Smooth pulled out glass-fiber surfaces and fractured surfaces are evidence of poor interfacial adhesion between matrix and glass fibers for PEK-C/GF [Fig. 2(a)]. For other samples, with increasing the PPS content from 5 to 30% in the matrix, rough pulled-out glass-fiber surfaces which were coated by the matrix can be found. This phenomenon should be responsible for the blending of PPS with the PEK-C matrix. It is believed that during fiber pulling out and failure initiation increased interfacial friction as a result of rough glass fiber surfaces, at least partly, corresponds to the enhanced mechanical properties.

Carbon, glass, and Kevlar fibers have been found to act as a nucleating agent for some semicrystalline polymers, which, in certain cases, can crystallize in the form of a sheath surrounding the fibers.[2-5] Figure 3 gives circumstantial evidence of this suggestion for glass fiber and PPS. As indicated by the arrow, there is a transcrystallinelike sheath, which is about 1.5 μm in thickness, surrounding the glass fiber. The polarizing optical micrograph of the PEK-C/PPS/GF composite with a 10% content of PPS in the matrix is shown in Figure 4. There is a crystalline sheath surrounding each glass fiber, whereas in the matrix, there exist many fine and evenly dispersed crystalline particles, i.e., a large part of the PPS in the composite distributes around the glass fibers in the form of a crystalline sheath. Also, a small part of PPS disperses evenly and finely in the PEK-C component, as shown by those microvoids existing on the fractured surface (Figs. 2 and 3) to form a multiphase matrix.
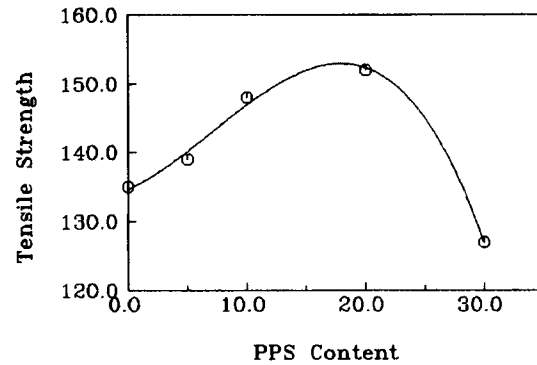

Figure 1 The tensile strength of PEK-C/PPS/GF composites as a function of PPS content in PEK-C/PPS matrix. Glass fiber concentration is 30%.

The miscibility and crystallization behavior of the PEK-C/PPS blend was reported by Li et al.[7] PEK-C was found to be immiscible with PPS. The degree of crystallinity of PPS in the blends decreased with the increase of PPS content. It is obvious that, for the PEK-C/PPS/GF composites, with increasing PPS content in the composite, most of PPS will disperse in the PEK-C/PPS matrix. The immiscibility of the PEK-C/PPS blend and the lower strength of PPS resin may lead to a decrease of the strength of the PEK-C/PPS matrix for the composite with a large content of PPS (Fig. 1). With these viewpoints and above morphological observations, the PPS component may crystallize on the glass-fiber surfaces and therefore improve the matrix/fiber interfacial adhesion. The optimum content of PPS in the PEK-C/PPS matrix should be 10–20% in order to improve the matrix/fiber interfacial adhesion without markedly decreasing the strength of the matrix.

The Fiber Aspect Ratio

The stress transmission in a composite, from the matrix to the fiber by the action of shearing forces across the interface, depends also on the fiber aspect ratio. There exists a critical fiber length which is the shortest fiber length for obtaining the maximum stress transmission from matrix to the fibers at the assumption of strong interfacial adhesion.[8] This means that a short fiber will not work to the full effect and the strength gain from the addition of fiber will be low. The fiber aspect ratio of PEK-C/PPS/GF composites with different PPS contents are shown in Figure 5. With increasing PPS content, the aspect ratio increases and a marked increase occurs after the PPS content exceeds 10%. This is due to the much lower melt flow viscosity of PPS at the processing temperature of the PEK-C composites.
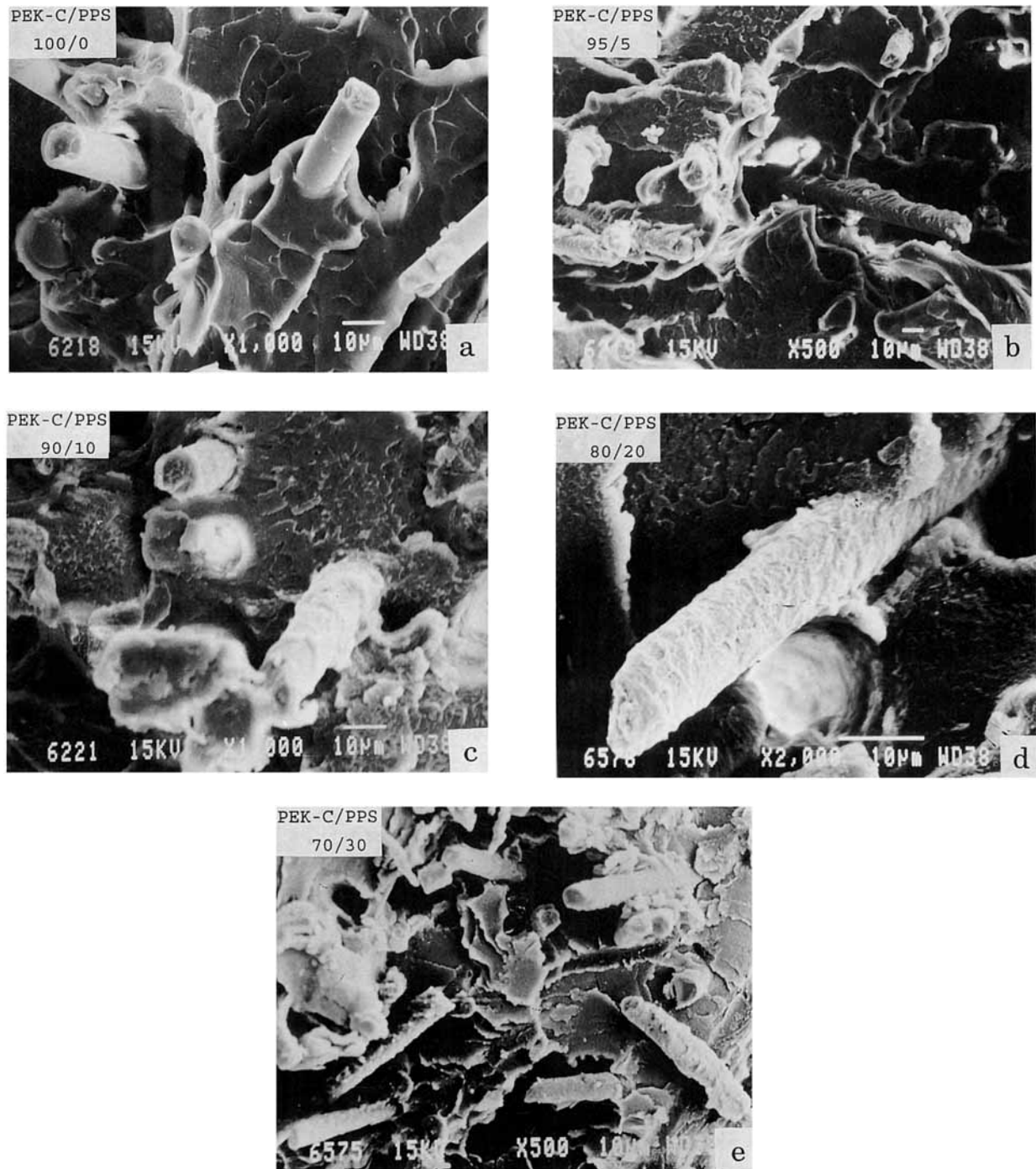
Figure 2   SEM photographs of fractured surfaces of PEK-C/PPS/GF composites with different compositions of the PEK-C/PPS matrix. The glass fiber concentration is 30% for all composites.

According to above results, the improvements of mechanical properties of glass fiber-reinforced PEK-C composites with addition of the PPS component may be attributed to the improvement of matrix/fiber interface and higher fiber aspect ratio.

Lowering of the melt flow viscosity of the matrix decreases the fiber breakdown during processing and is helpful for the even dispersion of fibers and orientation in the flow direction. On the other hand, from the viewpoint of processibility, the addition of PPS reduced the extruding temperature, torque, and melt pressure and, as a result, the processing temperature. This is similar to phenolphthalein polyethersulfone/PPS blends in
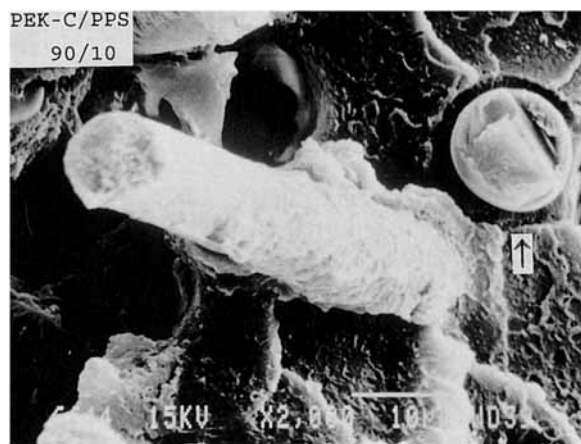
Figure 5   The fiber aspect ratio of PEK-C/PPS/GF composites.

Figure 3   SEM photograph of fractured surface of PEK-C/PPS/GF composite with 10% PPS content in PEK-C/PPS matrix.

which the PPS component also had a processing aid.[9]

CONCLUSIONS

In this study, we found that, instead of chemical treatment of glass fibers, blending a semicrystalline polymer, PPS, can improve the fiber/matrix interfacial adhesion and processing conditions of the glass fiber-reinforced PEK-C composites.
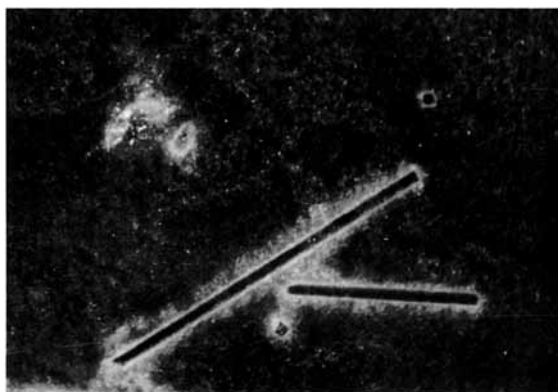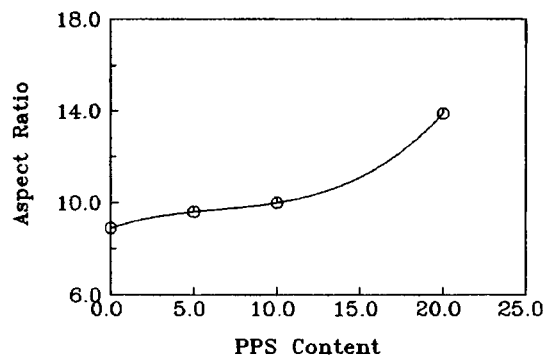
The PPS component in the PEK-C/PPS matrix can crystallize on the glass fiber surfaces and therefore improve the fiber/matrix interfacial adhesion. The improvement of mechanical properties of PEK-C/PPS/GF composites can be attributed to the good interfacial adhesion and high fiber aspect ratio resulting from the addition of PPS into the PEK-C matrix.

This study shows that, in general processing conditions, blending a proper semicrystalline polymer can enhance the mechanical properties of fiber-reinforced amorphous polymer-based composites and has a reasonable potential for application from the commercial viewpoint. To gain better understanding of above results, the crystalline behavior of PPS on the fiber surfaces and phase behavior of PEK-C/PPS blends need to be further studied.

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Figure 4   Polarizing optical micrograph of PEK-C/PPS/GF composite.