Mechanical Property and Fracture Morphology of Fiber-Reinforced Polysulfone Plasticized with Acetylene-Terminated Sulfone

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SYNOPSIS

The mechanical property and fracture morphology of glass fiber– (GF) and carbon fiber– (CF) reinforced polysulfone (PSF) blends with bis(4-(4-ethynyl phenoxy) phenyl) sulfone (ATS-C) have been investigated. Experimental results show that the tensile and flexural properties and impact strength of GF-reinforced ATS-C/PSF composites decrease as the processing temperature or/and the processing time increase, but CF-reinforced ATS-C/ PSF composites exhibit better mechanical properties. Although interlaminar shear strength (ILSS) for fiber-reinforced ATS-C/PSF composites decreases, scanning electron microscopy (SEM) observation of fracture surface indicates that the fractural model of fiber-reinforced PSF composites changes from the interfacial debonding fracture to the matrix fracture at the interfacial region with addition of ATS-C and the increase of the processing temperature. The end-use temperature of polysulfone can be retained and solvent resistance of polysulfone can be improved due to the formation of a semi-interpenetrating polymer network. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Interest has been generated in using thermoplastics as matrix resin for fiber-reinforced composites. The thermoplastic resins as matrix material for advanced composites have many advantages over thermosetting counterparts; fractural toughness, for example, is very high as compared with that of the thermosetting resins. The typical thermoplastics considered for such application should possess high glass transition temperature (T_g) to provide high end-use temperature. They include the polysulfones, principally bisphenol A polysulfone (PSF), polyethersulfone (PES), and polyarylsulfone (PASF). However, they require high processing temperature. In addition, these high-performance amorphous thermoplastic resins are susceptible to solvent-induced crazing, thus limiting their use. Therefore, for successful application of high-performance amorphous thermoplastic resins, it is required that the pro-

cessing temperatures be lowered and solvent resistance be improved while maintaining high end-use temperatures. This has been made possible by blending amorphous thermoplastic resins with reactive plasticizers, such as the acetylene-terminated oligomer.[1-5]

Like commercial plasticizers, the reactive plasticizer can also lower the glass transition temperature of thermoplastic resins by increasing the free volume. Consequently, the melt viscosity and processing temperature of thermoplastic resins can be lowered. Unlike the commercial plasticizers, the reactive plasticizer undergoes a thermally initiated crosslinking reaction during processing and subsequent cure treatment and forms a crosslinked network structure. This type of molecular structure caused by the reactive plasticizer is expected to improve the chemical resistance of thermoplastic resins.

The reactive plasticizer having ethynyl groups can be reacted through thermal cure to form a network. The network structure and property of the reaction product of the reactive plasticizer in blends depend upon the cure conditions.[2] This work was performed

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to study the effects of processing conditions on mechanical and thermal properties, solvent resistance, and fractural morphology of glass fiber– (GF) and carbon fiber– (CF) reinforced bis(4-(4-ethynyl phenoxy) phenyl) sulfone (ATS-C) plasticized PSF blend (weight ratio of ATS-C/PSF = 10 : 90) composites in order to select the reasonable processing conditions to prepare fiber-reinforced composite materials for different applications.

EXPERIMENTAL

Materials

The bisphenol A polysulfone (PSF) was obtained from Shuguang Chemical Factory, Shanghai, People's Republic of China. The bis(4-(4-ethynyl phenoxy) phenyl) sulfone (ATS-C) was provided by Changchun Institute of Applied Chemistry, Academia Sinica. The blend solution of 30% (g/mL) (weight ratio of ATS-C/PSF = 10 : 90) was prepared by dissolving the polysulfone and the ATS-C oligomer in 1,2-dichloroethane. Carbon fiber was provided by Liaoyany City Special Fiber Test Factory, People's Republic of China (σ_t = 2600 MPa). Glass fiber coated with KH-550 was obtained by Nanjing Glass Fiber Factory, People's Republic of China (σ_t = 2300 MPa).

Preparation of Composites

The resin-preimpregnated tapes (prepreg) were fabricated by impregnating a continuous unidirectional glass fiber and carbon fiber bundle into the above resin solution. The prepreg was dried at 100–120°C for 5 h. Then the prepregs were hand laid in a cold-matched metal die that was inserted into a press preheated to the processing temperature shown in Table I and the contact pressure was applied. A thermometer was attached to the die to de-

termine the thermal history. When the die temperature reached 240°C, 20 MPa pressure was applied. The temperature was continuously raised to the processing temperature and was cured for a certain time (shown in Table I) under 40 MPa pressure. When the die temperature cooled to 240°C, 60 MPa pressure was applied and the die cooled to room temperature, and the heat-pressured laminates were removed from the press. Composites with thicknesses of 2.1–2.4 mm were obtained. A fiber volume fraction was maintained at approximately 55%.

Characterization

Mechanical Properties

Flexural tests were made on a three-point loading fixture with a fixed span of 60 mm. The specimens were 6 mm wide by 90 mm long, and the thickness of the specimens was 2 mm. Measurements of interlaminar shear strength were carried out by using the short-beam three-point method at a constant span to a thickness ratio of 5.5. Flexural and interlaminar shear tests were performed on a DL-1000B electron tension machine with a crosshead speed of 5 and 1 mm/min, respectively. Tensile strength and modulus were measured on a Instron-8032 testing machine with a crosshead speed of 2 mm/min. The dimensions of the tensile sample were 180 × 6 × 2 mm. The impact tests were conducted using a XCJ-500 impact testing machine. Unnotched 60 × 6 × 2-mm bars were used at a span of 40 mm to measure the impact strength of composites. In the above experiments, five samples of each condition were tested and the results were averaged.

Solvent Resistance

The specimens (5 × 6 × 2 mm) were immersed in 1,2-dichloroethane at room temperature for a certain time and then dried at 100–120°C for 1.5 h. The weight loss due to the solvent extraction was deter-

Table I   Processing Temperatures and Times for Fiber-Reinforced PSF and ATS-C/PSF Composites

Processing				
Temperature (°C)	Time (h)	ATS-C/PSF	GF Reinforced	CF Reinforced
300	0	0 : 100	A	A'
300	0.5	10 : 90	B	B'
300	5	10 : 90	C	
360	0	10 : 90	D	D'

mined. The surface of the etched specimens was observed under scanning electron microscopy (SEM).

Thermal Properties

Differential scanning calorimetry (DSC) was carried out with a Perkin-Elmer model II thermal analyzer at a heating rate of 20°C/min. The glass transition temperature (T_g) was taken as the midpoint of the change in heat capacity. Thermogravimetric analyses (TGAs) were performed using a TGS-2 thermogravimetric analyzer (PE Co., Japan) at a heating rate of 10°C/min in flowing air. Isothermal aging in air at 200°C was performed. The test specimens were 35 × 6 × 2 mm in size.

Morphology

The fracture surface of impact specimens and the surface of etched specimens were coated with a thin layer of Au and examined using a HITACHI S-450 scanning electron microscope.

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties of fiber-reinforced PSF and ATS-C/PSF composites processed under different conditions are shown in Figure 1. It can be
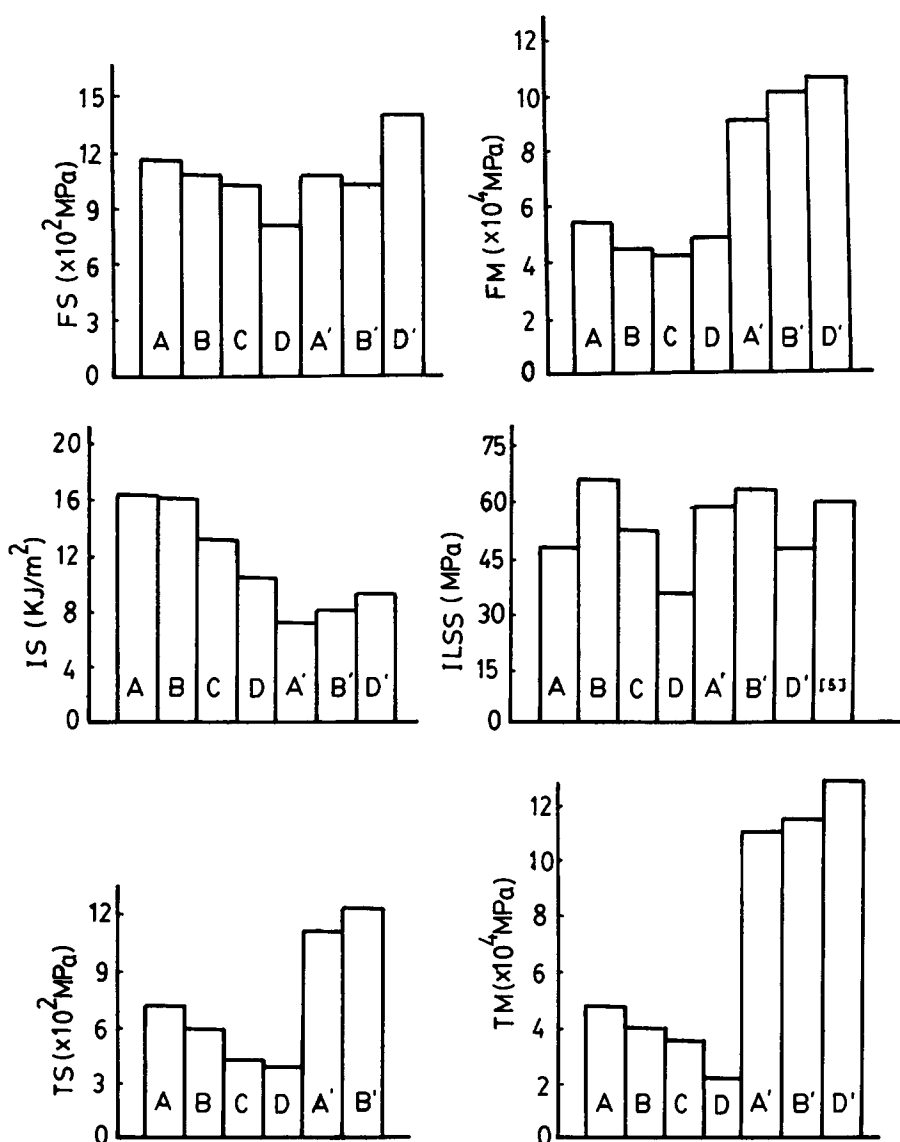
Figure 1   Mechanical properties of glass fiber– (A, B, C, D) and carbon fiber– (A', B', D') reinforced PSF and ATS-C/PSF composites processed at different conditions.
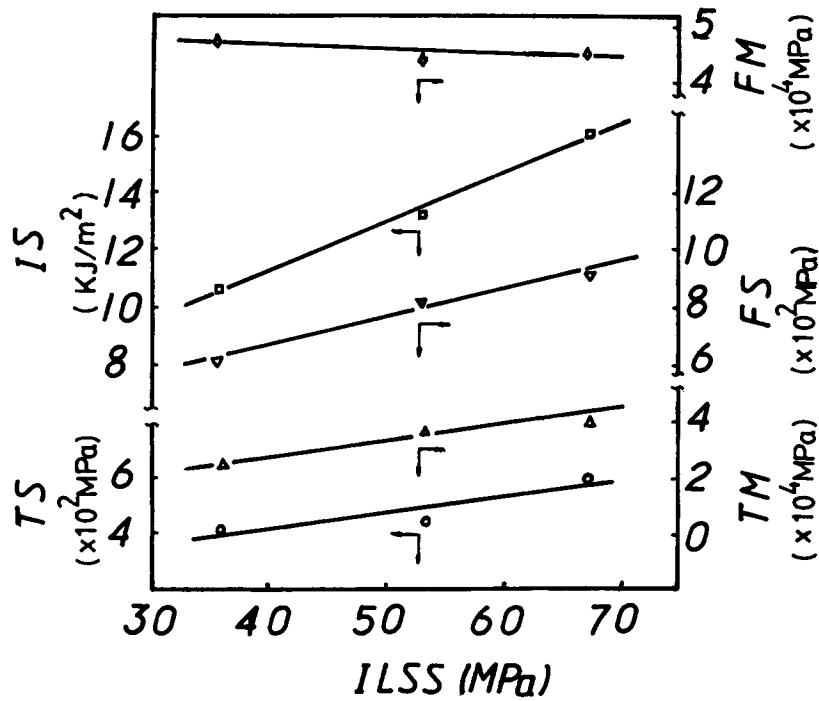
Figure 2   Relationship between mechanical properties and ILSS of fiber-reinforced ATS-C/PSF composites.

seen that the flexural strength (FS) of GF- and CF-reinforced PSF composites and the flexural modulus (FM) of GF-reinforced PSF composites prepared at 300°C for 0.5 h decrease by the addition of ATS-C

and the flexural modulus of CF-reinforced ATS-C/PSF composites increases. Flexural properties of GF-reinforced ATS-C/PSF composites tend to decrease with increasing processing time (sample C)
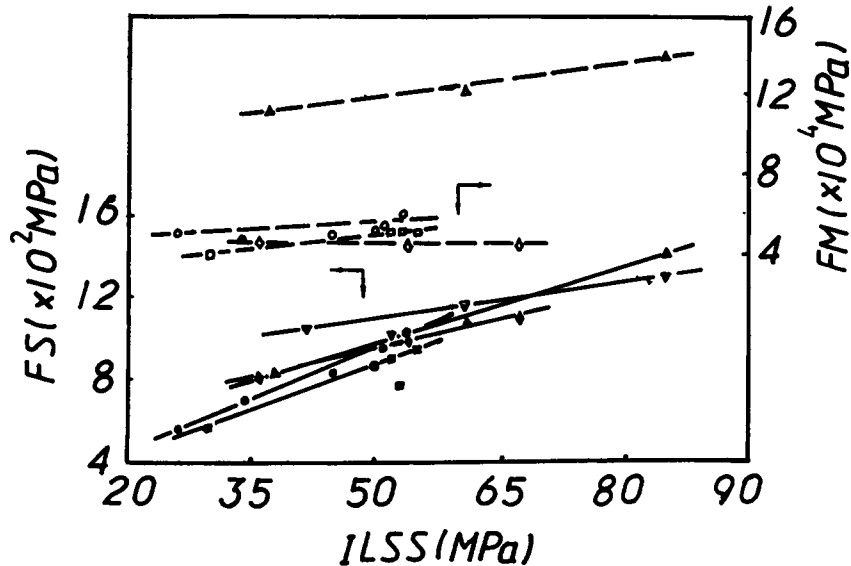

Figure 3   Relationship between flexural properties and ILSS of fiber-reinforced composites: (●, ○) ATPISi/graphite woven cloth[9]; (▲, △) ATPISi/HT-S graphite fiber[10]; (■, □) Thermid-600/ATPISi-2n blend/graphite woven cloth[9]; (▼) Thermid-600/graphite fiber[5]; (♦, ◇) this work.
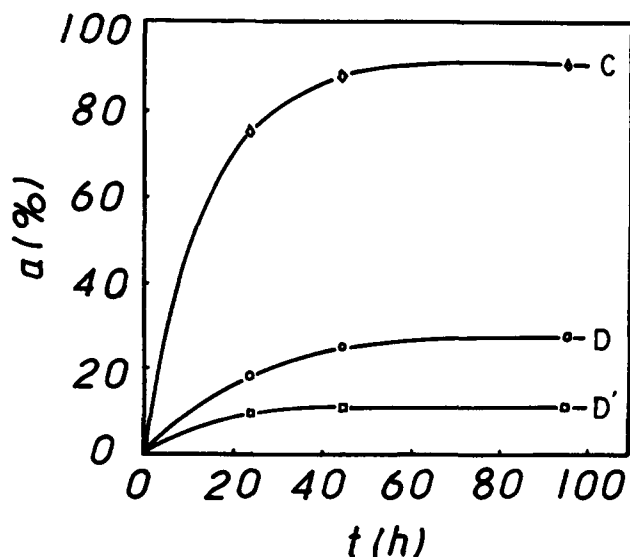
Figure 4 Relationship between soluble resin percent ($a\%$) and soluble time (t).

Table II Thermal Properties of GF-reinforced PSF and ATS-C/PSF Composites

Composites	T_g (°C)	Temperature (°C) of Weight Loss	
		At 5%	At 10%
A	190	458	500
B	188	460	486
C	191	444	478
D	189	450	482

and the processing temperature (sample D). However, flexural properties of CF-reinforced ATS-C/PSF increase with increasing processing temperature (sample D'). Similarly, tensile strength (TS) and tensile modulus (TM) and impact strength (IS) of GF-reinforced PSF decrease by the addition of AST-C and the mechanical properties of GF-reinforced ATS-C/PSF composites decrease as the processing temperature and time increase. However, tensile properties of CF-reinforced PSF increase with the addition of ATS-C and the mechanical properties of CF-reinforced ATS-C/PSF composites increase as the processing temperature and time increase. Above experimental results show that the tensile, flexural, and impact properties of GF-rein-

forced ATS-C/PSF composites decrease and CF-reinforced ATS-C/PSF composites exhibit better mechanical properties as the processing temperature and time increase. Interlaminar shear strength (ILSS) depends also upon the processing conditions. The ILSS of GF- and CF-reinforced ATS-C/PSF composites is higher than that of fiber-reinforced PSF composite prepared at 300°C for 0.5 h due to the plasticization of ATS-C to decrease the T_g of thermoplastic PSF resin and improve the interfacial property between matrix and fiber. However, the ILSS decreases with increasing processing temperatures and times. The reason may be that the internal stresses in the cured blends and the interface between matrix and fiber increase due to an increase in the extent of crosslinking of ATS-C at higher processing temperature and longer processing time. It can be seen from Figure 2 that the tensile, flexural, and impact properties increase as the ILSS increases. These results are similar to that of GF-reinforced epoxy composite and fiber-reinforced acetylene-terminated oligomer composites (Fig. 3). However, the results of SEM observation of the
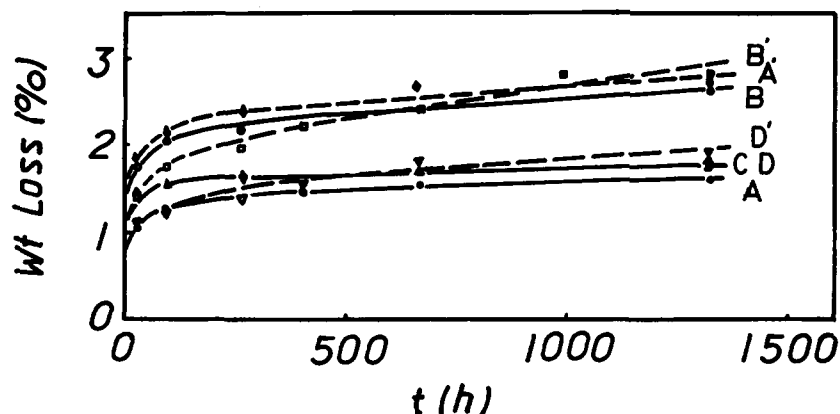

Figure 5 Relationship between isothermal weight loss and aging time (t) at 200°C.
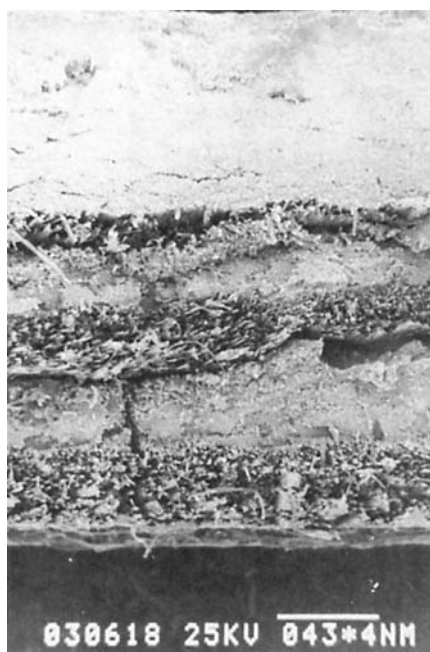
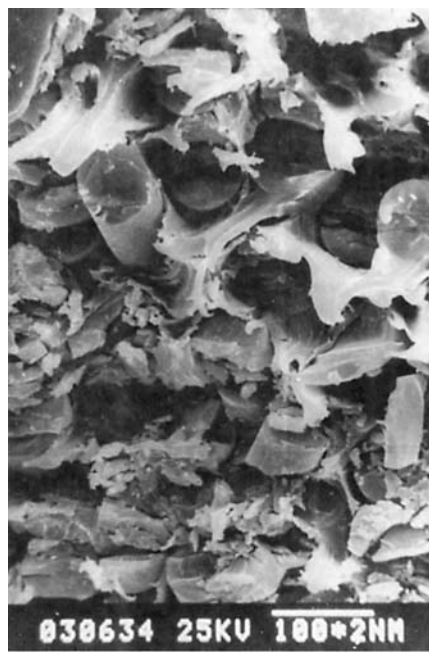**Figure 6** Fractural surfaces of impact specimens.

fractured surface of specimens (Fig. 7) show that fiber-reinforced ATS-C/PSF composites with higher ILSS do not exhibit better adhesion at the interface between matrix and fiber.
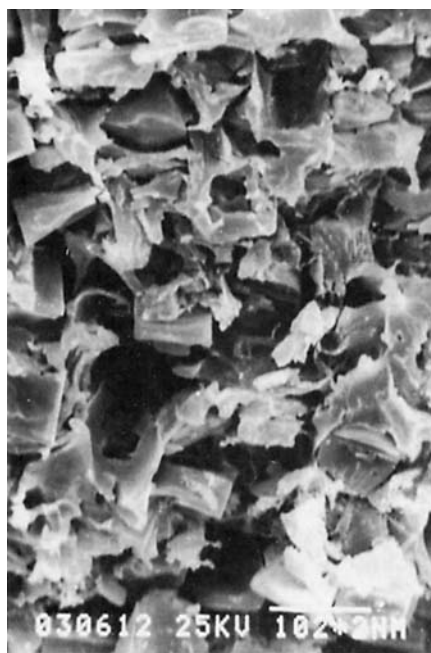
Solvent Resistance

During processing ATS-C in ATS-C/PSF blends undergoes reaction of cure and a semi-interpene-
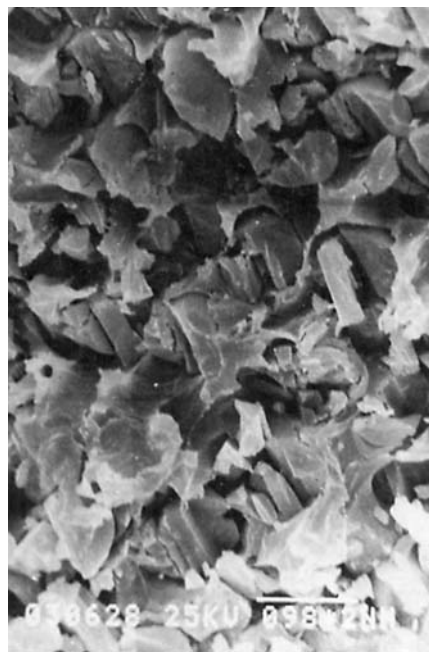
D'

B

C

D

Figure 6   (*Continued from the previous page*)

trating polymer network (semi-IPN) is formed. The chemical resistance of thermoplastic resin is improved. The solvent resistance of composites is characterized by the soluble resin percent in 1,2-

dichloroethane. It can be seen from Figure 4 that the solvent resistance of PSF composites prepared at 300°C for 0.5 h can be only slightly improved by addition of ATS-C. It is mainly due to ATS-C form-

D
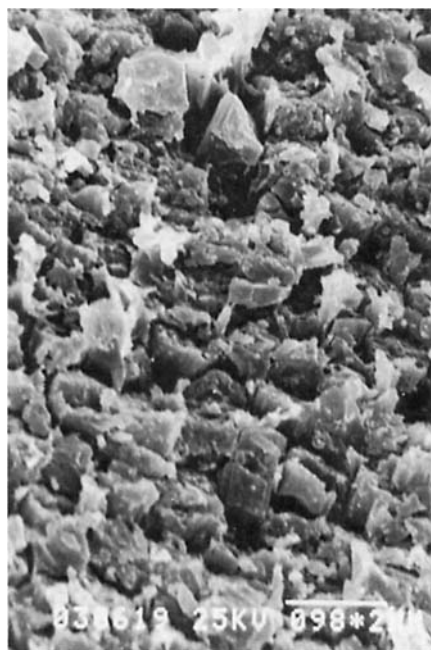
Figure 6 (*Continued from the previous page*)

ing little crosslinked network structure at lower processing temperatures. Solvent resistance of ATS-C/PSF composites can be dramatically improved by increasing the processing temperature. Soluble resin percent in 1,2-dichloroethane for 96 h of ATS-C/PSF composite prepared at 360°C is about 25% due to the increase in the extent of crosslinking of ATS-C network at higher temperature. These results indicate that the solvent resistance of amorphous thermoplastic PSF composite can be improved by addition of reactive plasticizer ATS-C and increased by increasing the processing temperature, which has much more of an effect on solvent resistance than does the processing time.

Thermal Properties

The apparent glass transition temperatures are obtained on DSC. Table II gives the T_g's and temperatures of weight loss by TGA for GF-reinforced PSF and ATS-C/PSF composites. The T_g's of fiber-reinforced PSF and ATS-C/PSF composites prepared at the above conditions are about 188–191°C (these T_g's are identical to those of the PSF phase in cured blends). No T_g of the ATS-C phase in cured blends is present.[2] Therefore, it is suggested that the end-use temperature of PSF composites cannot be lowered by addition of reactive plasticizer ATS-

C. TGA results show the temperatures of weight loss at 5% begin over 440°C and the temperatures of weight loss at 10% begin over 470°C for all specimens. However, ATS-C/PSF composites exhibit a lower degradation temperature than PSF composites. The experimental results of Hergenrother[6] also showed that the temperature of degradation of linear PSF was higher than that of acetylene-terminated polysulfone cured at 300°C for 0.5 h in air. The weight loss of PSF and ATS-C/PSF composites prepared at different conditions is about 3% at 200°C for 1300 h (Fig. 5) and weight loss of ATS-C/PSF composite can be decreased by increasing the processing temperature and time.

Fractural and Interfacial Morphology

Because the extent of crosslinking of ATS-C depends upon the cure conditions, the different processing conditions lead to different structure and morphology in the cured blends[2] and in the interface region between the matrix and the fiber. Therefore, ATS-C/PSF composites prepared at different conditions exhibit different mechanical and thermal properties and chemical resistance. It can be seen from Figure 6 that the fractural surface of the impact specimen for GF-reinforced PSF composite is very rough, and a great many of fibers are pulled out.

With addition of ATS-C, the fractural surface of fiber-reinforced PSF composites tends to be smooth. The surface of the fibers, which is pulled out, adheres much resi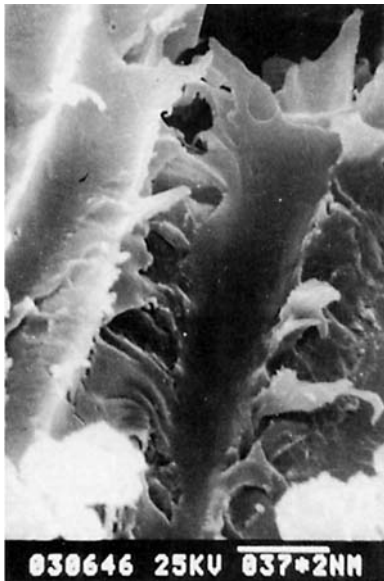n, and the resin adhered on the surface of the fiber increases with increasing processing temperature and time (Fig. 7). These results indicate that the fracture model of fiber-reinforced PSF composite changes from the interfacial debonding[7]
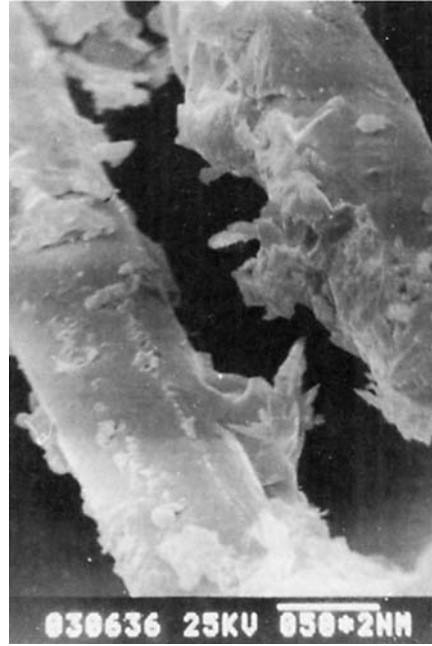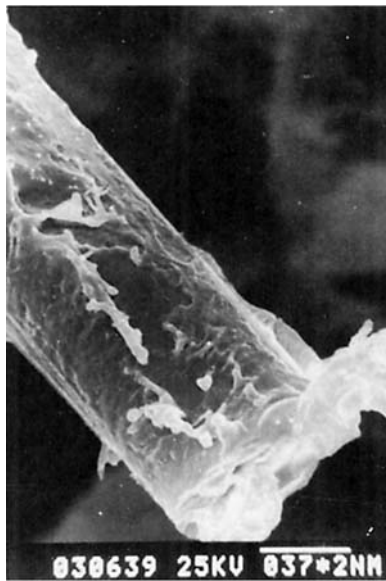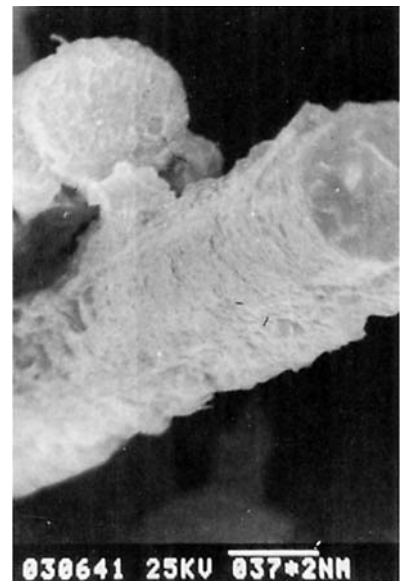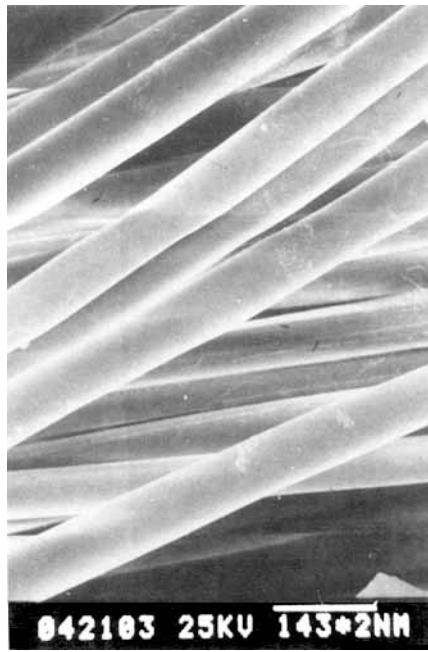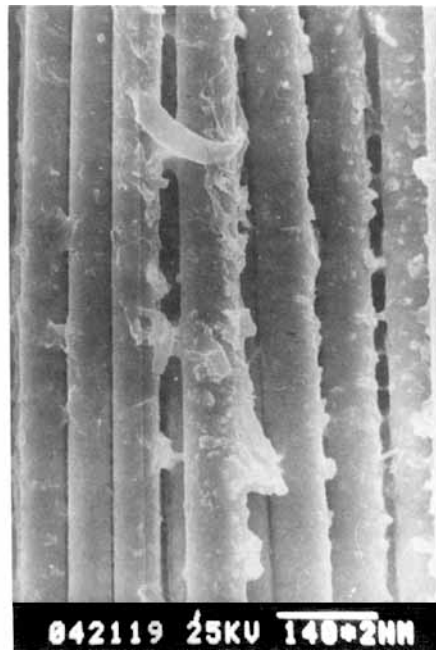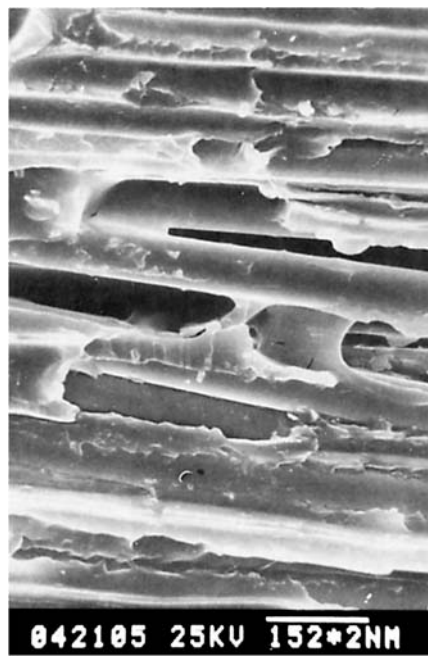

Figure 7   Interfacial bonding morphologies of impact specimens for fiber-reinforced PSF and ATS-C/PSF composites processed at different conditions.
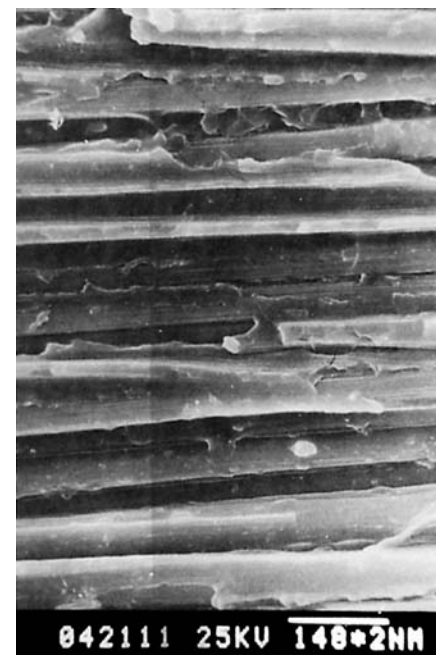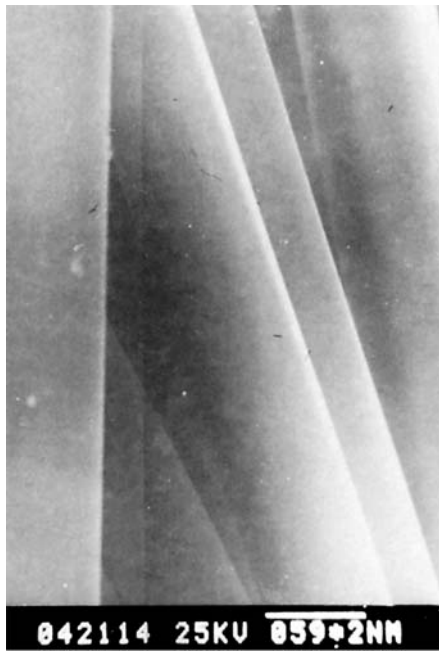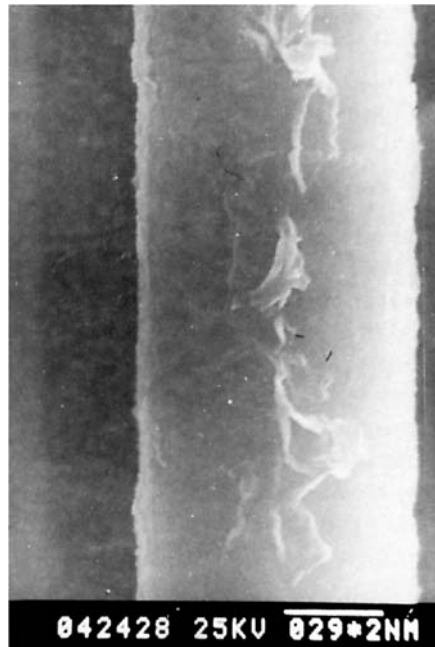
Figure 8 Surface morphologies of fiber-reinforced PSF and ATS-C/PSF composites etched in 1,2-dichloroethane for 96 h.

A

B

C

D

Figure 8   (*Continued from the previous page*)

into the matrix fracture at the interfacial region by addition of ATS-C and by increasing the processing temperature and time.

SEM observation of the surface of fractured specimen immersed in 1,2-dichloroethane for 96 h (Figs. 8 and 9) indicates that no resin is adhered on the fiber surface for GF-reinforced PSF composite. However, the resin adhered on the fiber surface of fiber-reinforced ATS-C/PSF composites increases as the processing temperature and time increase. It is suggested that ATS-C reacts to form crosslinked network structure in the cured blends and in the interface region between fiber and matrix (Figs. 10 and 11) to lead the formation of semi-interpenetrating polymer networks. This type of molecular structure caused by the reactive plasticizer can provide better chemical resistance, and the interfacial bonding and the property between fiber and matrix of fiber-reinforced composites can be improved.

SEM observation of fractured surface and the surface of etched specimens indicates that the interfacial bonding become stronger as the processing temperature and time increase. However, the ILSS of fiber-reinforced ATS-C/PSF composites de-

D'

Figure 10   Morphology of fractured specimen etched in 1,2-dichloroethane for 96 h.

creases. Lee[8] has also found that the tensile strength of acetylene-terminated sulfone cured at 250°C is lower than that of specimen cured at 200°C and the tensile modulus decreases with increasing cure time and temperature. The explanation for the decrease in properties of blends and composites cured at the higher temperature and longer time is that the network formed is "too tightly" crosslinked due to a higher extent of crosslinking. Previous work has shown that the extent of crosslinking of ATS-C in ATS-C/thermoplastic blends increases with increases in cure temperature and cure time.[2] It is possible that crosslinking causes stress concentration in the cured blends and in the interface region between fiber and matrix for fiber-reinforced composites so that the properties of fiber-reinforced ATS-C/PSF composites decrease as the processing temperature and time increase.

D'

Figure 9   Interfacial bonding morphologies of fiber-reinforced ATS-C/PSF composites etched in 1,2-dichloroethane for 96 h.

CONCLUSIONS

By addition of reactive plasticizer acetylene-terminated sulfone (ATS-C) oligomer, tensile, flexural
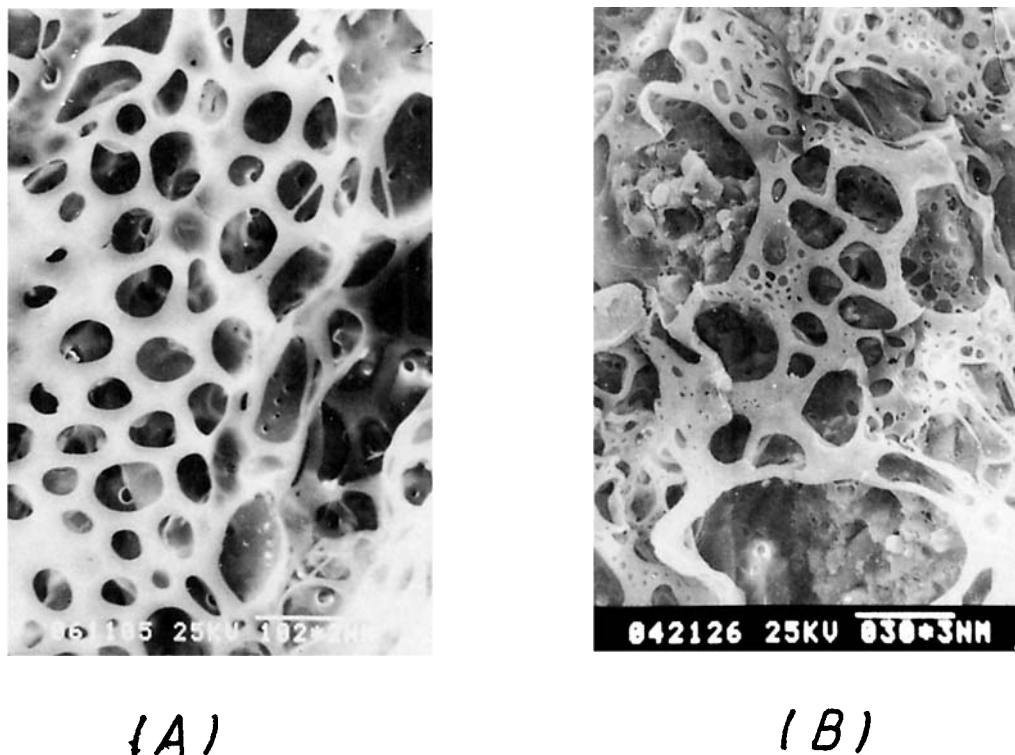
(A)   *(B)*

Figure 11 Network structure of (a) ATS-C/PSF blend and (b) fiber-reinforced ATS-C/PSF composite etched in 1,2-dichloroethane for 96 h.

properties and impact strength of glass fiber–reinforced polysulfone (GF/PSF) composites decrease and the mechanical properties of GF-reinforced ATS-C/PSF composites decrease as the processing temperature and time increase. However, carbon fiber–reinforced ATS-C/PSF composites exhibit higher mechanical properties, and the mechanical properties of GF-reinforced ATS-C/PSF composites increase as the processing temperature and time increase. Although the ILSS of composites decreases, interfacial bonding between fiber and matrix becomes stronger. The fractural model of fiber-reinforced PSF composites changes from the interfacial debonding fracture into the matrix fracture at the interfacial region by addition of ATS-C. The end-use temperature of polysulfone can be retained and solvent resistance can be improved due to the formation of a semi-interpenetrating polymer network.

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