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Toughening of Epoxy Composite by Dispersing Polysulfone Particle to Form Morphology Spectrum

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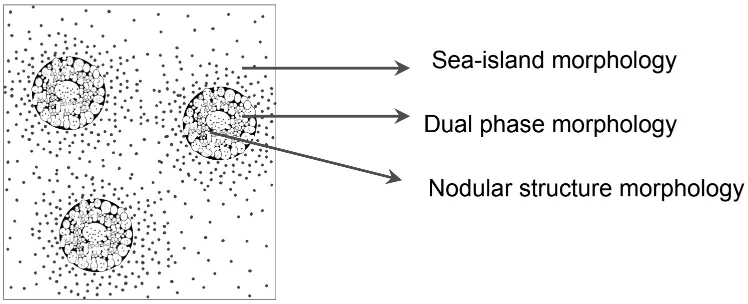
Summary

Fracture toughness of epoxy composite with polysulfone(PSf) particles to form morphology spectrum was investigated. The epoxy resin was based on diglycidyl ether of bisphenol-A(DGEBA type) and diaminodiphenylsulfone(DDS). 1K carbon fabric was used as the reinforcing material. The morphology spectrum which has gradual change of the morphological feature resulting from the concentration gradient of PSf in the composite can be obtained by spreading PSf particles in between the carbon fiber reinforced epoxy prepregs before cure. The relative rate of the dissolution and diffusion of the PSf particle in the epoxy determine the concentration gradient of the PSf. The fracture toughness of the composite with 21 wt % large size particles was 2.2 times higher than that of the unmodified composite. This result was ascribed to the plastic deformation of the continuous PSf rich phase formed inside the swollen PSf particle.

Introduction

It has been reported (1) that a semi-IPN with morphology spectrum could be obtained by dispersing thermoplastic particles in the epoxy oligomer before cure, three competing kinetics determime the morphology; 1) rate of dissolution/diffusion of thermoplastic, 2) rate of curing, 3) rate of phase separation. The semi-IPN prepared by dispersing thermoplastic particles has isotropic properties since the morphology spectrum is obtained in the radial direction. However the semi-IPN prepared by inserting thermoplastic film has anisotropic properties since the morphology spectrum is obtained in the thickness direction. Figure 1 shows the sketch of a morphology spectrum by the particle dispersion method (13).

To make isotropic properties with second phase dispersion, phase separation during the curing of initial homogeneous solution has been widely used. An alternative method includes introducing preformed spherical particles in thermoset formulation. For toughening the thermoset materials, acrylic elastomers (2-4), poly(butylenes terephthalate) (5), and core-shell particles with a rubbery core embedded in a compatibilizing thermoplastic shell (6-9) have been reported. In this case, the added



[Figure 1] Schematic illustration of the morphology spectrum by particle dispersion

particles remained in randomly dispersed state are immiscible with the thermoset resin, whereas in a few cases adding miscible thermoplastic particles with a diameter of 2 to 35 μm did not show any second phase.

The object of this paper is to toughened epoxy composite with the morphology spectrum by dispersing PSf particles between prepregs. The PSf particles were made by a milling machine. The fracture toughness of the composite is also discussed.

Experimental

Materials

1K plain woven carbon fabric (T300, Toray Co.) was used as a main reinforcing material. Diglycidyl ether of bisphenol-A (DGEBA) type epoxy resin (YD128, Mn=378, Kukdo Chemical Co., Korea) was used as a matrix resin and 4,4'-diaminodiphenylsulfone (DDS, Mn=248, Aldrich Co.) was used as a curing agent. The epoxy resin and the curing agent were mixed in 1:1 equivalent ratio. The thermoplastic modifier to toughen the epoxy resin was amorphous PSf (PSf, Udel P1700, Mn=29,400, Amoco Co.) with T_g of 190 ^{o}C. Chemical structure of the material is shown in Figure 2.

PSf particle

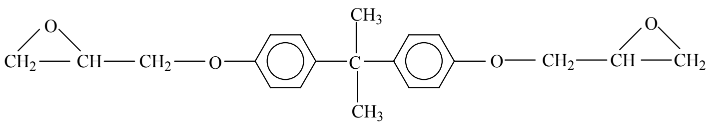
PSf pellets were milled by a 12,000 rpm milling machine. Sizes of the milled particles were analyzed in isopropyl alcohol by laser particle size analyzer (Analysette 22, Fritsch Co.). The particles were sieved to have uniform particle size range and dried at 150 ^{o}C under vacuum condition to remove remaining water. The particles were stored in a vacuum desiccator.

Carbon fiber/epoxy prepreg

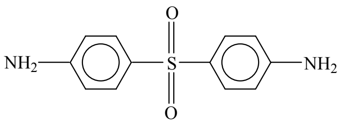
Prepreg was made by an automatic prepreg coating tower with 3 stage heating chamber. Heating temperature of the coating tower was 105 ^{o}C and the feeding speed of the prepreg was 1 m/min. Average resin content of the prepreg was 40.1 %, average volatile content was 1.92 %, and the average resin flow was 12.0 %. Degree of cure of the epoxy resin in the prepreg was 16 %, which was measured by DSC.

Composite specimen

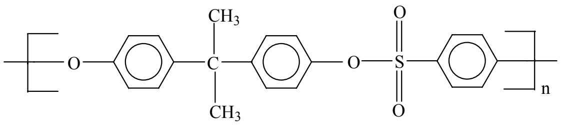
The prepreg was cut in size of 150 x 150 mm and 24 plies of the prepreg were laid up on the mold. The prepared PSf particles were dispersed between the 12th and 13th



Diglycidyl ether of bisphenol-A(DGEBA)

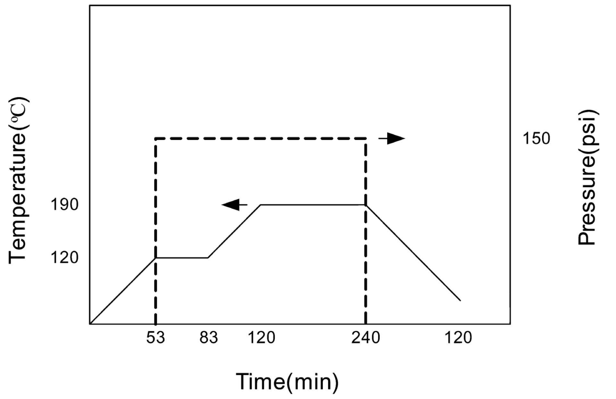


4,4'-diaminodiphenylsulfone(DDS)



Polysulfone(PSf)

[Figure 2] Chemical structure of the material

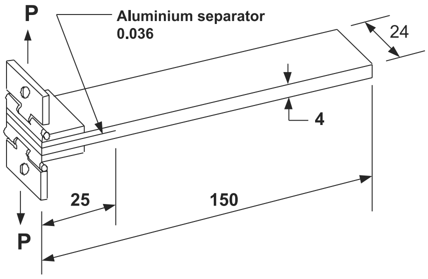


[Figure 3] Curing cycle of the composites

prepreg and the prepreg was cured at an autoclave. Curing cycle of the composite was shown in Figure 3.

Fracture toughness energy measurements

The mode I interlaminar fracture energy, G_{IC}, was measured by the tensile testing machine (Instron 1122) using a standard double-cantilever beam (DCB) specimen shown in Figure 4 (11,12). The crosshead speed was 2 mm/min. During each loading cycle, the displacement and the crack length were simultaneously monitored. Crack propagation was monitored with portable microscope situated in front of the specimen. The critical strain energy release rate, G_{IC}, was calculated from the following equation:



[Figure 4] DCB test specimen (dimensions in mm)

$$G_{IC} = \frac{P_C^{\;2}}{2w}\frac{dC}{da}$$

where P_C is the applied load, C is the compliance, a is crack length, and w is specimen width.

Morphology

The morphology of the specimen was investigated using a scanning electron microscopy (SEM, JSM-5610, JEOL Co.). The fractured surfaces of the semi-IPN were coated with a thin layer of a gold-palladium alloy (12). To investigate the morphology, the fracture surface of the specimens was etched with methylene chloride and dried for 1 hr at 100 ^{o}C in vacuum oven.

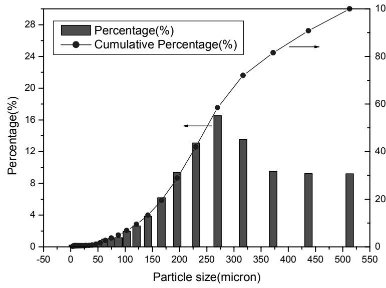
Results and discussion

PSf particle characterization

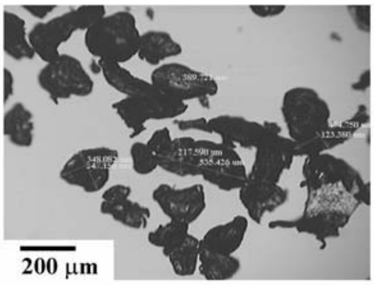
Figure 5 shows the result of the PSf particle size analysis and Figure 6 shows the photograph of the PSf particles by optical microscopy. The milled PSf particles have an irregular shape and the average aspect ratio was 1.96. Epoxy can diffuse only onto the surface of the PSf particles because there are no voids in the PSf particles. To investigate the effect of the PSf particle size, we used two groups of the PSf particles in size; one is small (50~150 μm) and the other is large (150~250 μm).

Formation of morphology spectrum

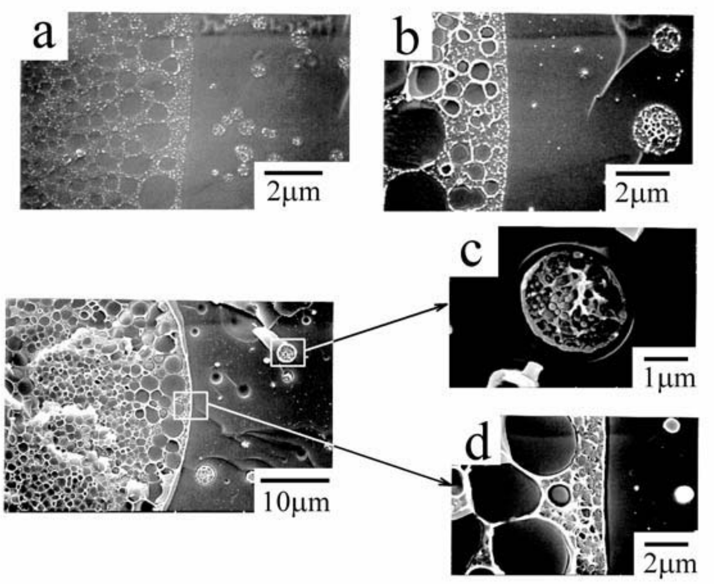
Min et al. (13) explained the formation of morphology spectrum by dispersing PSf particle in epoxy. To investigate the formation of the morphology spectrum, we quenched the specimen at constant time interval during the cure and observed the fracture surface by SEM. Figure 7 shows the SEM photographs of the morphology spectrum formed during cure. The curing temperature was 190 ^{o}C. Two minutes after curing started (Figure 7a), the nodular structure was formed inside the particle by the spinodal decomposition (SD) mechanism and the sea-island structure was formed in the matrix by the nucleation and growth (NG) mechanism. Inside the particle and close to the boundary, the PSf concentration is low and the viscosity is also relatively low, such that Figure 7b, the SD proceeds further to form larger domain and later undergoes secondary phase separation which forms small nodular structure in the PSf rich phase (Figure 7c). Figure 8 shows the conversion of epoxy resin with time at 190 ^{o}C.



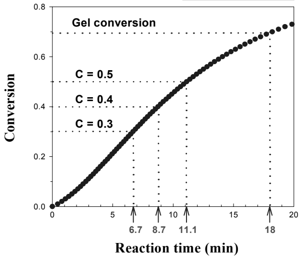
[Figure 5] Distribution of the PSf particles



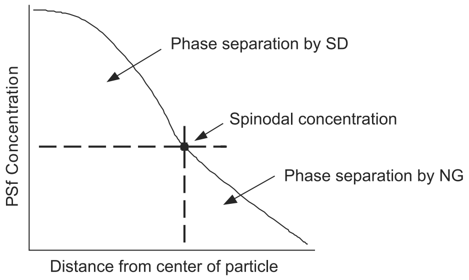
[Figure 6] Photograph of the PSf particles



[Figure 7] Morphology spectrum formation process; (a) 2 min (b) 4 min (c) 6 min (secondary phase separation in the sea-island structure) (d) 6 min (secondary phase separation in the nodular structure)



[Figure 8] Conversion of epoxy resin with time



[Figure 9] Phase separation with the PSf concentration

During the curing process of epoxy resin, the epoxy oligomer penetrates into the PSf particle and the dissolved PSf slowly diffuses out to the epoxy matrix. A concentration gradient is formed (Figure 9). Where the concentration of PSf at the core of the particle is high and the concentration gradually decreases in the radial direction from the center of the particle. When phase separation is started, the spinodal concentration will be the boundary. At high concentration than the spinodal concentration, phase separation occurs by SD mechanism and a co-continuous morphology is obtained. At lower than spinodal concentration, sea-island morphology is formed by NG mechanism. So the boundary shown in Figure 10 is not the boundary of the particle, but the boundary showing the spinodal concentration of the epoxy/PSf. As the epoxy curing is further proceeded and due to the high viscosity, secondary phase separation occurs and complex morphology is formed inside the as well as outside the particle.

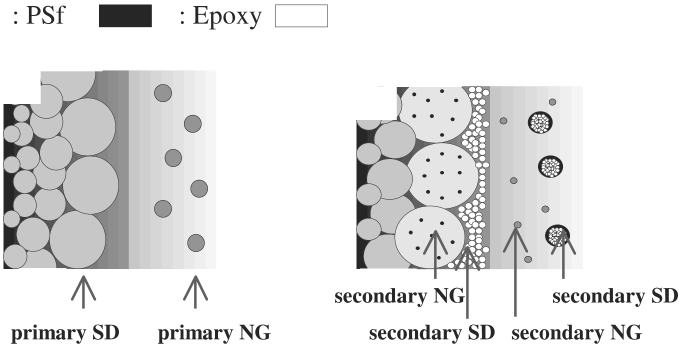
Mode I Fracture toughness (G_{IC}) of the composites

Figure 11 shows the critical strain energy release rate, G_{IC}, of PSf particles modified epoxy composites as a function of PSf content. The rectangular symbols are for the large size (150~250 μm) PSf particles and the circular symbols are for the small size (50~150 μm) particles. The G_{IC} of 20 wt % the large size PSf particle modified epoxy composite was 2.2 times higher than that of the unmodified epoxy.

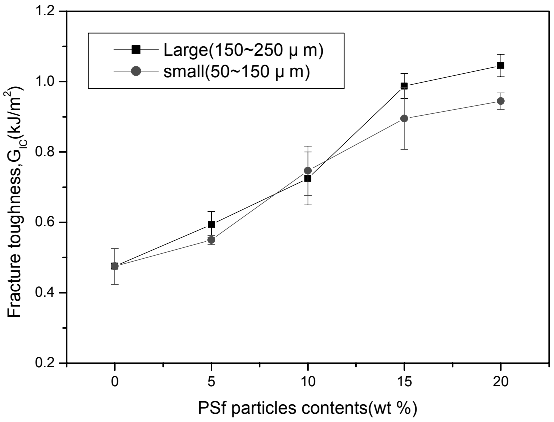
Two different size of the particle shows similar increasing pattern to 10 wt % of PSf. From 10 to 20 wt %, the G_{IC} value of the large size PSf particles was higher than that of the small size particles. It was reported by Kim et. Al. (1) that the fracture toughness was depended on the area of the co-continuous morphology. We can see that if the particle size is large, the diffusion and dissolution of the PSf particle is slow due to lower surface area of the particle, and the concentration inside of the particle at given time is higher in the case of the large particle size of PSf added. This higher concentration will give large area of the co-continuous morphology inside the particle.

Morphology of the fracture surfaces

Figure 12 shows the fracture surface of the PSf particle modified epoxy composite. SEM photographs of the fracture surface show that dual phase morphology made by the secondary phase separation was dominant on the fractured surface. The epoxy domains are spherical and the PSf domains are connected with each other. This dual phase morphology is the same as that obtained in Figure 7. The crack tip proceeded through the PSf and epoxy dual phase and the ductile deformation of PSf is observed.



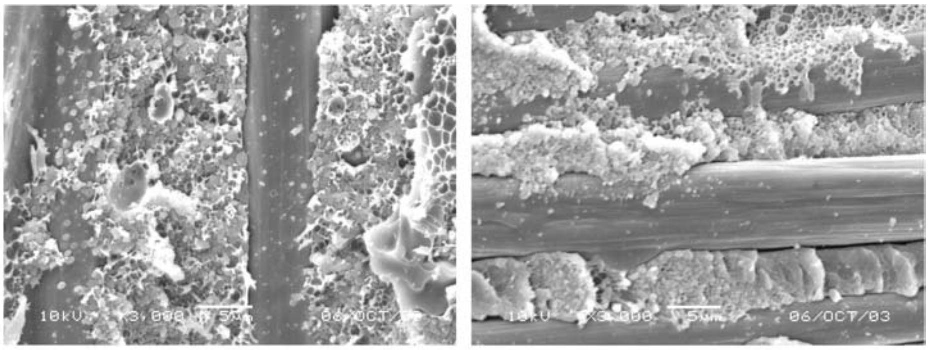
[Figure 10] Schematic illustration of the morphology spectrum by the particle dispersion



[Figure 11] Mode I Fracture toughness (G_{IC}) of the PSf particles modified epoxy composites

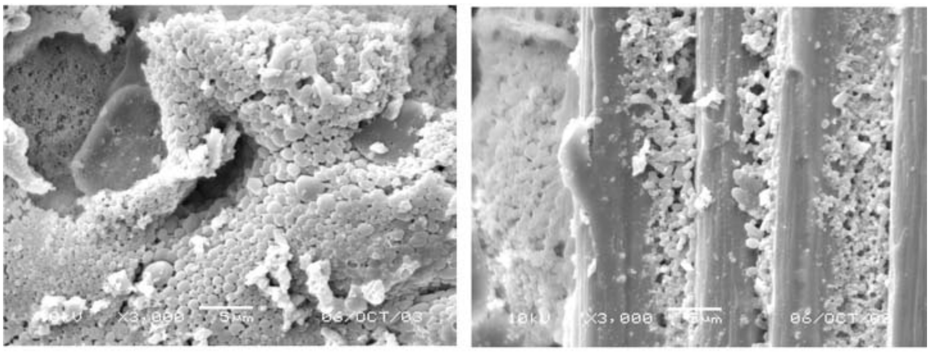
This result indicates that the PSf and epoxy form the morphology spectrum in the composite and it increases the G_{IC} value by absorbing the fracture energy.

To observe only the epoxy domains separate from PSf, the fracture surface was etched with methylene chloride at room temperature for 10 minutes. Figure 13 shows the etched fracture surface of the PSf particle modified epoxy composite. We can observe the nodular structure of epoxy at the fractured surface. This result indicates that the PSf and epoxy dual phase morphology contributes to the enhancement of the fracture toughness of the composite.



(a) (b)

[Figure 12] Fracture surface of the PSf particle modified epoxy composite (X3000); (a) 15 wt % (b) 20 wt %



(a) (b)

[Figure 13] Etched fracture surface of the PSf particle modified epoxy composite(X3000); (a) 15 wt % (b) 20 wt %

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