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# Fracture toughness of polysulfone/epoxy semi-IPN with morphology spectrum

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Summary

The fracture toughness of the semi-IPN's of crosslinked epoxy and linear polysulfone(PSf) having morphology spectrum was investigated. The epoxy resin was based on diglycidyl ether of bisphenol A(DGEBA) and diaminodiphenylsulfone(DDS). The morphology spectrum, which has the gradual change of the morphological feature resulting from the concentration gradient of PSf in the epoxy resin can be obtained by inserting a PSf film in DGEBA/DDS mixture before cure. The relative rate of the dissolution of the PSf in the epoxy oligomer and the rate of curing reaction determine the concentration gradient of the PSf. In the region where the PSf concentration is less then 5%, sea(epoxy)-island(PSf) morphology is observed. As the concentration of PSf increases, the morphology changes to nodular structure, inverted sea-island, and PSf/epoxy homogeneous phase. Up to overall 10wt% of PSf, the fracture toughness of the PSf modified epoxy with morphology spectrum was higher than that of the counterpart with uniform concentration of PSf. These results were ascribed to the plastic deformation of the continuous PSf rich phase which was present in the morphology spectrum.

## ***Introduction***

Recently, toughening of thermosets has been achieved by the incorporation of high performance thermoplastics such as polyetherimide(PEI)(1)-(5), polysulfone(PSf)(6),(7), and polyethersulfone(PES)(8),(9) etc. The fracture behavior of the thermoplastic modified thermoset is dependent upon the morphological feature categorized by the sea-island morphology, dual-phase morphology, and nodular structure. The sea-island morphology which was formed via nucleation and growth phase separation mechanism at low modifier content showed moderate increase in fracture toughness, while dual-phase morphology or nodular structure which was formed predominantly via spinodal decomposition mechanism at higher modifier content showed substantial increase. It is ascribed that when the thermoplastic rich phase becomes continuous, the toughening mechanism changes. That is, the plastic deformation of the continuous thermoplastic rich phase found in dual phase or nodular structure is more effective to enhance the fracture toughness than the crack pinning or crack path deflection which was observed in the sea-

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island morphology.
To expand the plastic deformation zone size, the technique of inserting a tough material into the composite laminate as an extra interlaminar layer, has been developed. Apart from that the inserted toughening layer remained a discrete layer within the interlayer in the selective toughening method, Johnston et al(10), reported that the gradient semi-interpenetrating polymer networks of which the concentration of thermoplastic increases gradually over the thermoset matrix as the distance increases could be applied to produce an enhancement in fracture toughness for the carbon fiber composite, despite their system did not exhibit any phase separated morphology because the miscibility of the two component was excellent. However, when the miscibility was not that good, concentration gradient may result in morphology spectrum. With this concept, we could expect the positive toughening effect of the thermoplastic modified thermoset at low modifier content because the capacity for absorbing fracture energy can be increased through nodular structure, and homogeneous region, which can only be achieved by having morphology spectrum caused by the concentration gradient of thermoplastic.

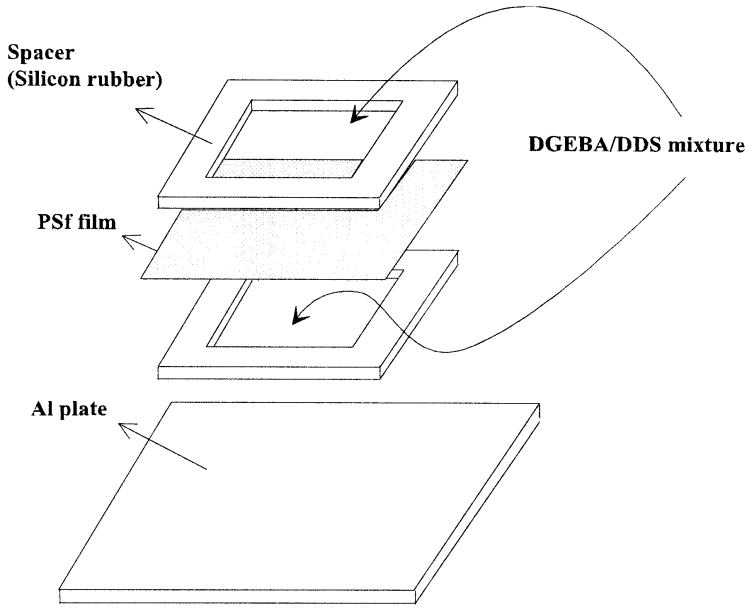
## ***Experimental***

### ***Materials***
Diglycidyl ether of bisphenol-A(DGEBA) epoxy resin(YD128, Kuk Do Chem.) with an aromatic amine curing agent, 4,4'-diaminodiphenyl sulfone(DDS, Aldrich Chem. Co.) were used as thermoset components. The thermoplastic modifiers used for toughening epoxy was amorphous polysulfone(PSf) (Udel 1700, Amoco). All materials were used as received.

### ***Specimen preparation***
PSf modified epoxy with morphology spectrum was prepared as follows. The PSf was dissolved in methylene chloride($CH_2Cl_2$) to obtain 10wt% solution. This solution was poured on a clean glass plate and casted by Gardener knife. The PSf solution casted was dried at room temperature for 2hr and heated slowly up to 150°C under vacuum condition to remove remaining solvent, and dry PSf film was obtained. Silicon spacers with 1mm thickness were attached on both sides of the PSf film. The epoxy resin was heated on a hot plate to 140°C, and stoichiometric amounts of DDS were added while stirring for about 7min. Firstly, DGEBA/DDS mixture was poured in the gap between aluminum plate and PSf film, and then the mixture was poured again onto the PSf film.(Figure. 1) Finally, the mixture was cured at 150°C for 6hr and postcured at 220°C for 1.5hr.
For comparison, a control sample of the PSf/epoxy semi-IPN's with uniform concentration of PSf was prepared by conventional solution-mixing techniques(11) under the same cure conditions.

### ***Measurement***
The critical stress intensity factors, $K_{IC}$, of the fully cured PSf modified epoxy were measured according to ASTM E399-78a. Measured $K_{IC}$ values were converted to critical strain energy release rate, $G_{IC}$, using the relationship [1].

$$G_{IC} = K_{IC}^2(1-\nu^2)/E \qquad [1]$$

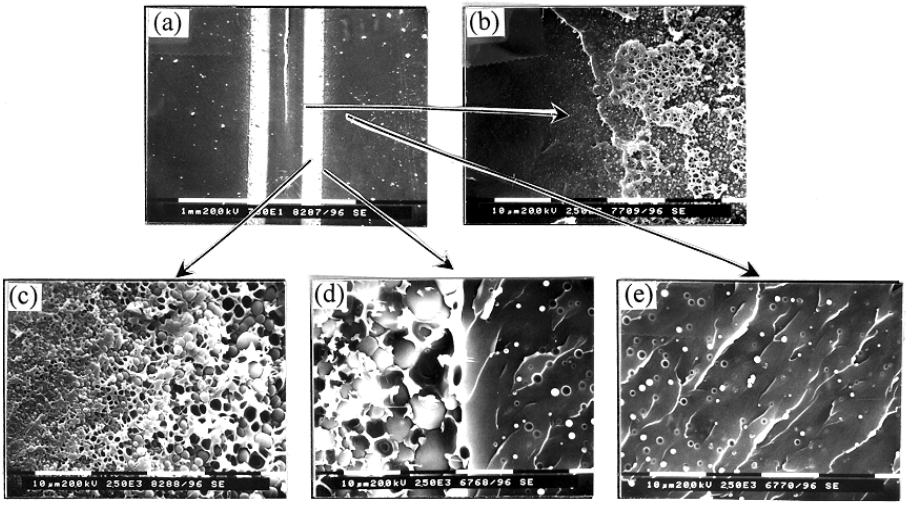



[ Figure 1 ] The schematic picture for sample preparation

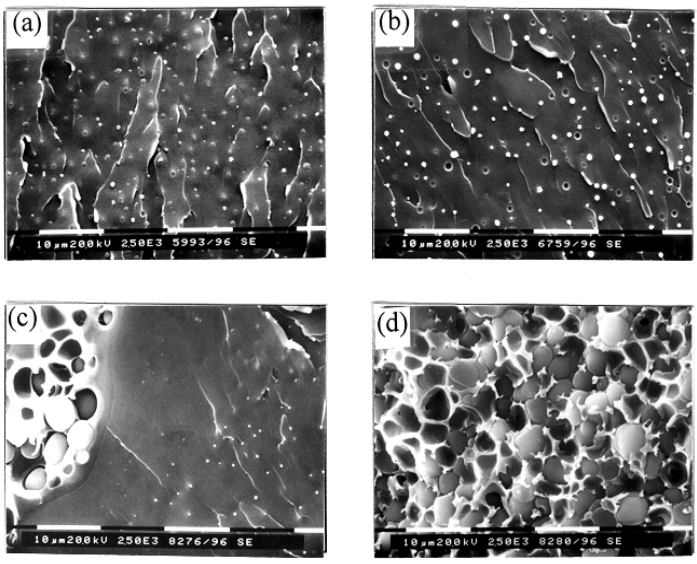
where Poisson ratio ν was taken as 0.35 for all samples, and E is Youngs modulus.
After the fracture test, the fracture surfaces were observed by Philips 535M scanning electron microscope(SEM).

***Results and discussion***

Figure 2 shows the morphology spectrum formed in postcured modified epoxy containing 8% overall PSf. The morphology spectrum consisted of 5 different regions from a macroscopic point of view. The PSf/epoxy homogeneous region, sea(PSf)-island(epoxy) morphology, nodular structure( co-continuous ), sea(epoxy)-island(PSf) morphology and neat epoxy region were observed starting from the center of specimen. As shown in Figure 3, considering the morphology of the PSf/epoxy blends having uniform PSf composition, morphology spectrum resulted from the concentration gradient of PSf component which was developed within the epoxy resin during the curing process. In the early stage of cure process, PSf film began to be dissolved from the interfacial region between PSf film and epoxy resin, and to be diffused by concentration gradient. In intermediate stage of cure process, the concentration gradient was developed in epoxy resin. It was already known that the phase separation mechanism depended upon the concentration of PSf. Therefore, in the region that the PSf concentration was below 10 wt%, sea-island morphology was developed by nucleation-growth mechanism. On the other hand, at the region where the PSf concentration was over 15 wt%, nodular structure was developed by spinodal decomposition mechanism. The dual phase morphology exhibiting coexisting phases of sea-island and nodular morphology was shown in Figure 3 at 15% PSf composition when the PSf composition is uniform. However, dual phase




[ Figure 2 ] Morphology of PSf modified epoxy with morphology spectrum( overall PSf content = 8wt%) : (a) low magnification (b) inverted sea-island morphology (c) nodular structure (d) boundary region (e) sea-island morphology



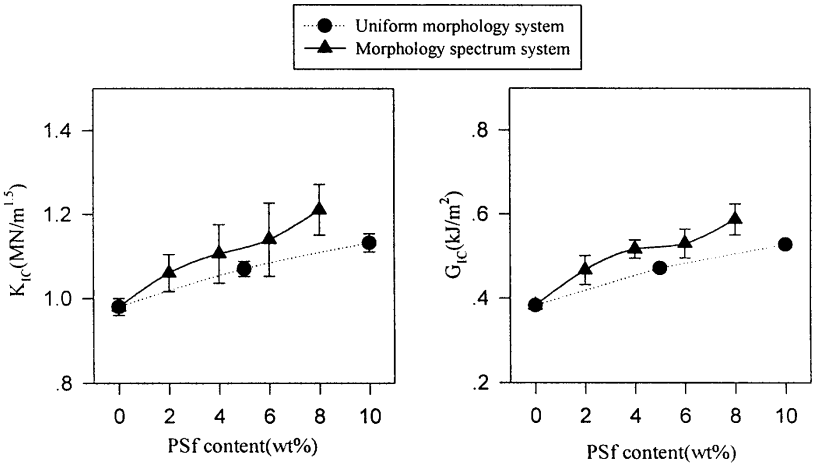

[ Figure 3 ] Morphology of PSf modified epoxy with uniform compositions :
PSf = (a) 5wt% (b) 10wt% (c) 15wt% (d) 20wt%

morphology was not clearly observed in the morphology spectrum since the concentration gradient was very steep around 15%.

The morphology of each region was observed as follows ; In homogeneous region, a small amount of epoxy component was dissolved in PSf rich phase not to show any phase separated morphology. In the inverted sea-island morphology, sea(PSf)-island(epoxy) morphology, the trace of spherical holes was found, which was thought of as the cavity that the dispersed epoxy rich domain was taken off when the fracture stress was applied. In nodular structure, it is noted that the size of nodules increased gradually from 0.1μm to 10μm due to the change in the viscosity of the reaction mixture as the PSf concentration varies, while the size of the spherical PSf rich domain in the sea-island morphology did not show large change in PSf domain size.

As shown in Figure 4, in the range of 2 - 8 PSf overall wt% composition, the fracture toughness of the PSf modified epoxy with morphology spectrum showed increased $K_{IC}$ and $G_{IC}$ values when compared to specimens having uniform PSf composition. The toughening effect of the morphology spectrum can be explained through the morphological analysis. In uniform morphology system, when the PSf content was less then 15wt% the dominant toughening mechanisms observed in Figure 3(a), (b) were crack path deflection mechanism and crack pinning, which are strongly dependent upon the domain size and the number of dispersed domains. However, because the size and the number of dispersed PSf domain slightly increased up to 10wt% PSf content, the $K_{IC}$ and the $G_{IC}$ of the uniform morphology system showed small increase in that compositional range. On the other hand, in morphology spectrum system with more than 4 wt% PSf content, not only sea-island morphology, but also other morphologies such as homogeneous region, inverted sea-island morphology and nodular structure were involved to absorb fracture energy. In Figure 2 (b)-(d), it was observed that the PSf continuous phase was deformed substantially. The main toughening mechanism of the semi-IPN's with morphology spectrum was observed to be the plastic deformation of the PSf rich phase. This plastic deformation was also observed in uniform morphology system when the PSf content was high, see Figure 3(c),(d).

By having the morphology spectrum, it was possible to obtain PSf continuous phase to induce plastic deformation with small amount of PSf modifier (2 to 8 wt%)




[ Figure 4 ] Fracture toughness of PSf modified epoxy with morphology spectrum compared with the counterpart with uniform morphology

[ Table 1 ] The thickness of different morphology layer observed in the morphology spectrum system

| PSf content (wt%) | 4 | 6 | 8 |
|---|---|---|---|
| Thickness of Morphology Layer | Nodular structure (240μm) | Homogeneous region (80μm) | Homogeneous region (180μm) |
| | | Sea(PSf)-island(epoxy) (20μm) | Sea(PSf)-island(epoxy) (20μm) |
| | | Nodular structure (240μm) | Nodular structure (240μm) |
| | Sea(epoxy)-island(PSf) (260μm) | Sea(epoxy)-island(PSf) (260μm) | Sea(epoxy)-island(PSf) (260μm) |

( overall thickness of the sample = 3000μm )

The thickness of the different morphology layer is lied in Table I. With only 4% of PSf, nodular structure showing continuous PSf phases was observed in about 10% of the specimen thickness. With 8% PSf, the continuous PSf phases occupied about 15% of the total thickness.

## ***Conclusions***

A novel method for toughening of brittle thermoset epoxy resin was developed by applying the morphology spectrum concept. For the formation of morphology spectrum, PSf film was inserted in epoxy resin before curing and by the competitive kinetics of PSf dissolution and epoxy curing, the concentration gradient of PSf was obtained, which induced morphology spectrum. In PSf/epoxy semi-IPN's with morphology spectrum having 6 wt% to 8 wt% PSf composition, 5 different morphologies, i.e., homogeneous region, inverted sea-island morphology, nodular structure, sea-island, and neat epoxy region, were found across thickness direction. The fracture toughness of 8 wt% PSf modified epoxy with morphology spectrum showed about 10% increase compared to the counterpart with uniform morphology. This increase was seen to be the result of the plastic deformation of the continuous PSf rich phase that was only found in morphology spectrum system when the amount of PSf modifier was less than 10wt%.

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