

# EPOXY RESIN TOUGHENED BY THERMOPLASTICS\*

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## ABSTRACT

Two kinds of tough ductile heatresisting thermoplastic, namely bisphenol A polysulfone (PSF) and polyethersulfone (PES) were used to toughen thermoset epoxy resin. A systematic study on the relationship between the molecular weight and the terminal group of the thermoplastic modifier and the fracture toughness of the modified resin was carried out. The morphology of PSF modified epoxy resin was surveyed. With the same kind of PSF the structure of the epoxy resin and the toughening effect of PSF was also investigated. The fractography of PSF particle modified epoxy was examined in detail with SEM. The contribution of every possible energy absorption process has been discussed. Crack pinning mechanism seems to be the most important toughening mechanism for tough ductile thermoplastic PSF particle modified epoxy system.

## INTRODUCTION

Epoxy resins are widely employed as the basis for adhesive compositions and as matrix material for composites.

In order to increase the crack resistance of the epoxies, rubber has often been used to toughen epoxy resin, one of the most successful cases is the use of carboxyl terminated nitrile rubber (CTBN) to toughen epoxy resin. Several mechanisms<sup>[1,2,3]</sup> have been proposed to explain the improved toughness of the rubber modified epoxy. Many researchers<sup>[4,5,6]</sup> consider that the toughness enhancement by rubber modification is principally due to the plastic deformation of the matrix and the rubber particles at the crack tip. Therefore the toughening ability of rubber was found to be highly dependent on the crosslink density of the epoxy matrix. Huang, Sun and Zhao<sup>[5]</sup> or Yee and Pearson<sup>[6]</sup> in their research work all proved that the structure of epoxy resin, especially the  $\bar{M}_c$  value (average molecular weight between two adjacent crosslinks) of the cured network has a marked influence on the toughening effect of rubber. This influence appears to be much more important than the other factors such as the composition and the volume fraction of the dispersed phase and the distribution of rubber particle sizes. In the case with very highly crosslinked rubber toughened epoxy resin, the epoxy matrix offers quite strong resistance against the voiding and shear yielding, therefore the enhancement of the fracture toughness by rubber is obviously lower. However in rubber modified epoxy resin, a small amount of rubber is dissolved in the epoxy matrix and makes the matrix flexible. Therefore the improvement in fracture toughness by rubber has usually been at the expense of the bulk properties especially the modulus and  $T_g$ . Especially for very high crosslinked epoxy resin, the fracture toughness of the rubber toughened epoxy will not enhance very much, but its modulus and  $T_g$  will reduce obviously (see Table 4).

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Recently another approach has been taken to modify the epoxy resin to meet the requirement of the high performance epoxy composite matrix. This approach seems to provide better improvement in the overall properties of the resulting network without any significant loss in modulus and  $T_g$ . In this method tough ductile chemically and thermally stable engineering thermoplastics have been utilized. Bucknall and Partridge<sup>[7]</sup> studied polyethersulfone (PES) modified trifunctional epoxy (ERL 0510) and tetrafunctional epoxy resin (MY720). Diamant<sup>[8]</sup> investigated polyetherimide (PEI) modified epoxy resin. Raghav<sup>[9]</sup> studied PES modified MY 720, aromatic anhydride was used as curing agent. McGrath et al.<sup>[10, 11, 12]</sup> have reported about amino or hydroxy terminated polysulfone (PSF) modified epoxy resin. They found that the fracture toughness of the modified materials was enhanced and suggested the ductile deformation (stretching and tearing) of PSF particle and the plastic deformation of the epoxy matrix around these particles were the main energy absorbing processes.

In our research work a systematic study on the relationship between the molecular weight and the terminal group of the thermoplastic modifiers and the fracture toughness ( $K_{Ic}$  or  $G_{Ic}$ ) of PES and PSF modified epoxy resin was carried out. The morphology of the PSF modified epoxy resin was studied. With the same kind of thermoplastic modifier, the structure of the epoxy resin and the toughening effect of the modifier was also investigated. The microstructure of the modified epoxy resin was examined with SEM and the toughening mechanism of these modified system was discussed.

## EXPERIMENTAL

### Material

Epoxy resin: E51 (diglycidyl ether of bisphenol A, mol. wt. 403) was supplied by Wu Xi Resin Factory. AG80 (tetraglycidyl 4, 4'-diaminodiphenyl-methane) was supplied by Shanghai Research Institute of Synthetic Resin.

Curing agent: 4, 4'-diaminodiphenylsulfone (DDS) and piperidine (Pip) were purchased (reagent grade).

Modifiers: Cl-PSF-Cl and HO-PSF-OH of various molecular weights were prepared in this laboratory. HO-PES-OH oligomer of various molecular weights were kindly provided by Ji Lin University. The  $\bar{M}_n$  of the above PSF and PES modifiers were measured either by potential titration of their end groups or by GPC. A higher molecular weight PSF was from Shanghai Shu Guang Chemical Industrial Factory. Carboxyl terminated nitrile rubber (CTBN) ( $\bar{M}_n = 3030$ , AN content = 30%) was made in this laboratory.

Synthesis of the neat and modified epoxy resin moulding material: The neat resin or the epoxy resin with the dissolved modifier was heated in a three neck flask to a certain temperature and then degassed. After that the curing agent was added and stirred thoroughly. Then the mixture was poured into a preheated steel mould and cured in the oven according to the following curing procedures:

For AG80/DDS 4h. /130 °C, 2h. /177 °C and post cured 1h. /200 °C

For E51/DDS2 -2.5h. /140 °C (until gelation), 2h. /190 °C.

For E51/Pip 16h. /120 °C.

### Measurements

**Fracture toughness:** Measured according to ASTM E-399-83. The dimension of three point bending specimen was  $5 \times 10 \times 55$  mm. The detailed testing method was given in reference [13].

**Young's modulus:** Measured according to ASTM D-790. The dimension of the three point bending specimen was  $5 \times 10 \times 80$  mm.

**Compressive yielding stress ( $\sigma_{cy}$ ):** The  $\sigma_{cy}$  of three neat epoxies rectangular ( $5 \times 5 \times 10$  mm) specimens were compressed between two polished steel plates.  $\sigma_{cy}$  was calculated by the formula  $\sigma_{cy} = \frac{p_y}{A_0} (1 - e_y)$ , where  $p_y$  and  $e_y$  are the load and strain at yielding respectively.  $A_0$  is the initial cross-section area of the specimen.

A cross-head speed of 1 mm/min. was chosen in both bending and compression tests.

**Glass transition temperature ( $T_g$ ):** Du pont 900 DSC was used, the temperature raising speed was 10 °C /min.

### Microstructure observation

Hitachi Model S-450 SEM was used, the fracture surfaces were sputter coating with gold.

## RESULTS AND DISCUSSION

### 1. PES modified E51/DDS systems

$k_{lc}$ ,  $E$  and  $T_g$  values of HO-PES-OH' modified epoxy resin are listed in Table 2. The fracture surfaces of these modified epoxy resins are very smooth. The SEM observation and dynamic mechanical analysis (see Fig. 1) of these materials all prove that they are homogeneous systems. The slight raise of  $K_{lc}$  of the modified system is owing to the blending of ductile PES with brittle epoxy resin. The ductility of PES is raised with the enhancing of PES's molecular weight. This is at no expense of  $E$  values for the modified systems. The  $T_g$  values of the modified systems are even higher than those of the neat epoxy resins, this is probably caused by the higher  $T_g$  of PES. There is no phase separation of PES in this modified system, therefore the toughening effect of thermoplastics is not significant.

This result agrees with those of Bucknall, Partridge<sup>[7]</sup> and Diamant<sup>[8]</sup>.

**Table 1**  $K_{lc}$ , Flexural modulus( $E$ ) and  $T_g$  of PES modified epoxy resins \*

| No | $M_n$ of PES | $K_{lc}$ (Mpa $\sqrt{m}$ ) | $E$ (Gpa) | $T_g$ (°C) |
|----|--------------|----------------------------|-----------|------------|
| 1  | Control      | 0.64                       | 3.2       | 192        |
| 2  | 4,360        | 0.70                       | 3.1       | 194        |
| 3  | 8,910        | 0.71                       | 3.2       | —          |
| 4  | 14,100       | 0.71                       | 3.2       | 196        |
| 5  | 20,000       | 0.83                       | 3.1       | 194        |

\* E51 : DDS : PES=100:31:15 (weight ratio)

### 2. PSF modified epoxy resin systems

(1) The effect of molecular weight and terminal group of PSF.

Fig.2 is the experimental results of PSF modified E51/DDS systems. The  $K_{lc}$  value is raised as the molecular weight of PSF increased. This might be

explained by the increase of ductility of PSF with its molecular weight.

Various PSF modifiers shown in Fig.2 have three different cases of terminal groups, namely all chloro, all hydroxyl and partly chloro partly hydroxyl. The PSF with mixed terminal groups has a higher molecular weight. Fig.3 and 4 are the morphologies of the fracture surface of Cl-PSF-Cl and HO-PSF-OH modified epoxy resin respectively. In Fig. 4 only dispersed convex PSF particles could be seen, however in Fig. 3 except the convex particles, the concaved hole could also be found. These depressions might be formed while the PSF particles being peeled off from the matrix. It is believed that the adhesion of Cl-PSF-Cl particles to the epoxy matrix is weaker than that of HO-PSF-OH's, because the hydroxyl group but not the chloro group has been proved to be reactive to epoxy resin. There is chemical bond between HO-PSF-OH and epoxy resin, the PSF particles can only be stretched and teared instead of being peeled off from the epoxy matrix. This might be the reason why the  $K_{Ic}$  of Cl-PSF-Cl modified epoxy resin is lower than that of HO-PSF-OH modified system. (see Fig.2)



Fig. 1 Fracture surface of PES modified E51/DDS Epoxy

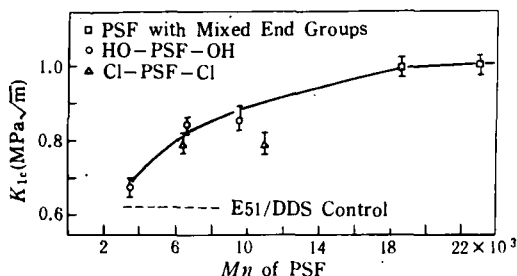


Fig. 2 The effect of  $\overline{M}_n$  and terminal groups of PSF Modifiers on  $K_{Ic}$  (15 parts of PSF was used)

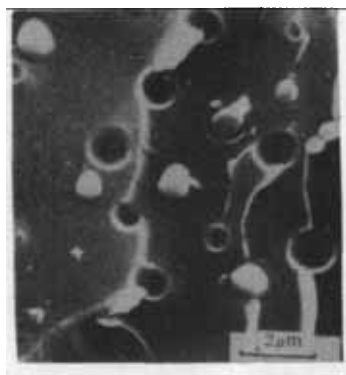


Fig.3 Fracture surface of Cl-PSF-Cl modified E51/DDS epoxy



Fig. 4 Fracture surface of HO-PSF-OH modified E51/DDS epoxy

## (2) The morphology of the PSF modified epoxy resins

In PSF modified epoxy resins three kinds of morphology were found. In type A, epoxy resin is the continuous phase and PSF small particles are dispersed phase as shown in Fig.5 and 6. When the content of PSF is less than 15%, this type of morphology is often got. The diameter of PSF particle is within several micrometers and depends on the molecular weight of PSF and the kinds of epoxy resins. The PSF modified epoxy with type A morphology can withstand the immersion of solvent such as chloroform. In type C, PSF is the continuous phase and epoxy resin is the dispersed phase as shown in Fig.8. The PSF content is usually greater than 20%. The dimension of the epoxy resin particles is rather large and these particles are packed together with a tiny amount of PSF filling in their interval. The PSF modified epoxy resin with C type morphology can not withstand the immersion of chloroform, the continuous PSF phase will dissolve in chloroform and the epoxy particles with the same dimension before immersion will be left. In type B(see Fig.7), it is a combination of type A and C. The PSF modified epoxy resin with type C morphology reaches a relatively high fracture toughness. This is probably owing to the different break form of this kind of material during fracture. The tearing of the PSF matrix and the peeling of the epoxy resin particles out off the PSF matrix may be the main energy absorbing processes.



Fig.5 Fracture surface of PSF ( $M_n = 18700$ , 10phr) modified E51/Pip epoxy (Type A)

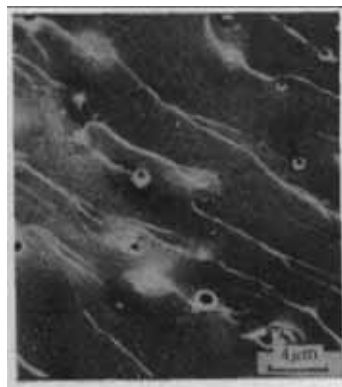


Fig. 6 Fracture surface of PSF ( $M_n = 18700$ , 10phr) modified AG80/DDS epoxy (Type A)

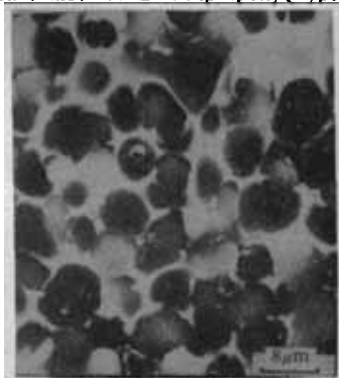


Fig. 7 Fracture surface of PSF ( $M_n = 18700$ , 20phr) modified E51/DDS epoxy (Type B)

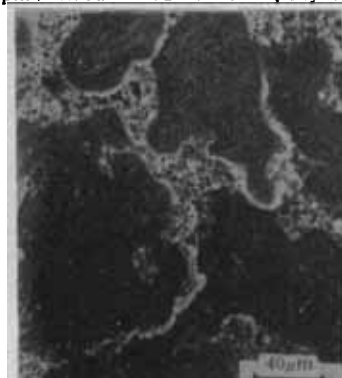


Fig. 8 Fracture surface of PSF ( $M_n = 18700$ , 20phr) modified E51/Pip epoxy (Type C)

### (3) Various epoxy resins modified by the same kind of PSF

Three kinds of epoxy resins were used. The  $M_n$  of PSF used was 18700. The experimental results are in Table 3. The crosslink density of E51/piperidine is the lowest and so is its  $T_g$ . The crosslink density of AG80/DDS is the highest and so is its  $T_g$ . The  $K_{Ic}$  values of the modified resins are all significantly higher than those of the neat epoxy resin. However it is different from the rubber modified system, the toughening ability of PSF was not found to be a strong function of the crosslink density of epoxy resin. The toughening abilities of PSF in different crosslink density epoxy matrices were nearly the same. The comparison between the PSF

and CTBN modified epoxy resins are listed in Table 4.

Fig. 5 and 6 are the SEM pictures of PSF modified fracture surface having a dispersed PSF second phase. For AG80/DDS system the dimension of the PSF particle was the largest ( $3\mu\text{m}$ ), voids could often be found within these particles. These might be caused by the contraction of PSF particles during cooling process. In these figures, it could be seen that the PSF particles were stretched and teared. No significant plastic deformation of the epoxy matrix could be found on the fracture surface. In addition, many characteristic tails or steps were found behind the PSF particles as shown in Fig. 9.

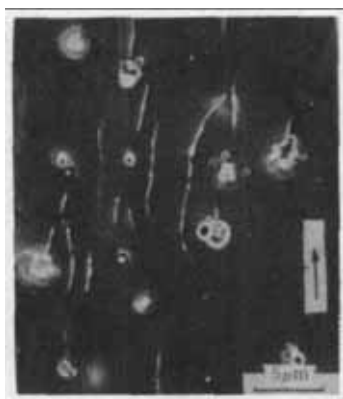


Fig. 9 Characteristic fracture surface of PSF modified AG80/DDS epoxy. The arrow represents the propagation direction of the crack.

Table 2 The properties of various PSF modified epoxy resins

| (a) PSF modified AG80/DDS epoxy resin |           |             |      |      |      |      |      |
|---------------------------------------|-----------|-------------|------|------|------|------|------|
| Contents of PSF                       | Phr wt. % | 0           | 5    | 10   | 15   | 20   |      |
|                                       |           | 0           | 3.45 | 6.67 | 9.68 | 12.5 |      |
| $K_{Ic}$ (MPa $\sqrt{m}$ )            |           | 0.51        | 0.67 | 0.67 | 1.0  | 1.0  |      |
| $G_{Ic}$ (J/m <sup>2</sup> )          |           | 54          | 96   | 97   | 209  | 219  |      |
| Type of Morphology                    |           | Homogeneous | A    | A    | B    | B    |      |
| (b) PSF modified E51/DDS epoxy resin  |           |             |      |      |      |      |      |
| Contents of PSF                       | Phr wt. % | 0           | 5    | 10   | 15   | 20   | 30   |
|                                       |           | 0           | 3.67 | 7.09 | 10.3 | 13.2 | 18.6 |
| $K_{Ic}$ (MPa $\sqrt{m}$ )            |           | 0.64        | 0.79 | 0.80 | 0.97 | 1.10 | 1.40 |
| $G_{Ic}$ (J/m <sup>2</sup> )          |           | 107         | 171  | 175  | 257  | 331  | 555  |
| Type of Morphology                    |           | Homogeneous | A    | A    | A    | B    | C    |
| (c) PSF modified E51/Pip epoxy resin  |           |             |      |      |      |      |      |
| Contents of PSF                       | Phr wt. % | 0           | 5    | 10   | 15   | 20   |      |
|                                       |           | 0           | 4.55 | 8.70 | 12.5 | 16.0 |      |
| $K_{Ic}$ (MPa $\sqrt{m}$ )            |           | 0.86        | 0.96 | 1.08 | 1.25 | 1.30 |      |
| $G_{Ic}$ (J/m <sup>2</sup> )          |           | 210         | 260  | 330  | 442  | 478  |      |
| Type of Morphology                    |           | Homogeneous | A    | A    | B    | C    |      |

**Table 3** The compositions and properties of three epoxy resin matrices

| Kinds of matrix | Epoxy Resin/Curing Agent | $T_g(^{\circ}\text{C})$ | $E(\text{GPa})$ | Poisson Ratio | Compressive Yielding Stress $\sigma_y(\text{MPa})$ |
|-----------------|--------------------------|-------------------------|-----------------|---------------|----------------------------------------------------|
| AG80/DDS        | AG80:DDS=100:40          | 223                     | 4.10            | 0.38          | 189                                                |
| E51/DDS         | E51:DDS=100:31           | 193                     | 3.20            | 0.38          | 107                                                |
| E51/Pip         | E51:Piperidine=100:5     | 83                      | 3.00            | 0.38          | 83                                                 |

**Table 4** The comparison of the toughening effect of PSF and CTBN in different epoxy matrices\*

| Epoxy matrix | Modifier | $G_{Ic}(\text{J/m}^2)$ | $T_g(^{\circ}\text{C})$ | $E_f(\text{GPa})$ |
|--------------|----------|------------------------|-------------------------|-------------------|
| AG80/DDS     | none     | 54                     | 223                     | 4.10              |
|              | PSF      | 209                    | 227                     | 4.07              |
|              | CTBN     | 110                    | 201                     | 3.22              |
| E51/DDS      | none     | 107                    | 190                     | 3.20              |
|              | PSF      | 257                    | 190                     | 3.10              |
|              | CTBN     | 317                    | 176                     | 2.95              |
| E51/Pip      | none     | 210                    | 96                      | 3.00              |
|              | PSF      | 442                    | 95                      | 3.10              |
|              | CTBN     | 1720                   | 92                      | 2.82              |

\* The contents of the modifiers are all 15 phr.

### 3. Toughening mechanism of thermoplastic modified epoxy resin

#### (1) Fractography of PSF particle modified epoxy resins

As mentioned before, with the lower content of PSF, a two phase structure is obtained where PSF particles disperse in the continuous epoxy matrix. On the fracture surface of most of this type of PSF modified epoxy systems, we can see the plastic deformation of PSF particles caused by the stretching and tearing of these particles at the crack tip (see Fig. 4, 5 and 6). Stretching and tearing of these thermoplastic particles have been thought to be responsible for the increase in fracture toughness in this kind of modified epoxy system by some researchers. Besides, on the fracture surface of most of this type of modified epoxy systems, no significant plastic deformation in matrix around PSF particles could be observed, this is quite different from the case of some rubber particle modified epoxy resins. Though there are some thin circular patterns around the PSF particles on the SEM photograph of the fracture surface of E51/DDS /PSF epoxy system as shown in Fig. 10, but we think that these circular patterns are most possibly the edges formed along the intersection of particle and matrix. However, a careful observation of these SEM pictures reveals that after the propagating of the crack, many characteristic tails or steps were formed behind the PSF particles (see Fig. 9). In some rigid glass bead filled epoxy systems, this kind of fractograph was also found and was explained as the evidence of crack pinning mechanism<sup>[14]</sup>. This crack pinning mechanism will be discussed in detail later.

Thus, in the PSF modified epoxy systems, the possible processes of toughening

include:

(a) Energy absorption in the dispersed PSF particles caused by ductile stretching and tearing of these particles.

(b) Increased plastic deformation in the epoxy matrix due to the dispersed particles.

(c) Interaction between the crack front and the dispersed PSF particles (crack pinning).

The importance of each process will be discussed.

## (2) Discussion on toughening mechanisms

The former researchers proposed that energy absorption by the stretching and tearing of thermoplastic particles and the plastic deformation of the matrix induced by the particle were responsible for the increase in fracture toughness. But according to our research work we believe that crack pinning mechanism may be the most important toughening mechanism in the thermoplastic modified epoxy resins.

To explain our point of view, the contribution of every energy absorption process will be discussed.

(1) Evaluation of the toughening effect of the particle stretching and tearing process.

The  $G_{lc}$  of a particle-filled composite can be expressed by:

$$G_{lc} = G_{lc}^* (1 - V_p) + \Delta G_{lc} \quad (1)$$

where  $G_{lc}^*$  is the  $G_{lc}$  of the matrix material,  $V_p$  is the volume fraction of the particles and  $\Delta G_{lc}$  is the  $G_{lc}$  increase caused by the present of particles. We think it is reasonable to evaluate  $\Delta G_{lc}$  caused by stretching and tearing of PSF particle in this way. Assuming that the whole particle reaches its maximum elongation when it is teared. Thus, the maximum increase of  $G_{lc}$  is given by

$$\Delta G_{lc} = 2\bar{r}V_p \int_0^{\epsilon_f} \sigma d\epsilon \quad (2)$$

For PSF particles, yield stress  $\sigma_y = 70$  MPa,  $\epsilon_f = 50 - 100\%$ , Young's modulus  $E = 2.5$  GPa. When  $r = 0.5 \sim 1.0 \mu\text{m}$ ,  $V_p = 10\%$ , according to the above equation the maximum evaluation of  $\Delta G_{lc}$  will be  $3 \sim 10 \text{ J/m}^2$ , this value is much smaller than the real one, so the particle stretching and tearing mechanism is not an important toughening mechanism here and is inadequate to explain the enhancement of fracture toughness in the ductile thermoplastic modified epoxy resin.

(2) The importance of PSF particle induced plastic deformation of epoxy matrix.

When a uniform remote tensile stress is applied to a two phase composite containing dispersed particles stress concentration is usually formed around the particles, this stress concentration sometimes induces or enhances localized plastic deformation of the matrix, such as crazing, shear yielding or voiding etc.. The extent of stress concentration depends on the difference of the moduli of the two phase materials. As we know, the difference of moduli between rubber and glassy

polymer is much larger. Using Goodier's solution<sup>[15]</sup>, the stress distribution in epoxy matrix around a PSF particle and a rubber particle under the applied uniform tensile stress were calculated, the stress concentration factor for rubber-epoxy system is about 2, while for the PSF-epoxy system it is only 1.1 ~ 1.2. This means that little stress concentration could be caused by PSF particles in epoxy matrix. Therefore PSF particle induced plastic deformation can not be an important energy absorbing process. On the other hand if the plastic deformation of the matrix induced by the PSF particles were the main source of energy dissipation, the structure of epoxy resin especially its crosslink density should have a marked influence on the toughening effect of the PSF particle, but the experimental results were not the case. In addition, no significant plastic deformation around particles could be observed on the SEM of the fracture surface.

### (3) Crack pinning mechanism in the PSF particle modified epoxy system

#### (a) Introduction

Crack pinning mechanism has been proposed to explain the toughening effect of the second phase particles to a brittle matrix in which they dispersed. It was proposed earlier by Lange<sup>[16]</sup> and has since been modified and extended by Evans<sup>[17]</sup> and Green et al. The two basic assumptions are (1) matrix brittle and (2) particles well-bonded to the matrix and impenetrable, i.e. they pin the crack but do not fracture themselves before they are circumvented by the crack. Thus as a crack begins to propagate in a stressed solid and meets an array of second-phase particles, the crack front bows out between the particles, forming secondary crack, while the main crack still remaining pinned at all positions where it encounters the particles, as illustrated in Fig. 11. Thus, new fracture surface is formed and the length of the crack front is increased due to its changes of shape. Energy is therefore not only required to create new fracture surface but also must be supplied to the newly formed nonlinear crack front, which is assumed to possess a line energy. The latter factor is suggested to be the primary contribution to the increased fracture energy.

An expression of  $G_{lc}$  of particle-filled composite was primarily derived by Lange<sup>[16]</sup>, but this equation has been found to be inadequate to describe the crack pinning mechanism. More satisfactory theoretical models have been derived by Evans and others. The result by Evans is given in Fig. 15, where  $K_{lc}/K_{lc}^0$  and  $G_{lc}/G_{lc}^0$  are the ratios of critical stress intensity factor and critical release rate of strain energy respectively.  $K_{lc}$ ,  $G_{lc}$  are for the composite,  $K_{lc}^0$ ,  $G_{lc}^0$  are for the pure matrix.  $D/d$  is the ratio of interparticle space to the particle diameter. Good agreements are obtained up to a certain volume fraction of particles for some composite systems, such as alumina trihydrate filled epoxy<sup>[17]</sup> glass beads filled epoxy<sup>[14]</sup> and others.

(b) The possibility of crack pinning of tough ductile thermoplastic particles to brittle epoxy resin matrix

Now we consider the case of tough ductile polysulfone particles modified epoxy resins. In this case the two basic assumptions are fulfilled, i.e. matrix brittle and particles impenetrable. Because epoxy is brittle and PSF is a high strength

and rather high modulus thermoplastic, it has a break elongation as high as 50 ~ 100%, if the PSF particles are well bonded to the epoxy matrix, they will not fracture until circumvented by the crack, so the PSF particles may have crack pinning effect to the brittle epoxy matrix.

(c) The experimental evidences of crack pinning mechanism in the PSF modified epoxy systems

First, let us analyse the possible characteristic features of fracture surface of crack pinning existing systems. When a crack propagates in a brittle material, characteristic "river" markings are always formed on the fracture surface. The line of "river" markings are perpendicular to the moving crack front and by using the pattern of the "river" markings on a fracture surface, the shape of the crack front at any moment during fracture can be determined by tracing a line perpendicular to the "river" line. Fig. 12 illustrates this and shows the interaction of crack front with a second phase particles. The thin solid lines indicate the "river" markings and the broken lines indicate the crack front at the different positions. In addition, characteristic step or tail behind the particle is also shown in this figure, which may be formed due to the meeting of the two arms of crack front (or two second cracks) when they propagate from different fracture planes on both sides of the particles. Fig. 10 shows these characteristic features on the fracture surface of PSF modified epoxy system. These evidences indicate the bowing of crack front on the two sides of the second phase particles. After further observation we finally found the direct evidence of the bowing out of crack front between PSF particles in the PSF modified epoxy system. Fig. 13 and 14 are the SEM of the fracture surface of PSF modified AG80/DDS epoxy resin. The half elliptical shaped curve lined between the PSF particles are the traces of crack front that are formed when the propagating crack paused at this position. Those are strong evidences of crack pinning mechanism. So crack pinning is indeed an operative mechanism in the PSF particle modified epoxy resin.

As reported before the molecular weight and the terminal groups of PSF modifier affected its toughening effect, the low  $\bar{M}_n$  PSF particle is brittle and the nonreactive end group PSF particle has poor adhesion to the epoxy matrix, both of the two factors can affect the crack pinning effect of the particles.



Fig. 10 Fracture surface of PSF ( $\bar{M}_n = 18700$ ) modified E51/DDS epoxy

furthermore, according to the experimental result, 10% PSF modified epoxy resins have nearly two-fold increase in  $G_k$  and the average ratio of interparticle space to particle diameter  $D/d$  is about 3 to 4. This result agrees with the Evans calculated theoretical result. Therefore crack pinning mechanism seems to be the most important one for the tough ductile thermoplastic modified epoxy system.

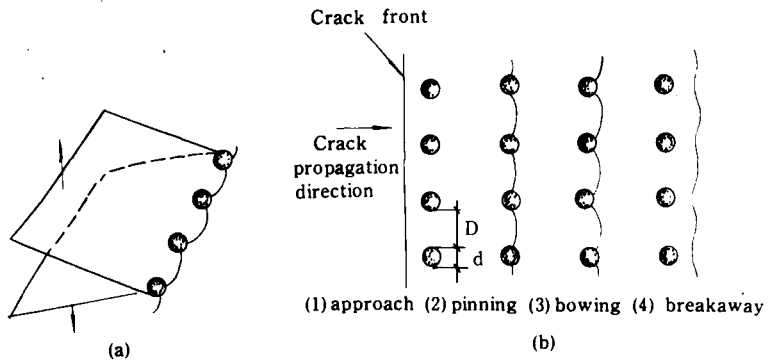


Fig.11 (a) An opening crack pinned by the second-phase particles.  
(b) Successive stages of a crack interacting with and passing through a row of second-phase particles

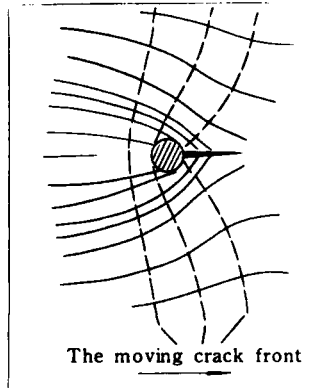


Fig.12 The characteristics of the fracture surface of the matrix with second phase particles having crack pinning mechanism. The arrow indicates the crack propagation direction



Fig. 13 and 14 The SEM fracture surface of PSF modified AG80/DDS epoxy  
(Direct evidence of the bowing out of crack front between PSF particles)  
These pictures were taken near the initial crack propagating line.

## CONCLUSION

The thermoplastic PES and PSF modified epoxies have enhancements on fracture toughness to different extent at no expense of  $T_g$  and Young's modulus. PSF has more significant toughening effect on epoxy resins than PES. The PSF modified systems have two phase structure. As the increase of PSF content, the morphology will change from a PSF-particle-dispersed structure to a PSF-continued structure. Contrary to the rubber modified epoxy systems, the crosslinking density and the yield ability of the epoxy matrices have little effect on the extent of toughening for the PSF modified ones. Crack pinning mechanism plays a very important role in the toughening of PSF particle modified epoxies.

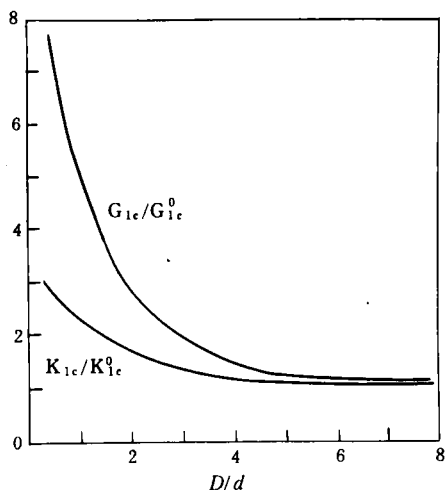


Fig. 15 The theoretical calculation results of crack pinning mechanism by A. G. Evans

## Keywords:

Polysulfone; thermoplastics; Epoxy resin; Toughening mechanism; Crack pinning

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