

# Toughening of Epoxy Resin by Poly(ether ether ketone) with Pendant Fluorocarbon Groups

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**ABSTRACT:** In this article, poly(ether ether ketone) (PEEK) with pendant fluorocarbon groups was synthesized to impart better impact resistance to diglycidyl ether of bisphenol-A (DGEBA) epoxy resins cured with 4,4'-diamino-diphenyl-sulfone (DDS). Mechanical properties were investigated as a function of the molecular weight and contents of PEEK. It was found that both impact strength and tensile strength varied with molecular weight and contents of PEEK. In the system of epoxies modified with  $M_n$  24,000 PEEK, drastic decline rather than increase of impact strength and tensile strength was observed, while impact strength was increased by 17% for the system of epoxies modified with  $M_n$  9500 PEEK at a relatively low PEEK content. To reveal the toughening mechanism, phase morphology of the modified epoxies were examined with scanning electron microscopy (SEM) and a two-phase morphology was observed. Ductile fracture mode was observed for the modified

epoxies and a rigid particle toughening mechanism was proposed. An image analysis software Quantlab-MG was used to analyze the dimension parameters of the dispersed particles for the epoxies modified with  $M_n$  9500 PEEK. A larger and more dispersed distribution of particles at higher thermoplastic content was found. Dynamic mechanical analysis (DMA) was employed to further study the phase behavior of  $M_n$  9500 PEEK modified epoxies. The observed phenomenon was interpreted by the reaction-induced phase separation mechanism. On the basis of the rubber elasticity theory, an indirect measurement of crosslinking density was taken and the results indicated that the incorporation of PEEK might reduce the crosslinking density of epoxies. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1758–1765, 2011

**Key words:** toughness; morphology; toughening mechanism; interfaces; mechanical properties

## INTRODUCTION

Toughening of epoxy resins with engineering thermoplastics has been actively studied since the early 1980s and considerable understanding has been made since then.<sup>1</sup> The main advantage in using thermoplastics to toughen epoxies lies in the fact that their incorporation need not result in significant decrease in desirable properties such as modulus, yield strength, and glass transition temperature as is generally the case when rubbers are employed as toughening agents. In the decades since the initial work on the thermoplastic toughening of epoxies was made,<sup>2</sup> there have been a variety of studies using different types of thermoplastics, which includes poly(ether sulfone) (PES),<sup>3–5</sup> polysulphone (PS),<sup>2,6</sup> polyimide (PI),<sup>7</sup> poly(etherimide) (PEI),<sup>8,9</sup> poly(aryl ether ketone) (PAEK).<sup>10–13</sup>

Poly(ether ether ketone) is a tough, semicrystalline high performance thermoplastic polymer with good thermomechanical properties. However, its semicrystalline nature and immiscibility with epoxy restricts its use as a modifier for epoxy resins. To improve the processibility and immiscibility, functionally terminated PEEK or PEEK with bulky pendant groups were used and had been approved to be effective by several researchers.<sup>14–19</sup>

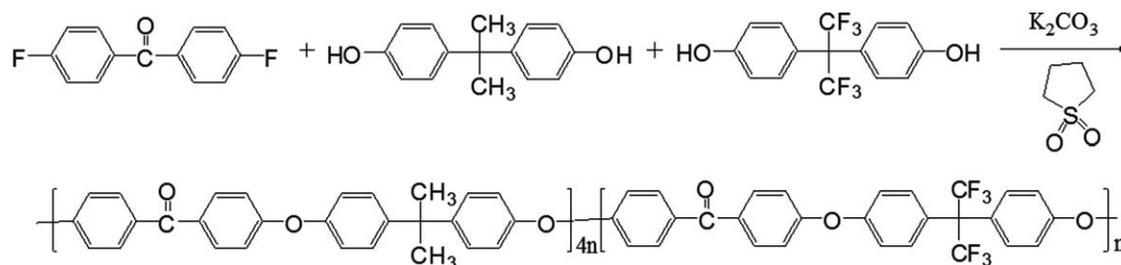
While, on the other hand, it is well known that incorporation of fluorine-pendant groups into polymers enhances thermal stability, chemical and flame resistance, and diminishes dielectric constants, surface free energy, water absorption and most importantly, crystallinity.<sup>20,21</sup> And the incorporation of fluorocarbon groups into polymers has already been reported in several literatures.<sup>21,22</sup>

In this article, poly(ether ether ketone) (PEEK) was used as the toughening agent. To improve the processibility and its immiscibility with epoxy, also to enhance its thermal and chemical stability, pendant fluorocarbon groups were incorporated into the thermoplastic and thus a novel soluble PEEK with pendant fluorocarbon groups was prepared. Mechanical tests were conducted to evaluate the effect of molecular

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**Figure 1** Reaction scheme for the synthesis of poly(ether ether ketone) with pendant fluorocarbon groups.

weight and contents of toughening agents. Phase morphology of the fracture surface was revealed by means of scanning electron microscopy (SEM) to interpret the toughening mechanisms. Dynamic mechanical analysis (DMA) was employed to study the effect of the incorporation of thermoplastics on the phase behavior of the toughened epoxies.

## EXPERIMENTAL

### Materials

4,4'-difluorobenzophenone (DFBP, analytical grade), bisphenol A (BA, analytical grade), hexafluorobisphenol A (HFBA, analytical grade), methylbenzene (MB, analytical grade) and tetramethylsulfone (TMS, analytical grade) was used for the synthesis of poly(ether ether ketone) with pendant fluorocarbon groups. Potassium carbonate ( $K_2CO_3$ , analytical grade) was dried at  $400^\circ C$  before using.

Diglycidyl ether of bisphenol-A epoxy (DGEBA, E-54, commercial grade) from Xingchen New Chemical New Material Co. LTD., China, was used as received. The curing agent was 4,4'-diamino-diphenyl-sulfone (DDS, commercial grade) from Beijing Chemical Factory, China, having the weight ratio of 33 : 100 to DGEBA.

### Synthesis of poly(ether ether ketone) with pendant fluorocarbon groups

The reaction route for the synthesis of poly(ether ether ketone) with pendant fluorocarbon groups is given in Figure 1. The synthesis was conducted in a clean and dry three-necked flask equipped with a mechanical stirrer, thermometer, and nitrogen inlet.

The flask was purged with dry nitrogen before starting the reaction and successively charged with 43.64 g (0.20 mol) of DFBP, 50.05 g (0.16 mol) of BA, 13.59 g (0.04 mol) of HFBA, 28.98 g (0.21 mol) of anhydrous  $K_2CO_3$ , 195 mL of TMS and 100 mL of MB. The reaction mixture was heated at  $120^\circ C$  for 2 h with constant stirring. Water formed during the reaction was removed. After that, the reaction temperature was heated at  $230^\circ C$  for 3 h and then cooled to room temperature. The polymer formed was precipitated by adding distilled water at room temperature. The precipitated polymer was grinded and purified by refluxing with distilled water to remove the residual TMS and  $K_2CO_3$ . Finally, the product was dried under vacuum at  $120^\circ C$  for 12 h. The molecular weight of the obtained polymer was controlled by the amount of BA and tested with LC-10A GPC (Shimadzu, Japan). In this article, PEEKs with two molecular weight ( $M_n = 24,000$  and  $9500$ , respectively) were synthesized. Their physical and chemical characteristics were shown in Table I. As indicated, elongation at break of PEEK approaches 55 and 58%, respectively, and both 5% weight loss temperatures exceeds  $480^\circ C$ , which demonstrated their good plasticity and thermal stability.

### Specimen preparation

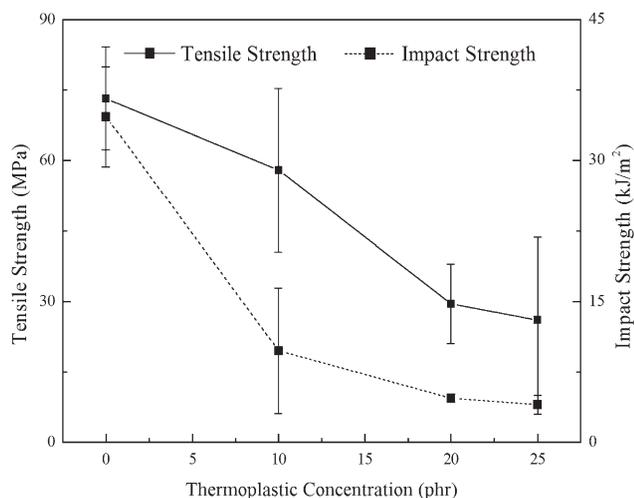
The prereacted specimen was prepared by dissolving various contents of thermoplastic in the epoxy for 30 min at  $130^\circ C$ . The DDS was then added and mixed for 20 min at  $130^\circ C$ . The mixture was transferred to an open mold and evacuated to a vacuum oven until no visible bubble could be found, then cured at  $180^\circ C$  for 2 h followed by postcure at  $200^\circ C$  for another 2 h. After postcure, the blends were

**TABLE I**  
Physical and Chemical Properties of PEEK

| PEEK     | Strength (MPa) | Modulus (GPa) | Elongation at break (%) | Glass transition temperature ( $^\circ C$ ) <sup>a</sup> | 5% weight loss temperature ( $^\circ C$ ) <sup>b</sup> |
|----------|----------------|---------------|-------------------------|--|--|
| Mn 24000 | 66             | 2.13          | 55.2                    | 134.7  | 493.4  |
| Mn 9500  | 68             | 2.10          | 58.4                    | 131.0  | 480.6  |

<sup>a</sup> Q800 DMA (TA, USA), film tension, strain 0.020%, 1 Hz,  $5^\circ C/min$

<sup>b</sup> Pyris Diamond TG/DTA (Perkin-Elmer, USA), nitrogen,  $10^\circ C/min$ .



**Figure 2** Impact strength and tensile strength of epoxies modified with contents of  $M_n$  24,000 PEEK.

allowed to cool slowly to room temperature. Contents of the added thermoplastic varied from 0 to 25 parts per hundred resin (phr) of epoxies.

### Mechanical test

Dumbbell shaped specimens with the dimension of 75 mm × 10 mm × 2 mm were prepared according to Chinese standard GB/T 16421-1996 for tensile tests. For impact test, unnotched specimens with the dimension of 80 mm × 10 mm × 4 mm were prepared according to Chinese standard GB/T 2571-1996, which used a pendulum impact machine to determine the energy to break standard test specimens of specified size (width and depth) under stipulated conditions of specimen. Experiments were performed in the technical Institute of Physics and Chemistry (IPC), Chinese Academy of Science (CAS).

### Morphology observation

FEG SEM Quanta 600 (Philips-FEI, Holland) was used. Failed specimens from impact test were etched with tetrahydrofuran for 48 h, after which the thermoplastic is supposed to be rinsed away. Normally, PEEK is a semicrystalline high performance thermoplastic polymer and is not soluble in tetrahydrofuran. However, the incorporation of flexible fluorocarbon groups disturbed its crystal regularity and improved its solubility. After thermoplastic being etched out, the specimens were sprayed with a gold coating on the fracture surface before being examined.

### Dynamic mechanic analysis

DMA Q800 (TA, USA) was used and specimens with the dimension of 35 mm × 12 mm × 2 mm were run in the single cantilever beam mode at a

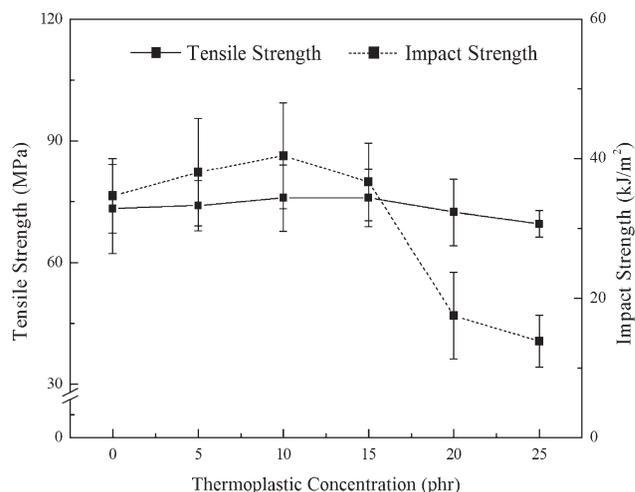
constant frequency 1 Hz and a stress amplitude equal to 0.5N during temperature sweeps (5°C/min, from 50°C to 300°C).

## RESULTS AND DISCUSSIONS

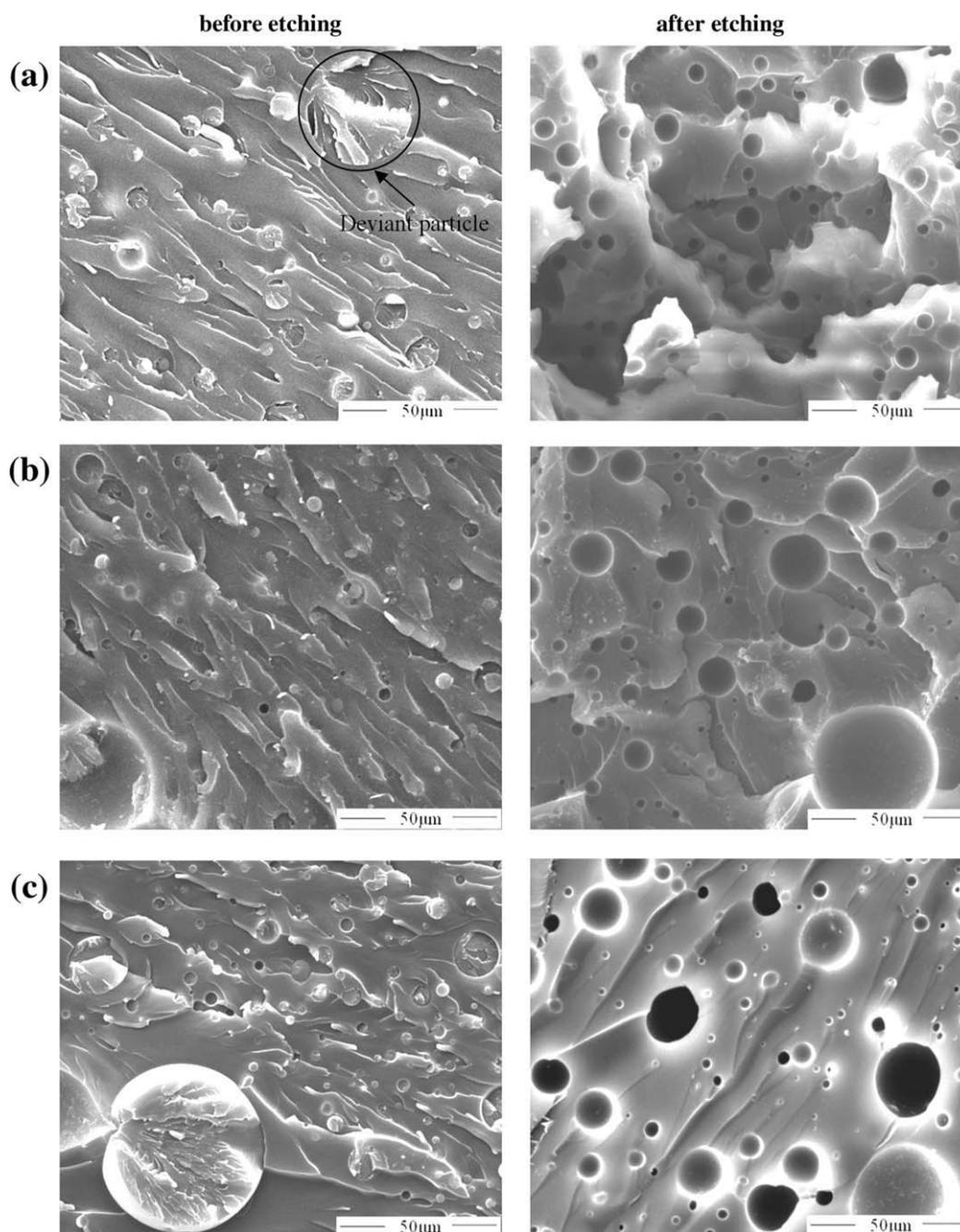
### Mechanical properties

To evaluate the effect of the molecular weight and contents of PEEK on the mechanical properties of epoxies, impact test, and tensile test were performed. Figure 2 shows the impact strength and tensile strength of the epoxies modified with contents of  $M_n$  24,000 PEEK. Apparently, the addition of  $M_n$  24,000 PEEK did not impart a better impact strength. On the contrary, the impact strength of the epoxies dropped drastically. The same tendency was found for the tensile strength of the modified epoxies.

The impact strength and tensile strength of epoxies modified with contents of  $M_n$  9500 PEEK are shown in Figure 3. It was observed that there is an initial increase in the value of impact strength, followed by a sharp decline. The slight increase of the impact strength from 34.6 to 40.4 kJ/m<sup>2</sup> may result from the low toughenability of DDS-cured epoxy.<sup>23</sup> While for the tensile property, the incorporation of  $M_n$  9500 PEEK did not cause any considerable decline of the tensile strength for the contents studied in this research. A moderate increase of the tensile strength, from 73.2 to 78.5 MPa could even be found at a low content of  $M_n$  9500 PEEK. All these behavior was distinguished from the former system modified with  $M_n$  24,000 PEEK, which might result from better immiscibility caused by the decrease of thermoplastic molecular weight.<sup>6</sup> This could be also understood in terms of interfacial interactions as more fluorocarbon groups, which would decrease the crystallization ability of the PEEK and improve



**Figure 3** Impact strength and tensile strength of epoxies modified with contents of  $M_n$  9500 PEEK.



**Figure 4** ESEM micrographs of the fracture surfaces of failed specimens from impact test for epoxies modified with (a) 10; (b) 20; and (c) 25phr of  $M_n$  24,000 PEEK (Left: before; Right: after etching; Magnification: 2000 $\times$ ).

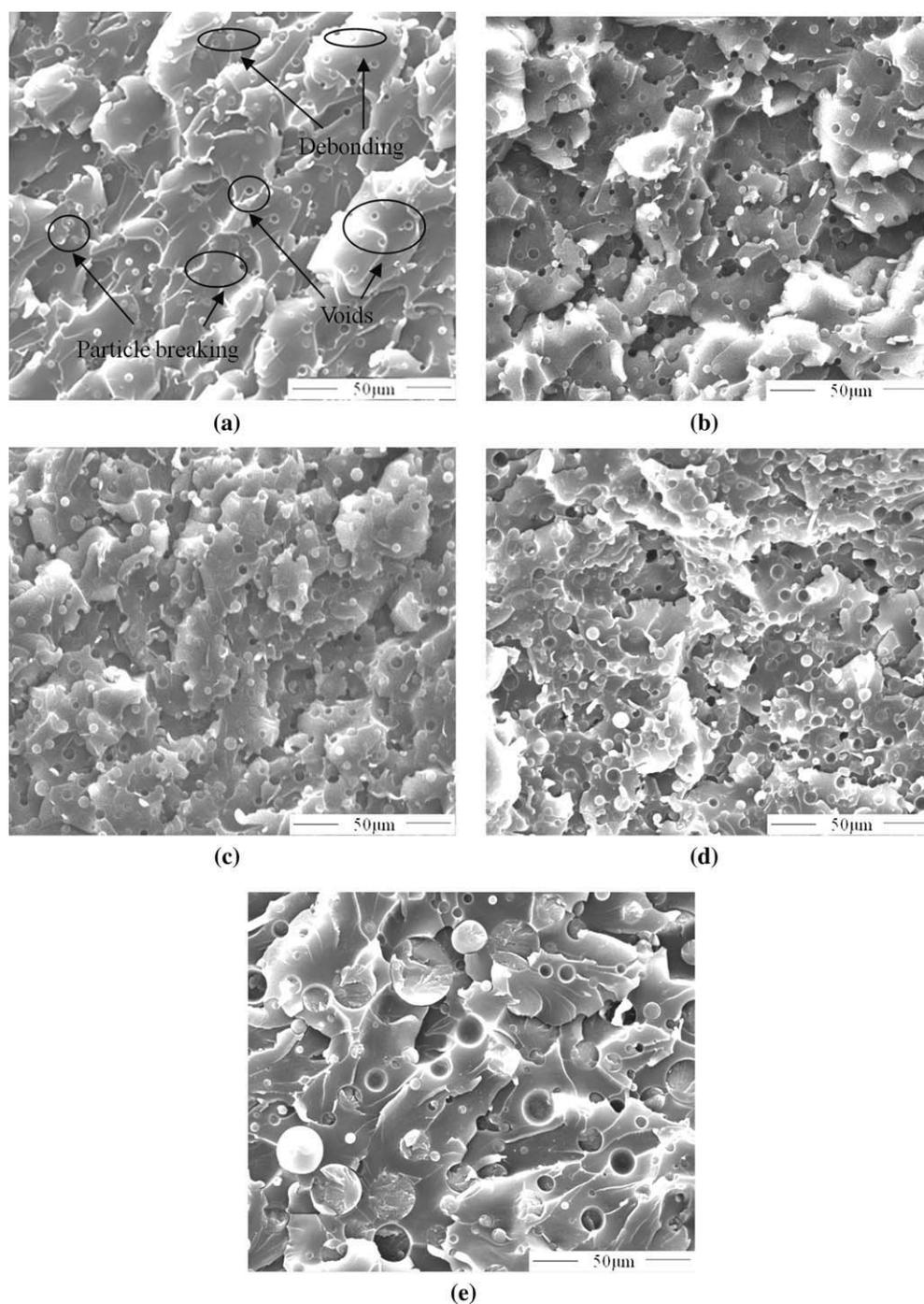
its interfacial interactions with epoxy, will be available when molecular weight decreases.

#### Phase morphology

Both the two systems of uncured blends prepared by melt-mixing were transparent at room temperature, even after settling down for a few days. No visual heterogeneity was observed, which showed the homogeneous nature of the uncured blends. While, the phase morphology of the cured blends

was influenced by many factors such as immiscibility of the modifier in epoxy, molecular weight, and amount of the modifier, and so forth.<sup>19</sup>

SEM micrographs of the failed specimens from impact test of epoxies modified with contents of  $M_n$  24,000 PEEK are shown in Figure 4. Two-phase morphology (known as isolated domain morphology) of the blends with dispersed thermoplastic particles in continuous epoxy matrix was observed. The impetus of the phase separation from homogeneity of uncured blends to heterogeneity of cured blends



**Figure 5** ESEM micrographs of the fracture surfaces of failed specimens from impact test for epoxies modified with (a) 5; (b) 10; (c) 15; (d) 20; and (e) 25 phr of  $M_n$  9500 PEEK (before etching; Magnification: 2000 $\times$ ).

was the increase in molecular weight of epoxies due to the curing reaction. This was the so-called “reaction-induced phase separation,”<sup>5</sup> which depicts the phase decomposition process of a blend system from homogeneity to heterogeneity, causing by the decreasing of conformational entropy of the blend with proceeding of curing reaction.

From Figure 4, it is observed that dimension of the dispersed particles increased with the content of  $M_n$  24,000 PEEK. Obviously, the morphology was

nonuniform. Some irregular particles existed and acted as macro stress concentrators, which well explains the sharp decrease of the impact strength and tensile strength after the incorporation of  $M_n$  24,000 PEEK.

To get information about the toughening mechanism responsible for the increase in impact strength of epoxies modified with  $M_n$  9500 PEEK, the fracture surface of failed specimen were also examined under SEM. Figure 5 shows the SEM micrographs of

**TABLE II**  
Diameter and Polydispersity Index of Dispersed PEEK Particles ( $M_n$  9500)

| PEEK content (phr) | $\bar{D}_n$ ( $\mu\text{m}$ ) | $\bar{D}_w$ ( $\mu\text{m}$ ) | PDI  |
|--------------------|-------------------------------|-------------------------------|------|
| 5                  | 1.79                          | 1.82                          | 1.01 |
| 10                 | 2.13                          | 2.18                          | 1.02 |
| 15                 | 2.16                          | 2.20                          | 1.02 |
| 20                 | 2.60                          | 2.72                          | 1.04 |
| 25                 | 3.77                          | 4.27                          | 1.13 |

failed specimen from impact test of epoxies modified with contents of  $M_n$  9500 PEEK. Again, a two-phase morphology of the blend system was observed, with discrete thermoplastic-rich phase dispersed in the continuous epoxy-rich phase. However, the irregular particles, which appeared in the epoxies modified with  $M_n$  24,000 PEEK, were not observed anymore. The fracture surfaces of the  $M_n$  9500 PEEK modified epoxies were rough and ridgy, which indicated the ductile nature of the fracture. Dispersed particle acted as micro stress concentrators on applying load, leading to micro-cracking and local plastic deformation around the particles. As the intensity of the dispersed particles increases, stress field created by each particle will interact with each other, resulting in the improved fracture resistance. Also, the thermoplastic-rich phase can bridge the crack to some extent and left tail marks behind the particles, which is the characteristic of a crack-pinning mechanism.<sup>24</sup> Particle breaking and particle debonding with the epoxy-rich phase can be observed, which may also attribute to the toughening effect. The presence of smooth cavities corresponding to thermoplastic particles extracted away, clearly shows that brittle failure of the interface occurred without yielding. All these indicated a rigid particle toughening mechanism, which may involve micro-cracking and crack-pinning.<sup>25</sup> Good interfacial adhesion is necessary to obtain substantial improvement in impact toughness. Hence, a lack of interfacial properties results in only moderate toughness improvement.

The dimensions of dispersed particles of epoxies modified with contents of  $M_n$  9500 PEEK were obtained by an image analysis software Quantlab-MG. Diameter and polydispersity index (PDI) were calculated using the following equations:

$$\text{Number Average Diameter, } \bar{D}_n = \frac{\sum n_i d_i}{\sum n_i} \quad (1)$$

$$\text{Weight Average Diameter, } \bar{D}_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (2)$$

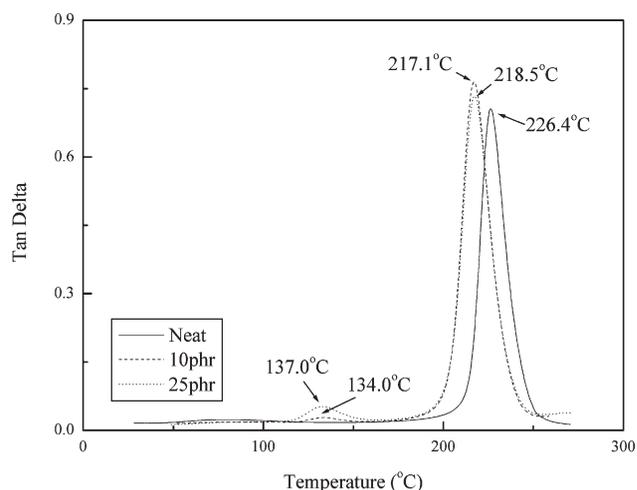
$$\text{Polydispersity Index, PDI} = \frac{\bar{D}_w}{\bar{D}_n} \quad (3)$$

where  $n_i$  is the number of particles having the diameter of  $d_i$ .

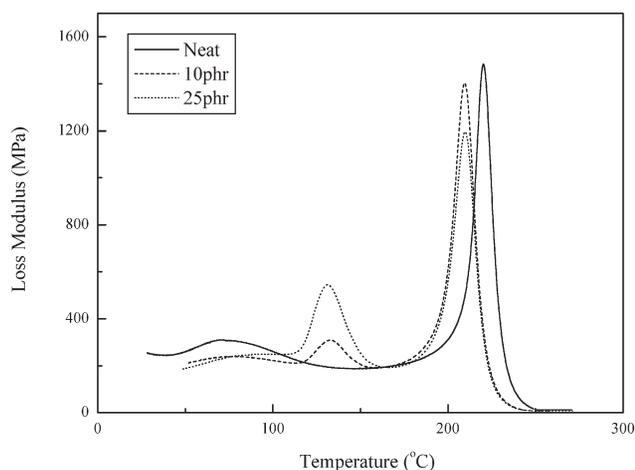
The values of  $\bar{D}_n$ ,  $\bar{D}_w$ , and PDI are summarized in Table II. Apparently, the particle dimension increased with the content of  $M_n$  9500 PEEK, from 1.79 to 3.77  $\mu\text{m}$  for number average diameter and from 1.82 to 4.27  $\mu\text{m}$  for weight average diameter. The increase of particle dimension was due to the coalescence of the particle after phase separation. As indicated, the polydispersity index also increased with the content of  $M_n$  9500 PEEK, from 1.01 to 1.03. Thus, a broader particle dimension distribution at higher content could be concluded. An explanation for this phenomenon could be given on the basis of phase separation mechanism governed by both thermodynamic and kinetic factors. It is known that reaction-induced phase separation occurs either by nucleation and growth or spinodal decomposition.<sup>5</sup> On the basis of the isolated domain morphology observed and poor immiscibility of the system reported,<sup>14-19</sup> nucleation and growth mechanism was preferred in this case. It is probable that not all the particles nucleated at the same time. Some particles might have formed at a later stage. However, the viscosity of the systems was increasing as a result of crosslinking, which would prevent isolated particle to coalesce. Hence the particle would not fully develop. This was even more prominent for the system with higher thermoplastic content, which resulted in a broader dimension distribution.

### DMA analysis

For a further insight into the phase behavior of epoxies modified with  $M_n$  9500 PEEK, dynamic mechanical analysis was performed to evaluate the glass transition temperature ( $T_g$ ) of the blends. Figure 6 shows the  $\tan \delta$  versus temperature spectrum of modified epoxies and compared with that of the neat one. Apparently, two relaxations were observed



**Figure 6**  $\tan \delta$  versus temperature spectrum of neat epoxy and epoxies modified with contents of  $M_n$  9500 PEEK.



**Figure 7** Loss modulus versus temperature spectrum of neat epoxy and epoxies modified with contents of  $M_n$  9500 PEEK.

for the modified epoxies. The peak at higher temperature range 210–220°C corresponds to the  $T_g$  of epoxy-rich phase and the peak at lower temperature range 130–140°C refers to the  $T_g$  of thermoplastic-rich phase. The peak values of the modified epoxies were found to be increased, which may be ascribed to the incorporation of the thermoplastics. The increase in  $T_g$  of thermoplastic phase when compared with that of pure thermoplastic (Table I) was due to the presence of trapped high- $T_g$  epoxy, which is caused by the increase of system viscosity when phase separation. The viscosity of the system increased with the thermoplastic content. A higher loading of thermoplastic must lead to a higher content of epoxy trapped in the thermoplastic-rich phase. This well explains the up-shift in  $T_g$  of thermoplastic phase for the epoxies modified with 10 phr and 25 phr  $M_n$  9500 PEEK, from 134°C to 137°C. While, the decrease in  $T_g$  of epoxy-rich phase for the modified epoxies was either due to the presence of low- $T_g$  thermoplastic trapped in the epoxy-rich phase or due to the decrease in crosslinking density as a result of the incorporation of thermoplastic.

Loss modulus of the modified epoxies and neat epoxy is shown in Figure 7. It is observed that the neat epoxy showed two peaks in loss modulus with the increase of temperature, with small and broad peak around 70°C, and the sharp peak near 220°C. This first peak should be corresponded to the epoxies with lower crosslinking density.<sup>26</sup> For the modified epoxies, the first peak was found at 130°C rather than 70°C, which should be designated to the relaxation of thermoplastic phase caused by glass transition at elevating temperature. The disappearance of the peak corresponding to epoxies with lower crosslinking density for the modified epoxies, was either due to the diminishment of epoxies with lower crosslinking density or due to the encapsula-

tion of low-crosslinking-density epoxies by thermoplastic.

Storage modulus of the modified epoxies and neat one is shown in Figure 8. For the neat epoxy, the first drop of storage modulus was around 70°C, corresponding to the glass transition of the epoxies with low crosslinking density. A followed and sharp drop was found near 220°C, which is governed by the glass transition of bulk epoxy with high crosslinking density. For modified epoxies, two drops were also observed, with the first corresponding to the thermoplastic-rich phase and the second referring to the epoxy-rich phase. All these showed good accordance with the  $\tan \delta$  versus temperature and loss modulus versus temperature spectrum (Figs. 6 and 7).

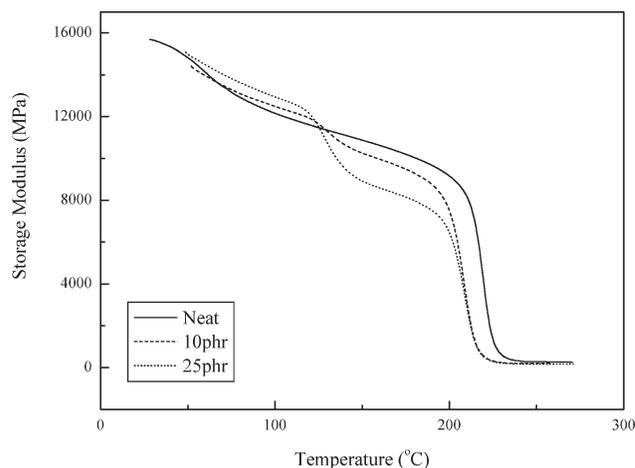
In principle, crosslinking density of a cured epoxy could be calculated from the theory of rubber elasticity. Shear modulus  $G$  of a crosslinked polymer is given by the following equation<sup>27</sup>:

$$G = \frac{\bar{r}_1^2 dRT}{\bar{r}_f^2 M_c} \left(1 - \frac{2M_c}{\bar{M}_n}\right) \quad (4)$$

where  $\bar{r}_1^2/\bar{r}_f^2$  is the ratio of the mean square end-to-end distance of the polymer chain to the same quantity in a randomly coiled chain,  $d$  is the density,  $R$  is the universal gas constant,  $T$  is the absolute temperature,  $M_c$  is the molecular weight between crosslinks and  $\bar{M}_n$  is the chain backbone molecular weight.

In this case,  $\bar{r}_1^2/\bar{r}_f^2$  was assumed to be 1.  $M_c/\bar{M}_n$  is supposed to be zero, for  $M_c$  is negligible when compared to  $\bar{M}_n$  as in the case of highly crosslinked epoxy system. Hence, eq. (4) could also be written as

$$G = \frac{dRT}{M_c} \quad (5)$$



**Figure 8** Storage modulus versus temperature spectrum of neat epoxy and epoxies modified with contents of  $M_n$  9500 PEEK.

**TABLE III**  
 **$M_c$  Values of Epoxies Modified with  $M_n$  9500 PEEK**

|                    |    |    |    |
|--------------------|----|----|----|
| PEEK content (phr) | 0  | 10 | 25 |
| $M_c$ (g/mol)      | 62 | 85 | 99 |

Thus,  $M_c$ , which can be taken as an indirect measurement of crosslink density of epoxies could be calculated from the following equation

$$M_c = \frac{dRT}{G} \quad (6)$$

One important thing that should be noticed is that  $G$  must be measured in the rubbery plateau above  $T_g$ , for eq. (4) is on the basis of the rubber elasticity theory. In this paper, shear modulus  $G$  could be taken as  $E'/3$ <sup>28</sup> and  $E''$  was measured at  $T_g + 40^\circ\text{C}$ . The values of  $M_c$  calculated from eq. (6) are given in Table III. It was found that  $M_c$  increased with the  $M_n$  9500 PEEK content. This implied that the incorporation of  $M_n$  9500 PEEK would probably decrease the crosslinking density of the epoxies and thus reduced the  $T_g$  of the modified epoxies (Fig. 6). The decrease of crosslinking density might be attributed to the restricted curing reaction caused by viscosity increases in the modified epoxies.<sup>6</sup>

### CONCLUSIONS

In the system of epoxies modified with  $M_n$  24,000 PEEK, the mechanical properties declined drastically with the incorporation of thermoplastic. For the system of epoxies modified with  $M_n$  9500 PEEK, impact strength was found to increase from 34.6 to 40.4 kJ/m<sup>2</sup> at 15 phr, which was followed by a sharp decrease at higher contents. While the tensile strength of the blends remained almost unchanged and did not show any significant decline.

A two-phase morphology was observed for the two modified systems. Fracture surfaces of modified epoxies showed a brittle nature of the fracture. A rigid particle toughening mechanism, which involve micro-cracking and crack-pinning was proposed. A larger and more dispersed distribution of particles at higher thermoplastic content was found with the aid of image analysis.

Two relaxations caused by the reaction-induced phase separation were observed for the modified epoxies by DMA. The glass transition temperature

of thermoplastic-rich phase shifted to a higher temperature at higher contents. On the basis of the rubber elasticity theory, an indirect measure of crosslinking density was employed and the results indicated that the incorporation of PEEK reduced the crosslinking density of epoxies.

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