Mechanical and Morphological Properties of Epoxy Resins Modified by Poly(phthalazinone ether sulfone ketone)

Yajuan Xu,[1] Gongxiong Liao,[1,2] Tiesheng Gu,[1] Liang Zheng,[1] Xigao Jian[1,2]

[1]Department of Polymer Science and Materials, Dalian University of Technology, Dalian 116012, China
[2]Liaoning Province Engineering Center of High Performance Resins, Dalian 116012, China

ABSTRACT: A series of blends have been prepared by adding a novel thermoplastic poly(phthalazinone ether sulfone ketone) (PPESK) in varying proportions to diglycidyl ether of bisphenol A epoxy resin (DGEBA) cured with p-diaminodiphenylsulfone (DDS). All the blends showed two-phase structures characterized by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). Addition of the PPESK resulted in great enhancement of glass transition temperatures (T_g) both in the epoxy-rich phase and in the PPESK-rich phase by reason of the special structure of PPESK. There was moderate increase in the fracture toughness as estimated by impact strength. Fracture mechanisms such as crack deflection and branches, ductile microcracks, ductile tearing of the thermoplastic, and local plastic deformation of the matrix were responsible for the increase in the fracture toughness of the blends. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2253–2260, 2008

Key words: PPESK/epoxy blends; morphology; fracture toughness

INTRODUCTION

Thermosetting epoxies possess many desirable properties such as high tensile strength and modulus, excellent chemical and solvent resistance, high dimensional and thermal stability, good creep resistance, and adhesive properties. These characteristics make them ideal candidates as matrices for many important applications, including adhesives, electronics encapsulate, and matrix resins for high-performance fiber-reinforced composites. However, the epoxy resins are generally brittle because of high cross-link densities, which limit their further proliferation into other applications that require more impact resistant or tougher materials. This drawback has prompted many studies, devoted to increasing their fracture toughness without compromising their desirable attributes, such as their high glass transition temperature (T_g), high modulus, and advantageous strength to weight ratios. In most cases, enhancement of these characteristics is not achieved only by improvement of the structure of epoxy resins. Modification by elastomers (rubbers) and thermoplastic polymers, therefore, has been investigated. The most common additives by far, have been liquid reactive rubbers, such as carboxyl-terminated butadiene rubbers (CTBN) and amine-terminated butadiene acrylonitrile (ATBN) copolymers; however, toughness improvements in most elastomer-modified epoxy systems usually lead to significant decrease in the thermal performance and mechanical strength of the cured epoxy resins.[1–3]

Fortunately, another toughening technology can enhance fracture toughness without sacrificing the mechanical properties of the thermosetting systems. This technology uses high-performance engineering thermoplastics with high glass transition temperatures (T_g's) and toughness, such as polysulfone (PSF),[4–6] poly(ether sulfone) (PES),[7,8] poly(ether imide) (PEI),[9–11] and poly(ether ether ketone) (PEEK).[12,13] However, it is generally agreed that the T_g's of the thermoplastic-modified epoxy resins are equal or only slightly higher than that of the unmodified epoxy resins.[7,14–18]

Poly(phthalazinone ether sulfone ketone) (PPESK),[19–21] a novel high performance thermoplastic, is developed successfully in recent years. Its special structure endows it with excellent comprehensive properties, such as outstanding thermal properties and good solubility. The PPESK and curing agent p-diaminodiphenylsulfone (DDS) used in this study could be dissolved in hot diglycidyl ether of bisphenol A (DGEBA) epoxy resin and melt-blended to form homogenous precursors without requiring any solvent. Of particular importance is that its T_g is about 280°C, much higher than that of the epoxy resin and other commercial thermoplastics, which will result in some special phase behaviors and outstanding properties of the PPESK/epoxy blends. Therefore, it is
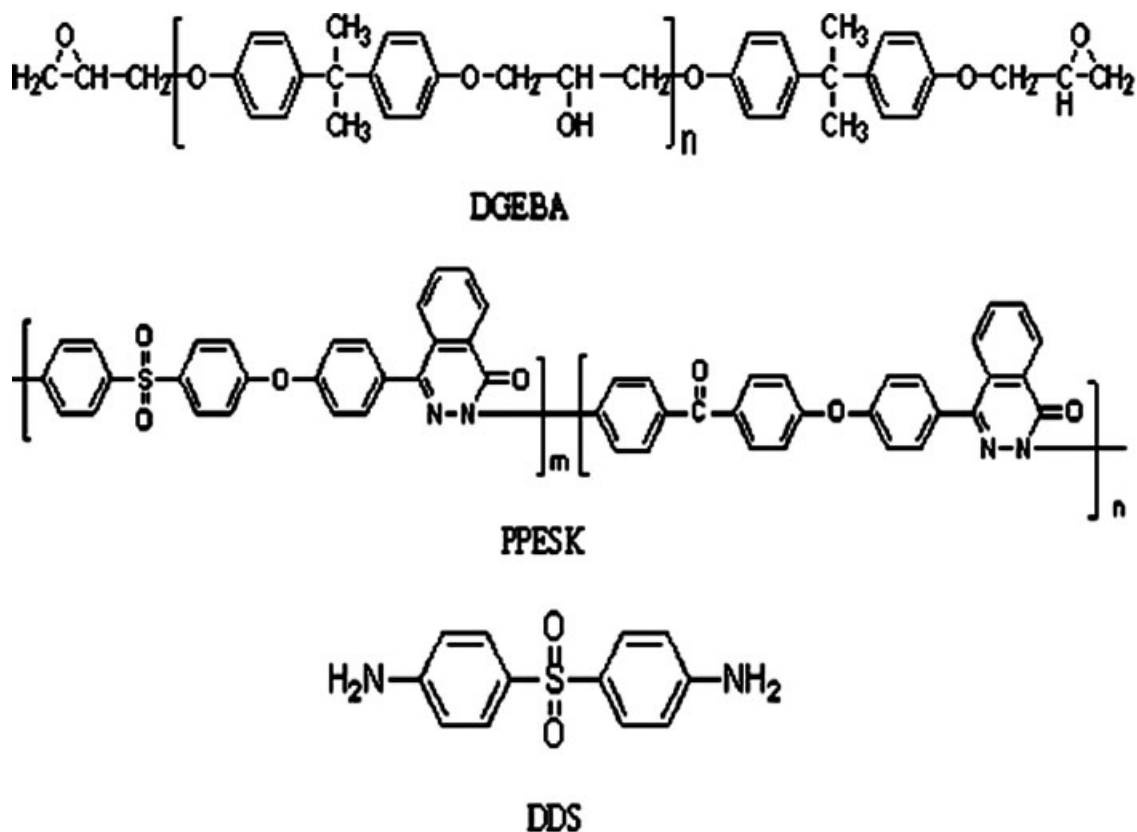
Figure 1 Chemical structures of DGEBA, PPESK, and DDS.

very necessary to investigate phase structures and properties of the PPESK/epoxy blends. However, there have been no reports published on the use of PPESK and its analogs as a toughening agent for epoxy resin.

Hence, this article reported here the toughening of DGEBA-type epoxy resin with PPESK and the relationship between the morphology and the thermal–mechanical properties of the PPESK/epoxy blends. We focused our attentions on the effect of the cure cycles on the phase structures and thermal–mechanical properties of the PPESK/epoxy blends. The toughening mechanisms were also investigated in detail.

EXPERIMENTAL

Materials

The epoxy resin used in this study was two DGEBA, a two functional, low viscosity, amber liquid sold as WSR618 (weight per epoxide = 185–208 g), supplied by Lanxing new materials resins factory of Wuxi, China. The curing agent was DDS (supplied by Shanghai Sanaisi Reagent Co. Ltd, China), a pale pink powder. The thermoplastic toughening agent was an amorphous PPESK (supplied by Dalian polymer novel materials company, China). The chemical

structure of DGEBA, PPESK, and DDS are shown in Figure 1, and the characteristics of PPESK are listed in Table I.

Sample preparation

Blending systems were prepared using a standard procedure. The PPESK and DGEBA were mixed together with the electric stirrer at 130°C, until the PPESK was completely dissolved and free of bubbles; the time which took depended greatly on the amount of PPESK added but was not longer than 30 min, even for the highest PPESK concentration. Once dissolved, the stoichiometric (corresponding to a 1 : 1 epoxy to amine molar ratio) hardener (DDS) was added and mixed continually until the DDS had also completely dissolved and the mixture was free of bubbles. The ternary blends were transparent and

TABLE I
Characterization Data of the PPESK

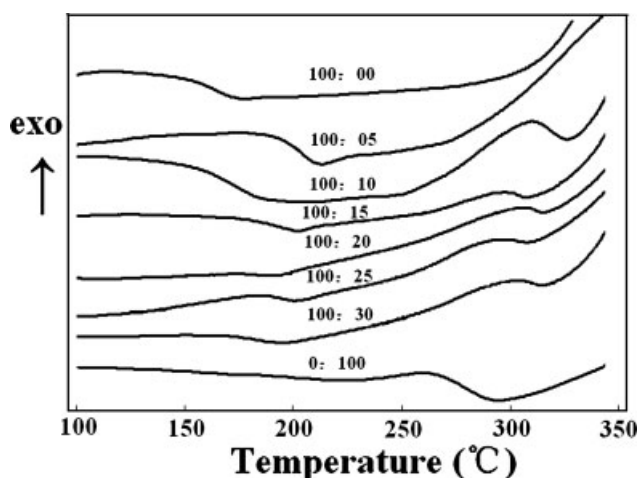| Viscosity (η)	0.42 dl/g
Molecular weight (M_w)	31,042 g/mol
Molecular weight (M_n)	5453 g/mol
Distribution (M_w/M_n)	5.69
T_g	280°C

Figure 2 DSC traces of DGEBA/PPESK blends cured in conditions C.

visually homogeneous. On curing, the blends became translucent, indicating heterogeneous morphology.

The samples were prepared with 0, 5, 10, 15, 20, 25, and 30 phr of PPESK in the DGEBA/DDS mixture, where phr represents the weight parts of PPESK per hundred parts of the DGEBA epoxy resin. Each sample was poured into an open chrome steel mold and put into a vacuum oven to degass, then to cure in an air circulating oven in four procedures. However, the phr-PPESK was no more than 15 phr for the charpy impact measurement because the high viscosity at the cure temperature of PPESK-epoxy-DDS formulations made it impossible to introduce more than a 15 phr mass fraction of PPESK for casting purposes. After curing, the oven was switched off, and the plaques were allowed to cool slowly to room temperature to prevent cracking. Four different curing conditions were used in the sample preparations as follows:

A. 150°C for 8 h.
B. 150°C for 5 h + 180°C for 3 h.
C. 150°C for 3 h + 180°C for 3 h + 200°C for 2 h.
D. 150°C for 2 h + 180°C for 2 h + 200°C for 2 h + 220°C for 2 h.

Characterization techniques

The thermal analysis work [glass transition temperature (T_g)] for the cured samples was carried out by using Mettler Toledo DSC822e at a heating rate of 10°C min^{-1} under nitrogen.

The fracture surfaces of cryogenically fractured specimens and failed specimens from toughness measurement were analyzed with a KYKY2800B scanning electron microscope (SEM). The morphology of the blend were analyzed by the cryogenically fractured specimens, which were etched with chloroform for 48 h to remove the PPESK phase, and then were dried in vacuum for 24 h to remove the solvent. All the specimens were sputter-coated with a layer of gold before they were examined by microscope.

The fracture toughness of the cured epoxy resins was evaluated from the impact strength according to the ASTM D 5942-96. The tests were performed using the charpy impact strength measurement set (XCJ-4). The specimen dimensions were 60 mm × 6 mm × 4 mm. There were 10 samples used to measure the average impact strength reported for each condition.

RESULTS AND DISCUSSION

Thermal properties analyses

To investigate the effect of the PPESK on the thermal properties of the blends, the glass transition temperatures (T_g's) of the cured samples in different curing conditions were measured by differential scanning calorimetry (DSC). Figure 2 shows the DSC traces obtained for the blends under curing conditions C. The same observations were noticed for the other three curing conditions. There was neither residual exothermic peak nor any endothermic peak observed. These values are presented in Table II. It

TABLE II
DSC Data for the E-51/PPESK Blends

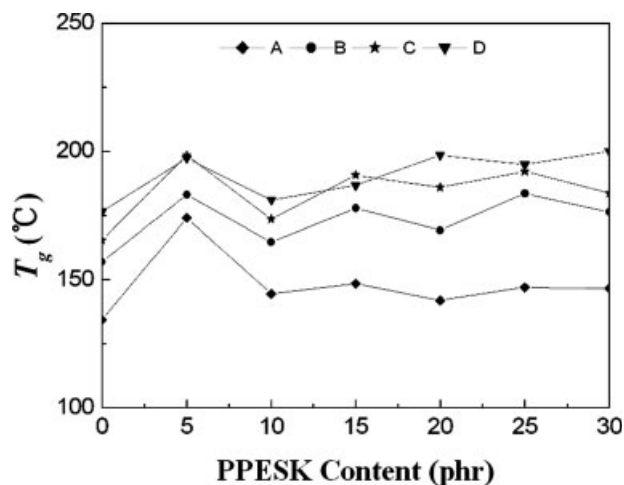| | Glass transition temperature (°C) | | | | | | | |
| | A | | B | | C | | D | |
phr-PPESK	α (epoxy)	β (PPESK)	α (epoxy)	β (PPESK)	α (epoxy)	β (PPESK)	α (epoxy)	β (PPESK)
0	134.3		157.0		165.4		176.5	
5	174.0		183.0		198.4		197.2	
10	144.5	324.1	164.7	322.9	173.6	321.0	181.0	318.1
15	148.5	309.7	177.8	309.0	190.7	304.6	186.7	312.7
20	141.9	314.2	169.2	314.9	185.9	312.7	198.5	304.3
25	147.0	308.4	183.5	311.8	192.1	303.8	194.9	304.4
30	146.6	308.3	176.3	313.9	183.6	310.8	200.0	299.7

Figure 3 Plot of T_g of epoxy-rich phase versus PPESK content for samples of varying cure conditions.

can be seen that the T_g of the blends was significantly higher not only in the epoxy phase but also in the PPESK phase than the pure epoxy and PPESK. The DSC spectra of the cured resins confirmed the existence of two-phase morphology by exhibiting two distinct glass transitions; one was due to the PPESK-rich phase (β phase) and the other was due to the epoxy-rich phase (α phase). However, the 5-phr PPESK showed a single glass transition. This did not mean that homogeneous phase occurred, but the concentration of PPESK was low and the majority of PPESK dissolved in the epoxy phase to form the fine dispersed particles [see Fig. 5(a)]. In this case, the PPESK phase was restricted in the epoxy cross-linked network to increase the T_g of epoxy-rich phase. At the same time, the particles of PPESK were embedded in the epoxy network and were not able to mobile. Therefore, the curve of DSC showed only one inflection in the 5-phr PPESK blend. The two-phase structures of blends were verified by the following micrograph of SEM (see Fig. 5).

Figure 3 shows the variation of the T_g in the epoxy-rich phase with cure temperature and PPESK concentration. At all the cure conditions, the T_g of the epoxy-rich phase was much higher than that of the neat epoxy. It is possible that hydrogen bonds formed between the hydroxyl of epoxy and carbonyl of the PPESK and the rigid chain of PPESK are bound to the epoxy network that limited the epoxy phase to move and accordingly increased the T_g of epoxy-rich phase. The T_g of the epoxy-rich phase reached the maximum value at 5-phr PPESK, and then decreased and showed no significant change with increasing content of PPESK. This indicated that the solubility of PPESK in the epoxy phase was limited and the epoxy phase seemingly became saturated by the excess of PPESK present. In addition, the T_g of the epoxy-rich phase increased with the

cure temperature, suggesting that temperature had a larger effect on the cross-link density than the effect of PPESK loading due to the reduced viscosity at higher temperature enabling the epoxy resin to overcome any steric hindrance, react further, and produce a higher cross-link density material.

Thus, the epoxy-rich phase showed similar behavior to a neat thermoset in that to reach higher glass transition, it was necessary to cure at higher temperatures. In contrast, the ultimate T_g of the PPESK phase (shown in Fig. 4) can be seen to be far less dependent on cure temperature and PPESK concentration than the glass transition temperature of the epoxy phase. The behavior of higher T_g of PPESK phase than that of pure PPESK was perhaps due to the lower mobility of thermoplastic in the epoxy network matrix and the PPESK matrix plastic deformation was constrained by the epoxy network. Furthermore, the T_g of β phase decreased with the increase of PPESK loadings on the whole. It could be attributed to the molecular weight distribution and the solubility of lower molecular proportions of PPESK. When the PPESK loadings were lower, most of the low-molecular proportions dissolved in the epoxy-rich phase, and the PPESK-rich phase involved nearly all of the high-molecular proportions, resulting in the narrow glass transition area and higher glass transition temperature (see Fig. 2). However, when the PPESK loadings were higher, the viscosity increased, and the low-molecular proportions became saturated in the epoxy-rich phase. Hence the PPESK-rich phase retained many low-molecular weight polymers, and the glass transition area became wide leading to the lower glass transition temperature. In addition, the glass transition temperature of PPESK phase changed little from cure conditions A to D in the same phr-PPESK. Thus, the PPESK-rich phase showed different
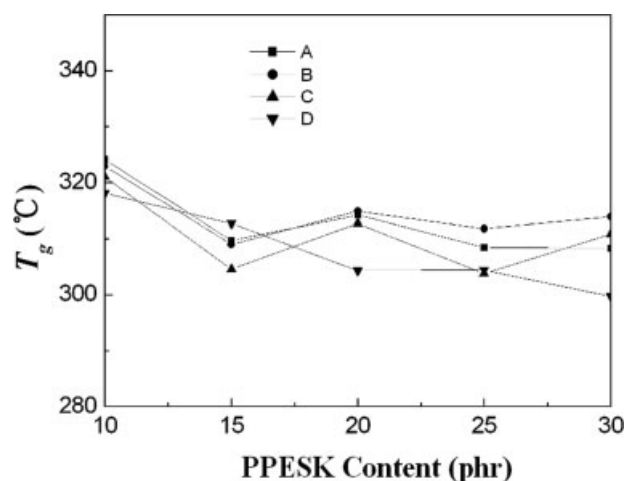

Figure 4 Plot of T_g of PPESK-rich phase versus PPESK content for samples of varying cure conditions.

behavior to a thermoset in that it was not necessary to cure at higher temperature to reach higher glass transition temperature. The relative small changes in the T_g of the PPESK phase compared with the changes observed in the epoxy phase suggested that PPESK was much more soluble in the epoxy phase than epoxy was in the PPESK phase, which is contrast to the study of Varley et al.[22] Their results suggest that PSF is much less soluble in the epoxy phase than epoxy in the PSF phase.

Morphological studies

It is well known that the final morphology of thermoplastic/epoxy blend is a result of competition between the molecular weight increase of the epoxy, leading to phase separation, and the simultaneous cross-linking which suppresses it. The morphologies of the PPESK/DGEBA blends cured in conditions C were analyzed by SEM. To get clear picture, the cryogenically fractured surfaces were etched with chloroform. The scanning electron micrographs of the 5-, 10- and 15-phr blends are shown in Figure 5. All the blends were heterogeneous after curing. However, the morphology of the final cured blends was found to be dependent on the content of PPESK. The fracture surface of the 5-phr PPESK blend consisted of a continuous epoxy matrix with the spherical domains of dispersed PPESK phase. The bright parts correspond to the PPESK-rich phase (β phase) and the dark parts correspond to epoxy-rich phase (α phase). Treatment of the fracture surface with a good solvent of PPESK chloroform had no effect on the spherical particles. It was clear that the dispersed PPESK phase also contained cross-linked epoxy resin, which probably reacted with the PPESK, rendering it insoluble. The morphology of 10-phr PPESK blend were two-phase interpenetrating, the epoxy phase and PPESK phase entangled with each other irregularly. The PPESK-rich domain was clearly mesh-like and interconnecting and thus continuous.

The 15-phr blend showed that the PPESK segregated into spherical domains in the continuous epoxy resins. The observed spherical cavities were due to the removal of the PPESK inclusions during solvent etching. This result indicated that the PPESK was not completely involved in the cross-linking reaction and hence it retained its ductility that deformed plastically under loading.

Fracture toughness

The fracture toughness is the resistance of a material to crack initiation and propagation. In the present case, the fracture toughness of the blends, expressed as un-notched impact strength, is plotted in Figure 6
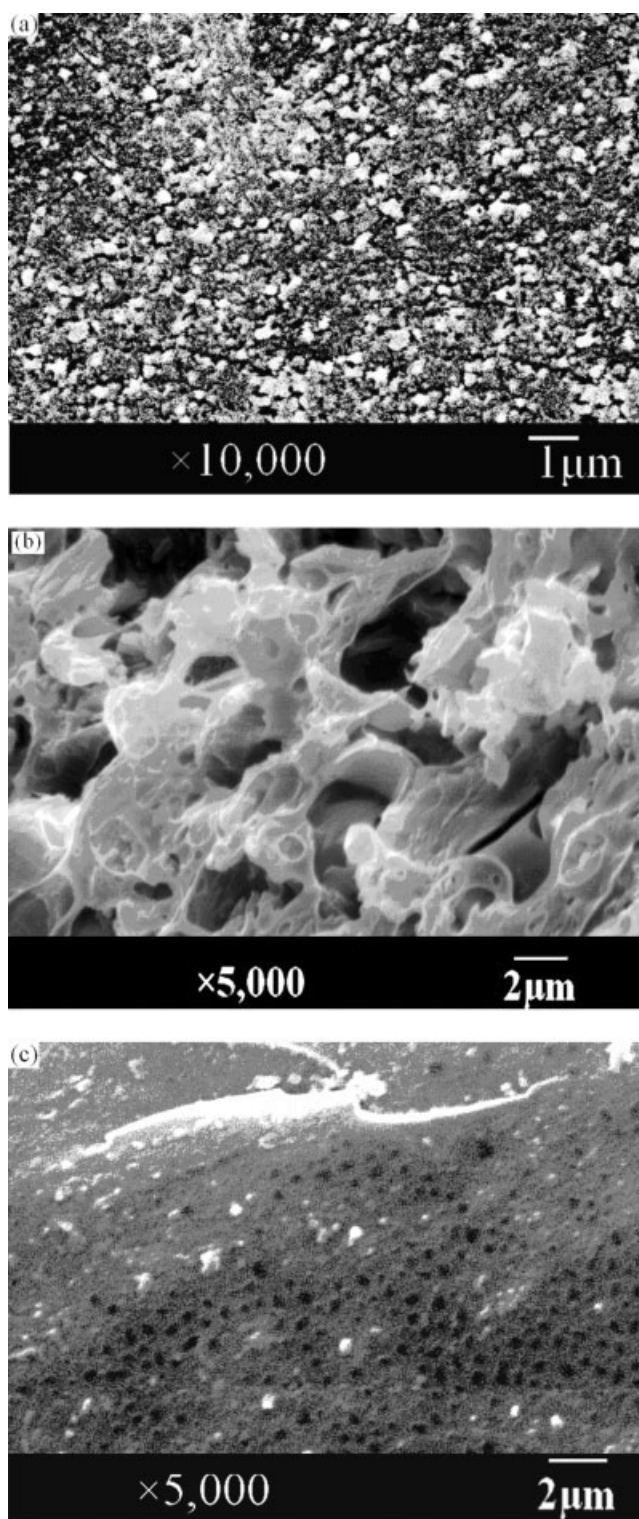

Figure 5 SEM micrographs of DGEBA/PPESK blends cured under conditions C: (a) 5-phr PPESK, (b) 10-phr PPESK, and (c) 15-phr PPESK.

as the function of the PPESK concentration at the different cure conditions. It can be seen that the maximum impact strength values of modified epoxy resins appeared at 5-phr PPESK in every cure conditions. However, there was no further improvement
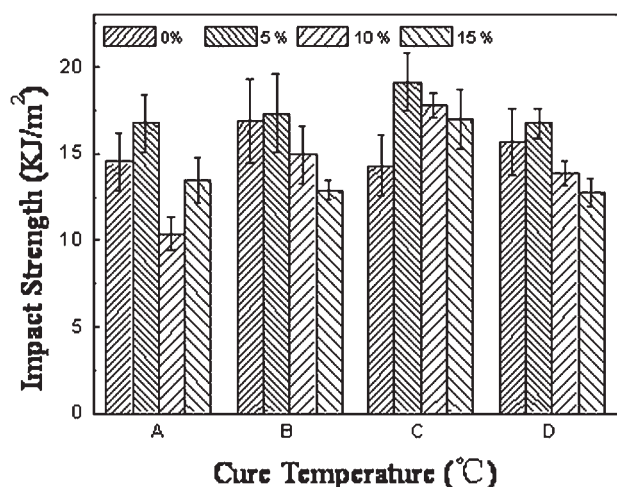
Figure 6 Impact strength of DGEBA/PPESK blends of varying cure conditions.

compared with the neat epoxy when the PPESK content was increased except curing condition C. It was also found that variation of the final postcure schedule did not have obvious effects on the impact strength and the curing conditions C resulted in higher toughness over the three other curing conditions. This was because increasing the postcure temperature caused an increase in the increasing in the cross-link density and hence a decrease in the mobility of the network, leading to a decrease in impact strength. At the same time, increasing the postcure temperature decreased the viscosity of the system and hence a more complete phase separation, leading to an increase in the impact strength. Therefore, this competition made the curing conditions C showed better toughness. Thus the further tests were conducted on the samples cured under the conditions C. Un-notched impact strength involves not only the initiation of the crack resulting from the growth of intrinsic defects but also its propagation. For the 5-phr PPESK blend, the fine particles phase of PPESK made it difficult to initiate cracks during un-notched impact test and the crack was split into some branches to avoid progressing through the dispersed particles. As a result, the particles of PPESK caused the drastic increase in the toughness of the resin. Moreover, the connected PPESK morphology enabled the cracks extension to grow further and thus consumed more energy when PPESK formed a continuous phase before failure occurred, which also caused the increase in the toughness of the blends. It is well known that a significant increase in toughness can be obtained when the thermoplastic/epoxy blends form co-continuous phase morphology.[23–25] However, in this study, the maximum value with 5-phr PPESK was about 33% higher than that of the unmodified epoxy resin. This weak improvement of fracture toughness compared with the glass transi-

tion temperature (T_g) was due to the rigid nonfunctionalized thermoplastic PPESK and the rigid matrix (as characterized by high T_g) was more difficult to occur displacement and deformation, leading to lower fracture toughness.

The increase in fracture toughness occurred for many reasons. One important requirement for obtaining enhanced fracture toughness in a thermoset/thermoplastic blend is a two-phase morphology.[26–30] The dispersed thermoplastic phase will initiate different process that will increase the fracture toughness. The scanning electron micrographs in Figure 5 had shown the two-phase morphology of the PPESK/DGEBA blends. To further investigate the toughening mechanisms, scanning electron micrographs were taken of the fractured surfaces of the failed specimens in different magnifications, which are shown in Figure 7. It can be seen that there was not plastic formation emerged on the fracture plane of the neat epoxy resin [see Fig. 7(a)], and the fracture plane was smooth and featureless. This was a kind of typical brittle rupture. Although the fracture surfaces of the cured epoxy blends with PPESK were different from that of the unmodified epoxy resin. The fracture surfaces were rough and river marks formed on the surfaces [see Fig. 7(b–d)]. These were evidences for the plastic deformation of the matrix, crack deflection, and ductile nature of the crack from the different multiple SEM images. Therefore, some explanations of the failure process were proposed. One factor responsible for the increase in the fracture toughness was the local plastic deformation of the matrix. PPESK, which diffused into epoxy resin, improved the plasticity of epoxy resin around the PPESK dispersed phase. These diffused PPESK particles could induce stress relaxation by way of local shear deformation. Furthermore, deformation energy was absorbed by the ductile drawing process of PPESK phase. In addition, the crack was split into some branches, deviated from their original plane and initiated more ductile microcracks, resulting in increased surface area of the crack, thereby increasing the toughness. All the aforementioned factors were favorable for the enhancement of the fracture toughness of the blends.

CONCLUSIONS

The mechanical behaviors of various content PPESK-modified-epoxy mixtures have been investigated for several cure schedules. Results have shown that the novel high-temperature-resistant high performance thermoplastic PPESK is an excellent candidate materials for improving the glass transition temperature and toughness of the epoxy–amine resin system. Results of this investigation can be summarized as follows:
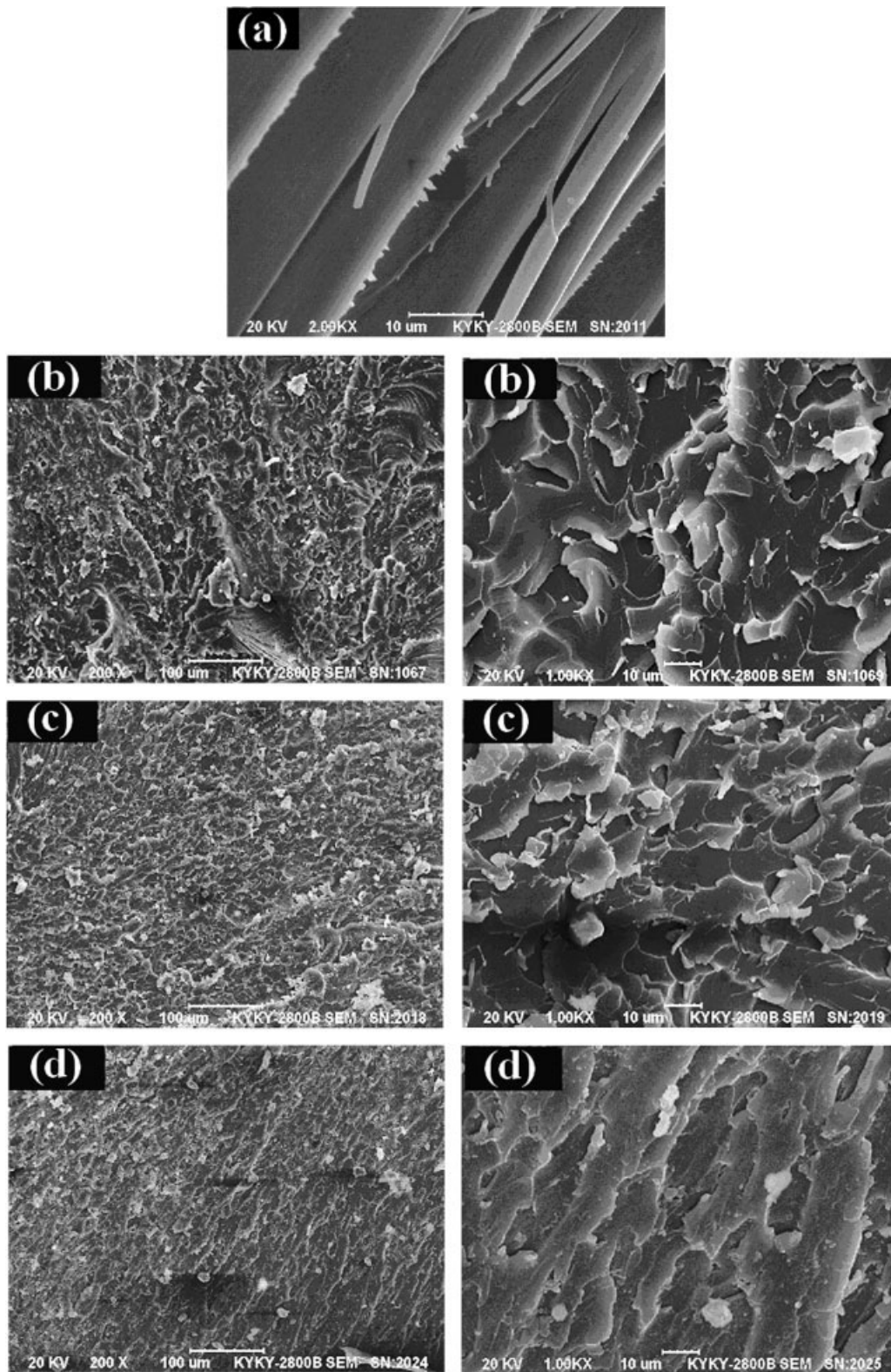
Figure 7 Scanning electron micrographs of failed surfaces of DGEBA/PPESK blends cured by conditions C: (a) neat epoxy resin, (b) 5-phr PPESK, (c) 10-phr PPESK, and (d) 15-phr PPESK.

- The DSC analysis of the blends gave two T_g's corresponding to epoxy-rich and thermoplastic-rich phases. The T_g of the blends was significantly higher not only in the epoxy phase but also in the PPESK phase than the pure epoxy and PPESK. The SEM micrographs of blends confirmed the results of DSC. All the blends exhibited heterogeneity and their morphologies

were found to be dependent on the content of PPESK.

- The fracture toughness of the modified mixtures with respect to the neat ones was accompanied by only slightly higher values, because of the high glass transition temperature of the matrix.
- Several toughening mechanisms such as local plastic deformation, crack deflection, and branches, ductile tearing of thermoplastic and the occurrence of ductile microcrack took part in improving the toughness of PPESK/epoxy blends.

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