Influence of Cyanate Content on the Morphology and Properties of Epoxy Resins with Phenolphthalein Poly(ether ketone)

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ABSTRACT: Phenolphthalein poly(ether ketone) (PEK-C) was blended with the diglycidyl ether of bisphenol A epoxy resin and bisphenol A dicyanate ester. The effect of cyanate content on cure behaviors, thermal and mechanical properties of PEK-C/epoxy/cyanate mixtures was investigated. As results, the increase of cyanate content slightly hindered the cure reaction of the mixtures. Fourier transform infrared results indicated that the curing reaction of the cured mixtures was complete. When the cyanate ester content increased, the flexural properties and T_g values were enhanced, and the initial thermal decomposition temperature was reduced. A significant improvement in fracture toughness was obtained when the cyanate group in the mixtures was excessive. The fracture toughness can be well explained by SEM observations. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 598–603, 2011

Key words: epoxy; toughness; blends

INTRODUCTION

Epoxy resins are widely used as resins matrix for structural composites and adhesives because of their ease of handling and processing. However, epoxy resins still have two drawbacks: (1) relatively high-dielectric loss and poor water absorption properties[1,2]; (2) brittlement because of high-cross-link densities.[3,4]

Cyanate ester resin, a relative newcomer to the composites industry, is an interesting modifiers for epoxy resin. In this way, a very complicated coreaction is involved in epoxy/cyanate ester blends since it involves[5,6]: (1) the formation of triazine ring through trimerization of cyanate ester; (2) oxazolidinone formation through the coreaction of epoxy and cyanate ester; (3) polyetherization. The appearance of linear chain (oxazolidone cycle) and cross-link network (triazine ring) permits us to obtain final products with completely different properties. As a result, epoxy resins with cyanate have better dielectric properties and higher thermal performances in hot/wet environments. Recently, this blend has been widely used in both the aerospace and the electronic industry.[7]

Toughening epoxy resins using rubbers has been known for a considerable time.[8] However, the use of rubber as toughening agent results in a significant decrease in modulus, yield strength, and glass transition temperature (T_g) of the cured epoxy resins. Thereby, toughening of epoxy resins is often explored by blending with high modulus and high T_g thermoplastics.[9–13] There are many reports on epoxy/cyanate or epoxy/thermoplastic blends. But few studies on thermoplastic/epoxy/cyanate ternary mixtures can be seen.[14,15]

Phenolphthalein poly(ether ketone) (PEK-C) is a high-performance thermoplastic with a T_g of 234°C[16] as measured by dynamic mechanical analysis (DMA). In the previous work,[17,18] we have studied the influence of PEK-C content on cure reaction, morphology and properties of the stoichiometric epoxy/cyanate blend. In this paper, the effect of cyanate content on the cure behaviors, mechanical and thermal properties of PEK-C/epoxy/cyanate mixtures was further investigated.

EXPERIMENTAL

Materials

Phenolphthalein PEK-C with an intrinsic viscosity of 0.81 dL g^{-1} was purchased from Xuzhou Chemical Factory, China. The diglycidyl ether of bisphenol A
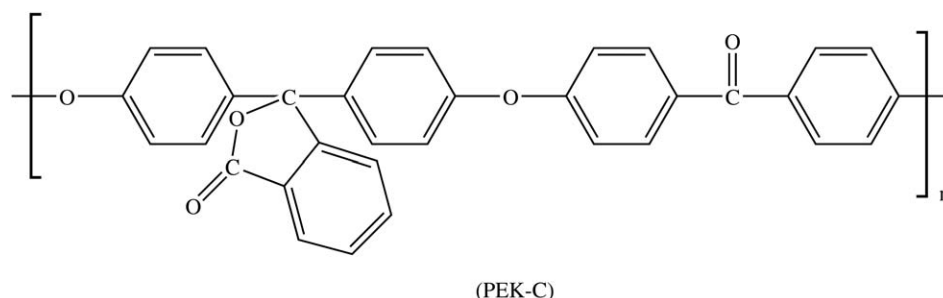
(PEK-C)

Figure 1 Chemical structure of PEK-C.

epoxy resin with epoxy equivalent 185–210, was supplied by Wuxi Resin Works, China. Bisphenol A dicyanate was provided by Shanghai Huifeng Technical and Business. All reagents were used as received. The chemical structure of PEK-C is given in Figure 1.

Sample preparation

PEK-C was first dissolved in the epoxy resin at 150°C with constant stirring. After complete dissolution, cyanate was dissolved in PEK-C/epoxy blend at 150°C in less than 1 min to minimize the curing reaction during the mixing for calorimetry measurements. Other samples were prepared by molding the mixture in Teflon molds and cured according to 150°C/4 h + 200°C/2 h + 230°C/4 h.

Three types of epoxy/cyanate network, named A, B, and C, were chosen as the studied targets, and the stoichiometry of cyanate to epoxy was 0.67, 1, and 2, respectively. The network A with 10 wt % PEK-C was designated as A-10. The meanings of other sample codes can be deduced by analogy.

Measurement

The cure behaviors of the ternary blends were monitored by differential scanning calorimetry (DSC, PE Diamond) at the heating rate of 10°C min^{-1} under N$_2$ atmosphere. Fourier transform infrared (FTIR) was performed with a Nicolet-20DXB using KBr pellets. The spectrums were taken using the following conditions: spectral width 4000–600 cm^{-1} and resolution of 4 cm^{-1}.

Thermogravimetric analysis (TGA) was performed with a Netzsch instrument model TG 209C thermal analyzer. The samples were heated from room temperature to 600°C at a heating rate of 10°C min^{-1} in N$_2$ atmosphere.

DMA was carried out on a TA Q800 instrument operating single-cantilever bending mode. The frequency used was 1 Hz, and the heating rate was set at 5°C min^{-1}. The specimen dimension was 31 × 10 × 3 mm^3.

Mechanical measurements were performed on a universal test machine in the three-point bending mode. The flexural tests were carried out at a cross-head speed of 2.0 mm min^{-1} with rectangular specimens of 80 × 10 × 4 mm^3 specimens. The loading span was 64 mm. The flexural strength and modulus were obtained from the stress–strain curve. The fracture toughness was measured by the single-edge-notched specimens of 58 × 12 × 6 mm^3 with a span of 48 mm at a constant cross-head speed of 1.3 mm min^{-1}. A notch of 6 mm was made at the center of one edge. The critical stress intensity factor (K_{IC}) and the critical strain energy release rate (G_{IC}) was determined using[19]

$$K_{IC} = \frac{P_c \cdot S}{B \cdot w^{3/2}} f(a/w)$$

$$G_{IC} = \frac{(1 - v^2)K_{IC}^2}{E}$$

where

$$f\left(\frac{a}{w}\right) = \frac{3(a/w)^{1/2}[1.99 - (a/w)(1 - a/w) \times (2.15 - 3.93a/w + 2.7a^2/w^2)]}{2(1 + 2a/w)(1 - a/w)^{3/2}}$$

P_c is the maximum load at fracture, and S, B, W, and a are the span width, thickness, width, and the crack length of the specimen, respectively. v is the Poisson's ratio, taken as 0.35. E is the average flexural modulus for each composition.

The fracture surfaces of the cured resins were investigated by using scanning electron micros-

copy (SEM; X-650 Hitachi). The fracture surfaces of samples were mounted and gold-coated by vapor deposition using a vacuum sputter. Some of the fractured samples were etched with tetrachloroethane at room temperature for 24 h before they were gold-coated and examined by microscopy.
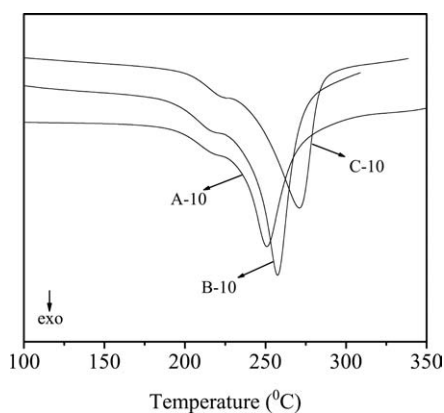
Figure 2 DSC curves of various epoxy/cyanate mixtures with 10 wt % PEK-C at the heating rate of $10°C \ min^{-1}$.

RESULTS AND DISCUSSION

Cure reaction

Various epoxy/cyanate mixtures with 10% PEK-C were subjected to dynamic DSC measurements to investigate the effect of cyanate content on cure reaction. Figure 2 displays the dynamic DSC curves for the three studied mixtures at a heating rate of $10°C \ min^{-1}$. All the DSC curves produced a broad exothermic peak with a small shoulder at lower temperature, suggesting similar curing pathways. But the peak maximum temperature (T_p) of the mixtures shifted to higher temperature with increasing the cyanate ester content. This phenomenon indicates that the increase of cyanate content resulted in a retardation effect on the cure reaction, probably due to the decrease of effective catalysts (—OH groups) in the initial mixtures.[5] A similar trend has been observed in the epoxy/cyanate systems catalyzed by lanthanum acetylacetone.[20]

Furthermore, FTIR studies were conducted to examine the completion of curing reaction and the chemical structures of the cured mixtures. Figure 3 shows FTIR plots of the cured mixtures and PEK-C. It is obvious that the absorption peaks of epoxy group (at 916 cm^{-1}) and oxazolidinone (at 1758 cm^{-1})
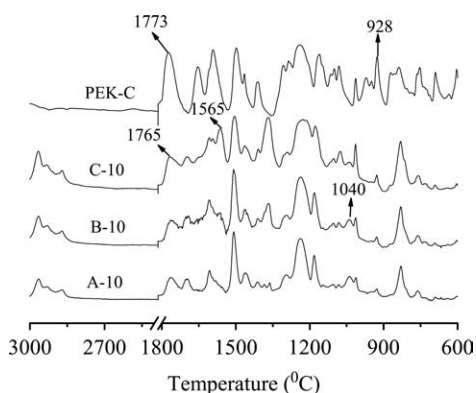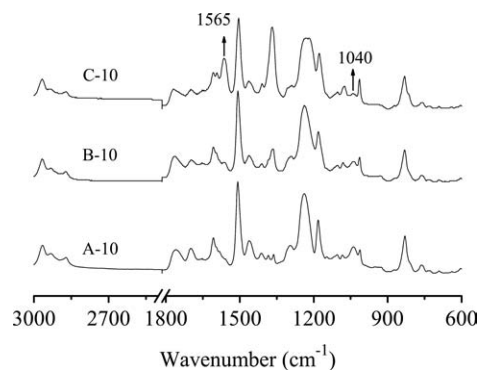

Figure 4 The subtracted FTIR spectra of the cured mixtures.

overlap with those of PEK-C (at 928 and 1773 cm^{-1}). Thus, a subtraction technique was used to subtract the PEK-C component from the mixtures.[21] The subtracted FTIR spectra of the cured mixtures were given in Figure 4. From Figure 4, it can be seen that there was no characteristic epoxy peak at 916 cm^{-1}, indicating that the curing reaction was complete. As can be expected, triazine rings increased and polyether structure decreased with the increase of cyanate ester content in the initial mixtures. This behavior can be well explained in light of the cure mechanisms and the functionality of the monomers.

Thermal stability

The thermal degradation behaviors of various epoxy/cyanate mixtures with 10% PEK-C were studied with TGA at a heating rate of $10°C \ min^{-1}$, and the results are shown in Figure 5. All the thermal degradation proceeded in a single step process. Thermal stability factors, including the 5% weight loss temperature ($T_{5\%}$), the temperature at the maximum weight loss (T_{max}) and char yield of the mixtures can be determined from TGA thermograms, and these parameters are summarized in Table I. As a result, $T_{5\%}$ and T_{max} decreased as the content of cyanate ester increased. It may be related with

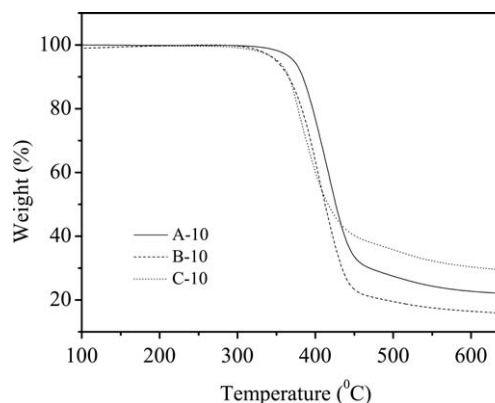**Figure 3** FTIR plots of the cured mixtures and PEK-C.

Figure 5 The TGA curves of various epoxy/cyanate mixtures with 10 wt % PEK-C.

TABLE I
Thermal Stability Factors of Various PEK-C/Epoxy/
Cyanate Mixtures Calculated from TGA Curves

Samples	$T_{5\%}$ (°C)	T_{max} (°C)	Char yield (%)
A-10	372	410	23
B-10	350	400	17
C-10	353	377	31

the phase structure and the thermal stability of PEK-C. All the cured PEK-C/epoxy/cyanate blends were thermally stable up to about 350°C.

Dynamic mechanical properties

Figure 6 shows the temperature dependence of the tan δ and storage modulus for PEK-C/epoxy/cyanate mixtures. The storage modulus values (E') of the blends at 50°C (at glassy region) and 270°C (at rubbery region), as well as T_g values obtained from the maximum in tan δ curve are presented in Table II. It can be seen that tan δ spectra of all epoxy/cyanate blends remained single peak and T_g of the cured blends increased with increasing cyanate ester content. Meanwhile, the A-10 and B-10 sample also showed a single tan δ peak, indicating a miscible structure. But appearance of a shoulder peak adja-

TABLE II
Dynamic Mechanical Properties of Various PEK-C/
Epoxy/Cyanate Mixtures Obtained from DMA Curves

Samples	Storage modulus (MPa)		T_g (°C)
	Glassy (50°C)	Rubbery (270°C)	
A	2040	57.1	223
A-10	2055	46.8	224
B	2340	46.6	232
B-10	1926	37.6	234
C	2294	47.2	241
C-10	2162	27.2	230, 240

cent to the major peak observed in C-10 sample suggests occurrence of some degree of phase separation. The one at high temperature is attributed to the T_g of the thermoset-rich domain, and the one at low temperature is associated with the T_g of the thermoplastic-rich phase. In all cases, T_g value of the modified mixtures remained close to that of the unmodified epoxy/cyanate blends.

With respect to E' curves, as the temperature increases, all the studied systems showed a gradual drop. In the glassy region, the storage moduli of B and C sample were greater than that of A sample, which may be due to the presence of more rigid triazine and oxazolidinone. Compared with the corresponding epoxy/cyanate blend, the storage modulus of A-10 sample was hardly changed, whereas those of B-10 and C-10 sample were reduced. The decrease of storage modulus in B-10 and C-10 sample was probably due to lower E' value of pristine PEK-C. Cross-link density of the blends can be calculated from the storage modulus values in the rubbery plateau region.[22] In general, an increase of storage modulus may be related to a reduction of cross-linking density. Thus, as evidenced by Table II, B and C sample in three epoxy/cyanate blends exhibited lower cross-link density than A sample, and the crosslink density for all epoxy/cyanate blends was found to slightly decrease with the increasing of PEK-C loading.

Mechanical properties

The mechanical properties of the different PEK-C/epoxy/cyanate mixtures are given in Table III. The addition of PEK-C had no significant effect on the flexural strength and modulus of various epoxy/cyanate blends, whereas the increase of cyanate ester content in either epoxy/cyanate or PEK-C/epoxy/cyanate blends led to enhancements of the flexural properties. This may be attributed to the change of the network structure in the blends with the increase of cyanate content.[23]

Fracture toughness is the resistance of a material toward crack initiation and propagation, and it is often expressed as K_{IC} and G_{IC}. As seen in Table III,
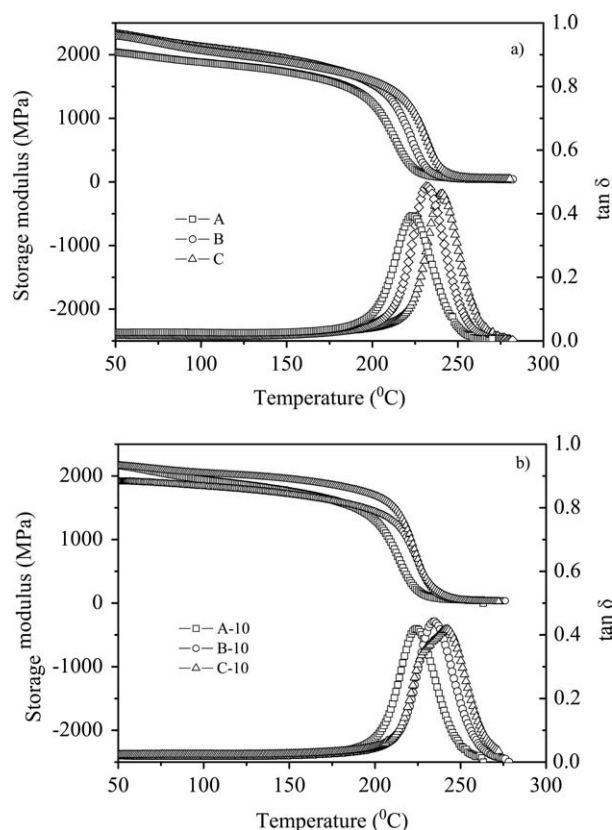

Figure 6 Dynamic mechanical properties of (a) A, B, and C sample and (b) A-10, B-10, and C-10 sample.

TABLE III
Mechanical Properties of the Various PEK-C/Epoxy/Cyanate Mixtures

Samples	Flexural strength (MPa)	Flexural modulus (GPa)	K_{IC} (MN/m$^{3/2}$)	G_{IC} (J m^{-2})
A	114 ± 8	2.7 ± 0.1	0.82 ± 0.06	211 ± 30
A-5	115 ± 8	2.7 ± 0.1	0.88 ± 0.10	236 ± 70
A-10	117 ± 7	2.8 ± 0.1	0.92 ± 0.10	258 ± 60
B	130 ± 14	2.9 ± 0.1	0.99 ± 0.10	281 ± 70
B-5	140 ± 7	2.9 ± 0.1	1.06 ± 0.07	332 ± 70
B-10	122 ± 10	2.9 ± 0.1	1.06 ± 0.09	329 ± 50
C	133 ± 9	3.1 ± 0.1	0.96 ± 0.04	252 ± 30
C-5	130 ± 10	3.0 ± 0.1	0.99 ± 0.10	267 ± 50
C-10	128 ± 9	3.1 ± 0.1	1.27 ± 0.05	433 ± 30

in the case of neat epoxy/cyanate blends, the fracture toughness of B and C sample was greater than that of A sample. In all cases, the fracture toughness of epoxy/cyanate blends increased with modification of PEK-C, while the toughening effect of PEK-C depended on the amount of cyanate ester resin. The improvement of fracture toughness in the A-10 and B-10 sample was modest, while higher improvement was achieved in C-10 sample. Accordingly, maximum K_{IC} and G_{IC} values of 1.27 MPa·m$^{1/2}$ and 432.8 J m^{-2} were obtained in C-10 sample.

The toughness behaviors can be explained in the terms of morphology with SEM, and Figure 7(a–f) shows the SEM photographs of various composition
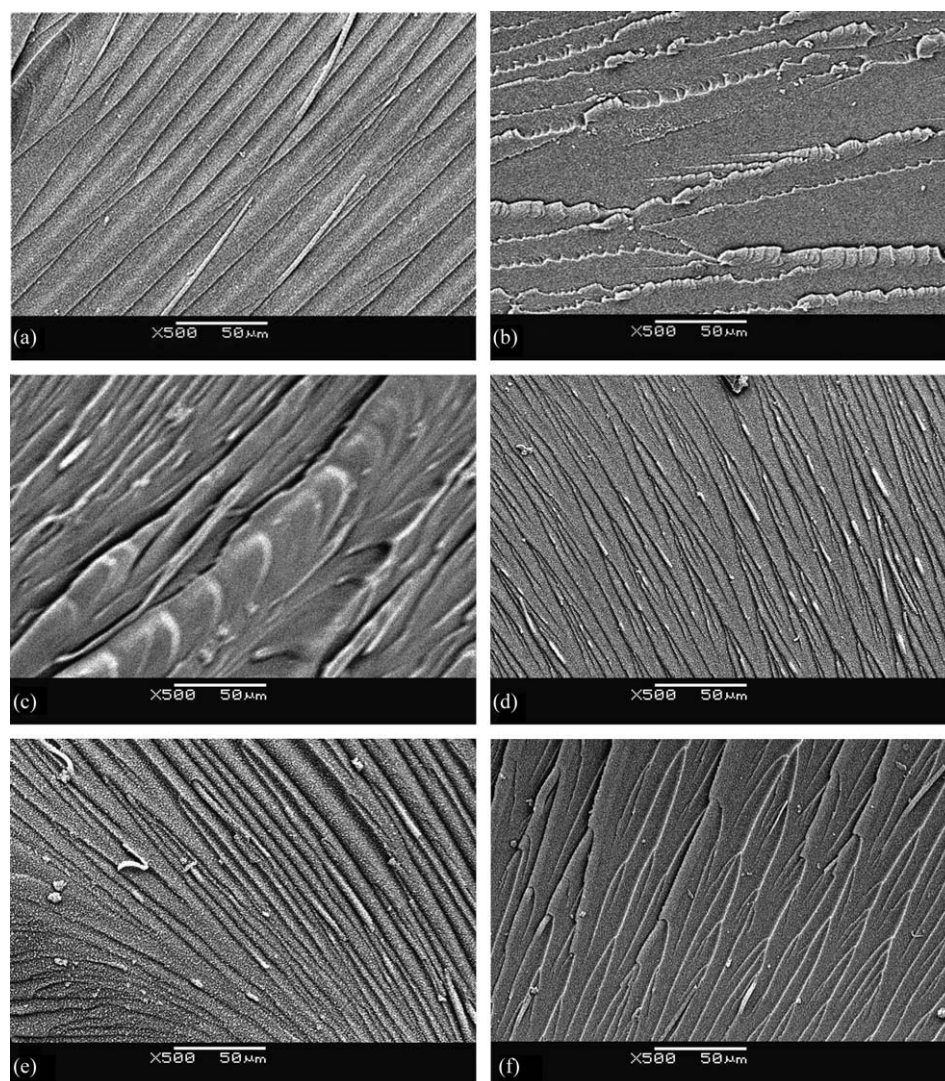

Figure 7 SEM micrographs of (a) A, (b) A-10, (c) B, (d) B-10, (e) C, and (f) C-10 sample.

mixtures. The fracture surfaces for epoxy/cyanate blends were smooth and the crack propagation was basically uninterrupted. This is typical of brittle fracture. But compared with A sample, the fracture surfaces of B and C sample were rougher and exhibited more cracks. Correspondingly, B and C sample had higher K_{IC} and G_{IC} values, probably due to the decrease in cross-link density as evidenced by E' in rubbery region. In addition, the toughening effect of thermoplastic resins strongly depends on the phase separation of the cured mixture. As shown in Figure 7(b), the crack for A-10 sample was basically extended in uniform direction with a homogeneous aspect, and only some ridge patterns were observed along the crack propagation path; hence, its fracture toughness got limited improvement correspondingly. However, phase separation and branches appeared on the fracture surfaces of the B-10 and C-10 curing systems. These branches effectively dispersed the energy responsible for crack initiation, resulting in the higher fracture toughness.[24–26]

CONCLUSIONS

In this study, a high-temperature resistant and toughened epoxy resins matrix was prepared by melt-blending epoxy resin with cyanate ester and phenolphthalein PEK-C. The effect of cyanate content on the cure behaviors, mechanical and thermal properties of the blends was investigated. A delay in the curing rate was observed with increasing cyanate ester content. FTIR spectra of the cured mixtures indicated that triazine rings increased and oxazolidinone decreased with the increase of cyanate content. Meanwhile, as the cyanate content increased, the T_g and flexural properties increased, whereas the thermal stability decreased. In all cases, the fracture toughness of epoxy/cyanate blends increased with incorporation of PEK-C, whereas the toughening effect of PEK-C strongly depended on the amount of cyanate ester resin. The considerable toughening effect appeared at an excessive amount of cyanate group case, probably due to the formation of phase-separated structure as evidenced by DMA and SEM. Ultimately, the optimum properties were obtained in the blend of 1 : 2 epoxy/cyanate with 10 wt % PEK-C.

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