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ORIGINAL CONTRIBUTION

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Morphology and mechanical properties of poly (ether-imide)-modified polycyanurates

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Abstract A high temperature thermosetting bisphenol A dicyanate (BADCy) was modified with a novel thermoplastic poly(ether-imide) (PEI) at various compositions. Fourier transform infrared spectroscopy was used to measure the conversion of BADCy. Curing kinetics of the BADCy/PEI blend were studied by the dynamic differential scanning calorimeter method. Morphologies of PEI-modified polycyanurates were investigated by scanning electron microscopy (SEM). It was found that the phase structures of the blends changed dramatically with the PEI content and molecular weight. The tensile results showed that the mechanical properties could be correlated with the morphologies. The blend with cocontinuous morphology had the highest tensile strength and elongation at break while the blend with ribbon-like morphology had the lowest one despite PEI molecular weight.

Keywords Blends · Phase separation · Morphology

Introduction

Thermosetting polycyanurates prepared from polycyclotrimerization of aromatic cyanate resins have drawn increasing attention due to their important application in industry. This cross-linked polycyanurates distinguished themselves from other thermosetting polymers by their excellent dielectric properties, thermal and dimensional stability, and low moisture absorption, which facilitated their applications in the electronic and composite areas. Though cyanate resins are known to be relatively tough compared with other thermosetting polymers, some applications required improved fracture toughness [1, 2].

The toughening of polycyanurates was achieved by the incorporation of thermoplastics without the reduction of polycyanurates' thermal and mechanical properties. These thermoplastics included polysulfones [3–5], poly(ether sulfone) [6, 7], polyarylates [8], poly(ether-imide) (PEI) [3, 9, 10], and so on. Generally, the cyanate and thermoplastic blend was homogeneous at the beginning of curing. As cure proceeded, the increasing molecular weight of the cyanate resins initiated phase separation to generate heterogeneous two-phase morphologies. Two main factors affect the morphology of the blend: thermodynamics and the kinetics of phase separation during curing. Therefore, the morphology could be changed by the content and molecular weight of the thermoplastic in the blend and/or curing conditions. The generated morphologies would have a great effect on the mechanical properties of the blends. It was reported that the fracture toughness could be dramatically improved in the case of the thermosetting/thermoplastic blend with cocontinuous or phase-inversion morphology [11].

In this study, a soluble PEI was used to modify the polycyanurates. Conversion of bisphenol A dicyanate (BADCy) was measured by Fourier transform infrared (FT-IR) spectroscopy and curing kinetics of the BADCy/PEI blend were studied by the dynamic differential scan-

ning calorimeter (DSC) method. The effects of morphologies and PEI molecular weight on the mechanical properties of the cured blends were studied.

Experimental

Materials

The BADCy with a cyanate equivalent of 139 g/eq was supplied by Beijing Aeronautical Manufacturing Technology Research Institute. The PEI was synthesized in one step from bisphenol A dianhydride (BISA-DA) and 4,4′-[1,4-phenylenebis(1-methylethylidene)bisaniline (BISP) in *m*-cresol at 200 °C for 6 h. With variations of stoichiometric ratio of BISA-DA and BISP, PEI polymers with two kinds of molecular weight were obtained. The inherent viscosity of PEI was determined at 30 °C in *N*-methyl-2-pyrrolidone as solvent. The PEI was designated as PEI (χ) where χ represented the inherent viscosity (in dl/g). Figure 1 shows the chemical structures of BADCy and PEI.

Mixing and curing procedure

PEI was dissolved in methylene chloride (CH_2Cl_2) and mixed with BADCy at room temperature. The residual solvent was removed under vacuum at 90 °C for 1 h after most of the solvent was evaporated at 40 °C. The mixtures were molded and then cured at 150 °C for 6 h.

FT-IR measurement

The sample films were prepared by solvent casting of a film onto aluminum foil from a methylene chloride solution (10wt% blend). The infrared spectra of the samples were recorded with a Nicolet Magna-IR 550.

Differential scanning calorimetry

Differential scanning calorimetry measurements were performed with DSC (Setaram 141). The DSC was calibrated with high-purity indium. Around 10 mg of samples were weighed into small DSC aluminum lids and experiments were conducted under a nitrogen flow of 40 ml/min.

SEM analysis

The morphology of the cured samples was investigated by scanning electron microscopy (SEM) (Philips XL39). The cured samples were fractured in liquid nitrogen and then the fracture surface was coated with a fine gold layer.

Mechanical properties testing

The specimens for mechanical properties testing were prepared by solvent casting of a film onto glass substrate from a methylene chloride solution (10wt% blend). The blend films were dried under vacuum at room temperature for 2 days to remove the solvent, then cured at 150 °C for 6 h, and then postcured at 210 °C for 2 h. The films used were around 0.1-mm-thick and were rectangular in shape (35×9 mm). Testing of the mechanical properties of the blends was performed using an Instron tensile tester (model 1121) at a constant temperature. A gauge length of 15 mm and a crosshead speed of 1 mm min^{-1} were used. All the reported results are averages of five specimens.

Results and discussion

FT-IR measurement

The conversion of the BADCy/PEI blend can be measured by the FT-IR method. The BADCy monomer had a characteristic C≡N stretching doublets at 2,270 and

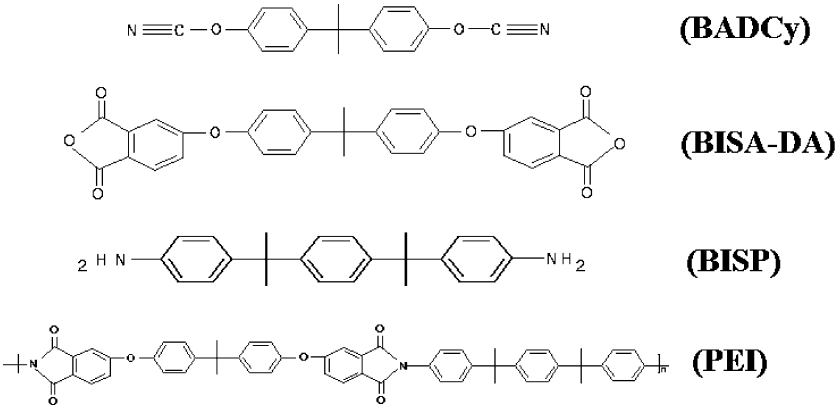

Fig. 1 Chemical structures of BADCy and PEI

2,235 cm^{-1}. As a triazine ring formed, the characteristic absorption peak at 2,270 and 2,235 cm^{-1} decreased gradually. Therefore, conversion can be calculated using the height of 2,270 cm^{-1} band with respect to the height of the reference band (the side-chain methyl stretching vibration) at 2,970 cm^{-1}. The conversion of BADCy monomer at different times was calculated as follows:

$$\chi = 1 - \frac{A(t)_{2,270}/A(o)_{2,270}}{A(t)_{2,970}/A(o)_{2,970}}$$

where $A(t)_{2,270}$ is the absorbance intensity at 2,270 cm^{-1} at time t, $A(t)_{2,970}$ is the absorbance intensity at 2,970 cm^{-1} at time t, $A(0)$ is the initial absorbance intensity, and χ is the extent of conversion of BADCy monomer.

Figure 2 shows that the variation of the absorbance intensity at 2,270 cm^{-1} was obvious in the infrared spectroscopy of the blend with 10wt% PEI (0.5) before and after curing. The conversions of all the BADCy/PEI blends after curing at 150 °C for 6 h or curing at 150 °C for 6 h and postcuring at 210 °C for 2 h are listed in Table 1. It was found that the blend composition had no obvious effect on the conversion both in the BADCy/PEI (0.5) and the BADCy/PEI (0.3) blends. For the BADCy/PEI (0.5) blends, however, the conversions were higher than the BADCy/PEI (0.3) blends, which might be attributed to their extent of phase separation. The BADCy/PEI (0.5) blends showed a higher extent of phase separation than the BADCy/PEI (0.3) blends as indicated in the results of SEM analysis. After postcuring at 210 °C for 2 h, the conversions of all the blends increased to more than 90%. Thus, the postcuring step is essential to attain excellent mechanical properties.

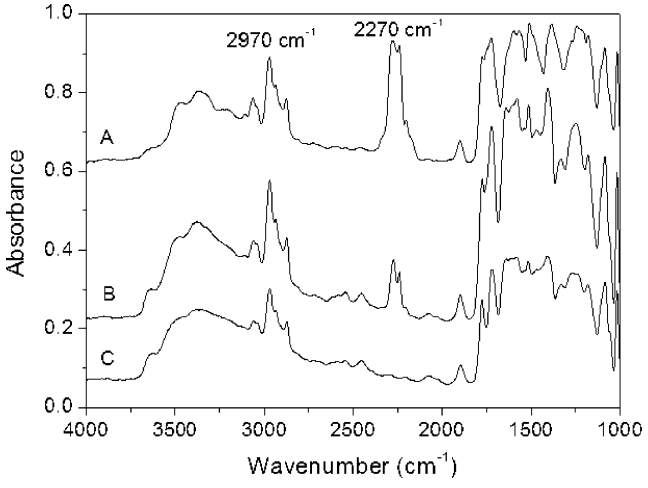

Fig. 2 FT-IR spectroscopy of the blend with 10wt% PEI (0.5): *a* before curing, *b* after curing at 150 °C for 6 h, *c* after curing at 150 °C for 6 h, and postcuring at 210 °C for 2 h

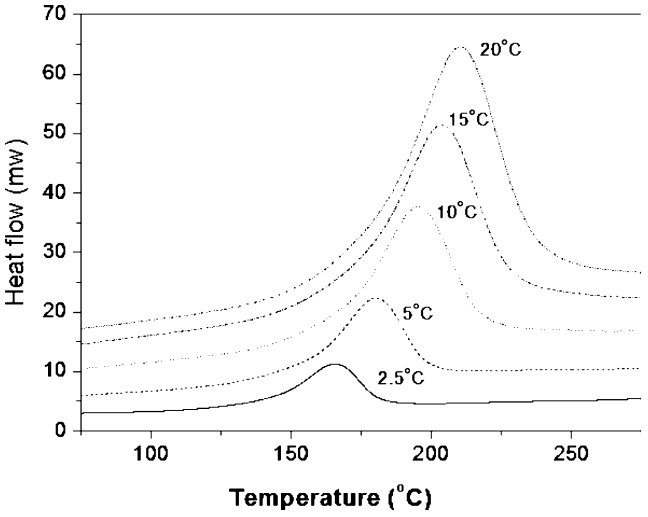

Fig. 3 The heat flow curves of the blend with 15wt% PEI (0.3) at various heating rates

Curing kinetics

The reaction activation energy of the curing reaction can be obtained by dynamic DSC. For example, the DSC heating traces of the blend with 15wt% PEI (0.3) at various heating rates (2.5, 5, 10, 15, and 20 °C/min) are shown in Fig. 3.

The data from dynamic DSC measurements were analyzed by the Kissinger method as follows [12]:

$$-\ln\left(\frac{\varphi}{T_P^2}\right) = \ln\left(\frac{E}{R}\right) - \ln(An) - (n-1)\ln(1-\alpha)_P + \frac{E}{RT_P}$$

where ϕ is the heating rate, T_P is the peak temperature of the DSC exothermic curves, α is the conversion, E is the reaction activation energy, and R is ideal gas constant.

If plots of $-\ln\left(\varphi/T_P^2\right)$ against $(1/T_P)$ is linear, the reaction activation energy can be obtained from the slope of the corresponding straight line. Figure 4 show the plots of $-\ln\left(\varphi/T_P^2\right)$ against $(1/T_P)$ for the BADCy/PEI (0.3) blend and BADCy/PEI (0.5) blend, respectively. The reaction activation energies calculated from Fig. 4 are listed in Table 2.

The results in Table 2 showed that the addition of PEI into BADCy resin resulted in the increase of the reaction activation energy of the curing reaction. Moreover, the reaction activation energy for the BADCy/PEI (0.5) blend was higher than the BADCy/PEI (0.3) blend. These were attributed to the effect of diffusion control in the late stage of the curing reaction. As cure proceeded and the resin was cross-linked, the glass transition temperature (T_g) of the curing system gradually increased. For cure temperature

Table 1 The conversion of all the blends during various curing conditions

Sample	Curing condition	PEI content		
		10wt%	15wt%	20wt%
BADCy/PEI (0.3)	150 °C×6 h	51.9	49.4	53.4
	150 °C×6 h +210 °C×2 h	96.1	96.5	99.2
BADCy/PEI (0.5)	150 °C×6 h	63.3	62.5	62.9
	150 °C×6 h+210 °C×2 h	94.8	94.2	93.2

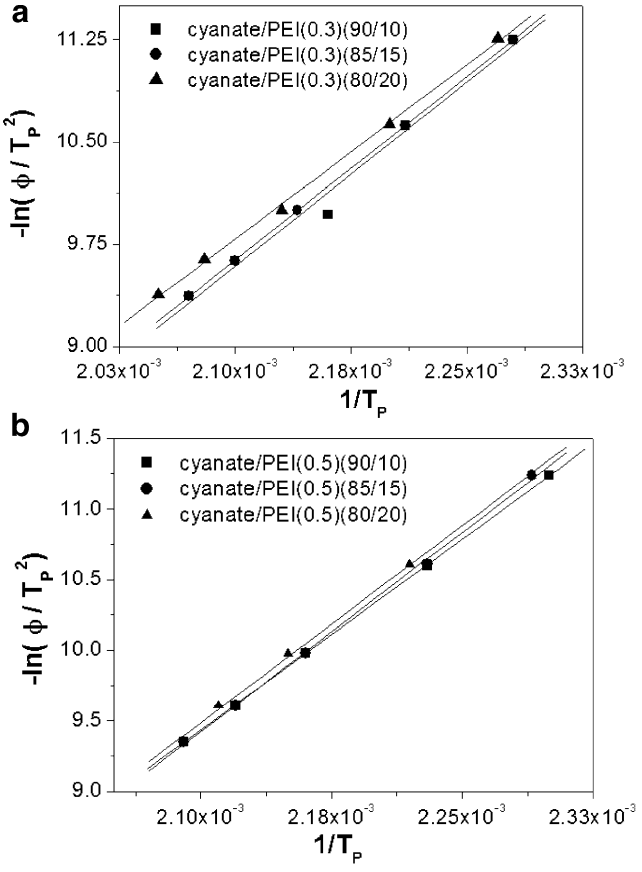

Fig. 4 Plots of $-\ln\left(\varphi/T_P^2\right)$ against $(1/T_P)$ for **a** BADCy/PEI (0.3) blend and **b** BADCy/PEI (0.5) blend

well above T_g, the reaction rate between cyanate groups was chemically controlled. When T_g approached the curing temperature, the curing reaction became diffused controlled by the viscosity of blend, and became very slow, and finally stopped. Thus, the increase of viscosity of the BADCy/PEI blends could account for the variation of the reaction activation energy owing to the presence of PEI and increasing PEI molecular weight.

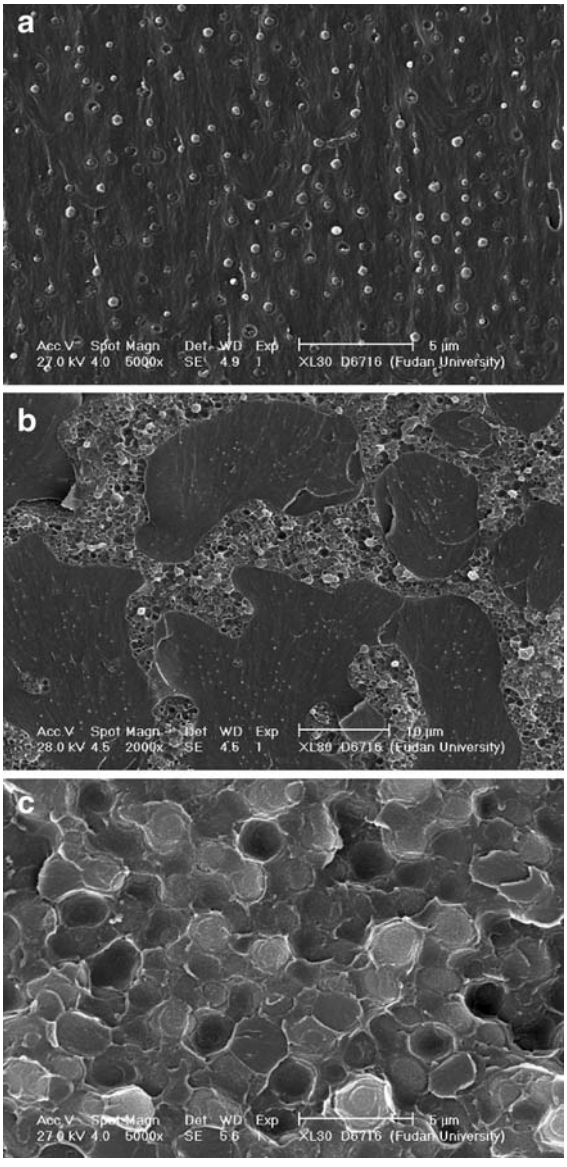

Fig. 5 Morphologies of the BADCy/PEI (0.3) mixtures cured at 150 °C with various PEI content: **a** 10, **b** 15, and **c** 20wt%

Table 2 The reaction activation energy of the curing reaction for the BADCy/PEI blend

System	The activation energy (kJ/mol)			
	0	10wt% PEI	15wt% PEI	20wt% PEI
BADCy/PEI (0.3) blend	58.0	74.8	74.5	72.3
BADCy/PEI (0.5) blend		74.9	78.2	77.3

Morphology analysis

The morphologies of the cured blends changed drastically, depending on PEI molecular weight and the blend composition. Figure 5a–c presents the morphologies of the BADCy/PEI (0.3) blends curing at 150 °C for 6 h. The blend with 10wt% PEI (0.3) had spherical domains of around 0.5 μm in diameter dispersed in the BADCy-rich matrix. When the PEI content was increased to 15wt%, the morphology of the blend showed a cocontinuous phase structure. Many dispersed small PEI particles can be seen in the BADCy continuous phase. Meanwhile, spherical BADCy particles are dispersed in the PEI continuous phase. The blend with 20wt% PEI showed complete phase inversion, the BADCy appeared as big interconnected spherical domains of around 2 μm in diameter.

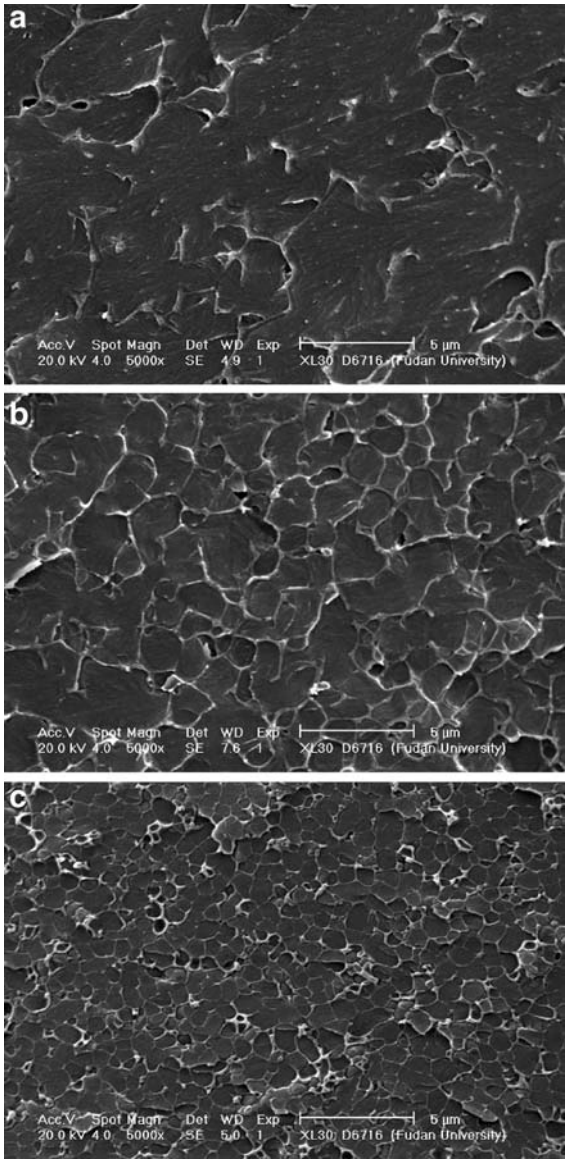

Fig. 6 Morphologies of the BADCy/PEI (0.5) mixtures cured at 150 °C with various PEI content: **a** 10, **b** 15, and **c** 20wt%

Figure 6a–c shows that the morphologies of the BADCy/PEI (0.5) blends were different from those of the BADCy/PEI (0.3) blends. Some ribbon-like domains of PEI dispersed in the BADCy-rich matrix in the blend with 10wt% PEI (0.5). Moreover, phase inversion occurred both in the blend with 15 and 20wt% PEI (0.5). In the case of the blend with 20wt% PEI (0.5), the BADCy particle size was much smaller than the blend with 20wt% PEI (0.3). It suggested that phase separation ended earlier and smaller BADCy particle could not merge further in the BADCy/PEI (0.5) blends due to the increase in viscosity with PEI molecular weight.

Independent of the mechanism by which phase separation is produced, the final morphologies of the thermoset/thermoplastic (TS/TP) blend depended primarily on the location of the trajectory in the conversion vs composition transformation diagram. If the initial TP content was located in the off-critical region to the left of the critical TP content, then the final morphology would consist of a dispersion of thermoplastic-rich particles in a thermoset-rich matrix. When the initial TP content was located in the off-critical region to the right of the critical TP content, phase inversion structures were obtained. In a composition region close to the critical point, a variety of morphologies, including cocontinuous structures, double-phase morphologies, and ribbon-like structures, may form [13].

Based on the above hypothesis, it could be found that the critical point should be around 15wt% for the BADCy/PEI (0.3) blend. When the molecular weight of PEI increased, the critical point decreased to around 10wt% for the BADCy/PEI (0.5) blend. Thus, the shift of the critical point with PEI molecular weight could be the main reason why both the blend with 20wt% PEI (0.3) and the blend with 15wt% PEI (0.5) showed the similar morphologies-phase inversion. Figure 7 shows a schematic diagram of the

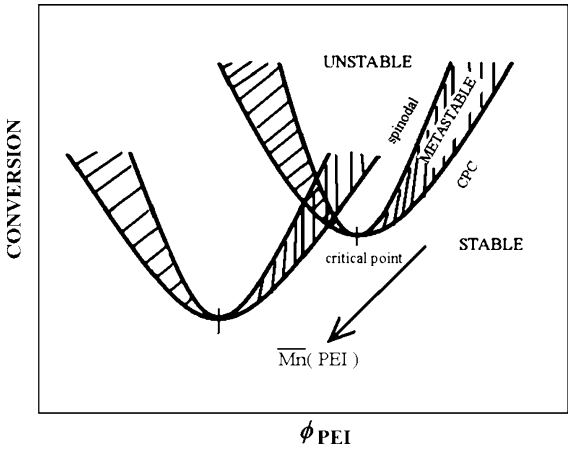

Fig. 7 Schematic diagram of the conversion vs composition transformation curves of the BADCy/PEI blend changing with PEI molecular weight

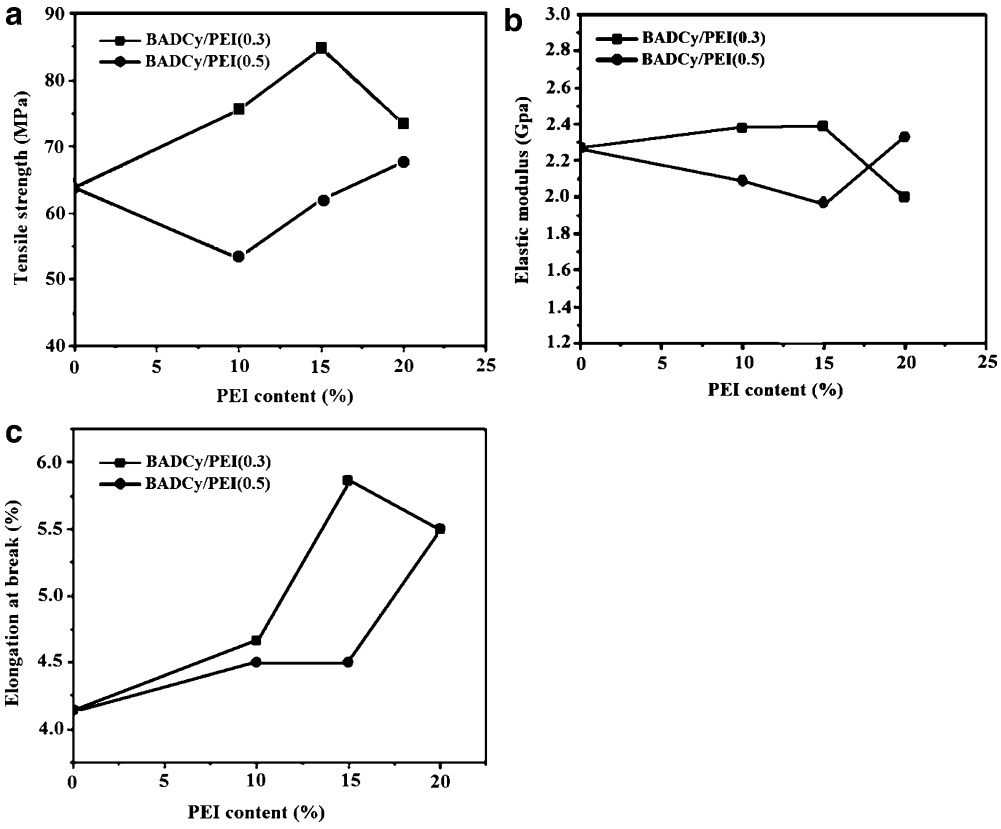

Fig. 8 Composition dependence of tensile strength of **a** BADCy/PEI (0.3) and BADCy/PEI (0.5) blends, **b** BADCy/PEI (0.3) and BADCy/PEI (0.5) blends, and **c** BADCy/PEI (0.3) and BADCy/PEI (0.5) blends

conversion vs composition transformation curves of the BADCy/PEI blend with PEI molecular weight.

Mechanical properties

The tensile properties of the BADCy/PEI (0.3) and BADCy/PEI (0.5) blends were investigated to discuss the effect of the blend morphologies on the mechanical properties. As shown in Fig. 8a, it was found that the blend with 15wt% PEI (0.3) had the maximum tensile strength, while the blend with 10wt% PEI (0.5) had the minimum one. Combined with SEM results, it can be concluded that the blend with cocontinuous morphology had the maximum tensile strength and the blend with ribbon-like morphology had the minimum one, regardless of the PEI molecular weight. In addition, the blend with PEI particle or phase inversion morphology had an intermediate tensile strength. It indicated that the control of the BADCy/PEI blend morphology was crucial to improve tensile properties.

As shown in Fig. 8b,c, the tensile modulus of the BADCy/PEI blend had little change and the elongation at the break of the BADCy/PEI blend increased with respect to neat BADCy resins. This demonstrates that the toughness of the polycyanurate can be improved without the expense of the modulus by the incorporation of PEI. It was also noticed that the blend with 15wt% PEI (0.3) had the largest elongation at break.

Conclusion

Soluble PEI was used to modify the BADCy resin. The conversion of the neat BADCy resin and the blend with varying PEI content was examined by FT-IR. The conversions of the BADCy/PEI (0.5) blends were higher than the BADCy/PEI (0.3) blends, which might be attributed to their extent of phase separation. Curing kinetics of all the BADCy/PEI blends were studied by DSC. The reaction activation energy of the curing reaction for the BADCy/PEI (0.5) blend was higher than the BADCy/PEI (0.3) blend due to the effect of the blend viscosity. It was found that the phase structures of the blends changed with the PEI content and molecular weight. The blend with 15wt% PEI (0.5) showed a phase inversion morphology similar to the blend with 20wt% PEI (0.3), which could be attributed to the critical point of the phase diagram shifted to lower PEI

concentration with the increase of PEI molecular weight. The tensile mechanical properties could be correlated with the morphology variation. It proved further that the blend with cocontinuous morphology had the highest tensile strength while the blend with ribbon-like morphology had the lowest one, regardless of PEI molecular weight.

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