

# The Study on Poly(ether sulfone) Modified Cyanate Ester Resin and Epoxy Resin Cocuring Blends

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**ABSTRACT:** Poly(ether sulfone) terminated with phenolic hydroxyl groups modified cyanate ester resin and epoxy resin cocuring blends were investigated by differential scanning calorimetry, Fourier transform infrared spectroscopy, scanning electron microscopy, rheometry, and mechanical properties measurement. The results suggested that poly(ether sulfone) (PES) could accelerate the polycyclotrimerization reaction of cyanate ester and cocuring processes between cyanate ester and epoxy of modified blends because of the presence of phenolic hydroxyl groups at the end of the PES molecules. It was found that the evolution of the morphologies and complex viscosities of the modified blends sensitive to molecular weight and content of PES, the

tensile strength and elongation at break of the modified blends were correlated with the morphologies of modified blends. Moreover, the evolution of complex viscosities of the modified blends also showed an exponential growth at the early stage of phase separation, which demonstrated experimentally that the coarsening processes of droplets of bisphenol-A dicyanate and diglycidyl ether of bisphenol A and the final morphologies obtained in the blends modified with PES were affected by viscoelastic behavior. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 60–70, 2009

**Key words:** poly(ether sulfone); molecular weight; cyanate ester; epoxy; modification

## INTRODUCTION

Cyanate ester resins have drawn increasing attention due to their important application in industry, including encapsulants of electronic devices, high temperature adhesives, and structural materials of aerospace because of their outstanding mechanical, thermal, and adhesive properties. In general, the inherent brittleness is a major drawback with most crosslinked thermosetting polymers, and some applications require improved fracture toughness.<sup>1,2</sup> One of the toughening methods of polycyanurates is physical blending with high performance thermoplastics, which toughen polycyanurates without excessive sacrifice on thermal and mechanical properties of the cyanate matrix. These thermoplas-

tics include polysulfone,<sup>3,4</sup> poly(ether imide),<sup>5,6</sup> poly(ether sulfone) (PES),<sup>7,8</sup> and so on.

Although the thermoset epoxy resin also hold similar properties with cyanate ester resin, it can be used to modify cyanate ester resin because the triazine groups and the epoxy groups could form oxazolidinone and provide cured resin products with cost and performance intermediate between the epoxies and the generally more expensive cyanate homopolymers.<sup>9</sup> The cyanate ester resin and epoxy resin cocuring blend have low order of toxicity compared with aromatic diamine curing agents for epoxy resin.<sup>10</sup> Moreover, high performance thermoplastics, such as polysulfone,<sup>11</sup> poly(ether imide),<sup>12</sup> poly(ether ether ketone),<sup>13</sup> poly(phenylene ether),<sup>14,15</sup> copolyethersulphone,<sup>16</sup> and PES<sup>17</sup> were also used to modify epoxy resin.

In the thermoplastics modified thermosets blends, the reaction-induced phase separation during the curing process has been reported previously.<sup>17,18</sup> Generally, the blend of cyanate ester resin and thermoplastic was homogeneous at the beginning of curing. As curing reaction proceeded, the compatibility of thermoplastic and cyanate ester resin became worse due to the molecular weight increase of the cyanate ester growing chain, and then phase separation occurred and resulted in heterogeneous multiphase morphologies.<sup>19,20</sup> The morphology could be changed either by the content and molecular weight

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of the thermoplastics in the blend or by curing conditions.<sup>3,4</sup> The morphologies would have a great effect on the mechanical properties of the blends. In fact, it was reported that the fracture toughness could be dramatically improved in the case of the thermosetting/thermoplastic blend with bicontinuous or phase inversion morphology.<sup>21</sup>

Moreover, besides morphology and mechanical properties, it is also crucial to study rheological behavior of thermosets and the blends of thermoplastic modified thermosets in industry because it can allow the estimation of the optimal process according to which the blends should be heated or molded. The rheological behavior of cyanate ester resin<sup>22</sup> and epoxy resin<sup>23</sup> have been carefully studied, which indicated that profound rheological changes were inevitably exhibited during polymerization.<sup>24</sup> However, the modification of thermosets with thermoplastics would change their rheological behavior. Pascault and coworkers<sup>25</sup> reported the rheological behavior of thermoset/thermoplastic blends during isothermal curing and Recca and coworkers<sup>26</sup> reported the rheological behavior of blends of novel thermoplastic copolymers and epoxy resins. The phase separation has a great effect on the rheological behavior of the blend. For example, in the blends with thermoplastic-dispersed structure, Kim and Char<sup>27</sup> reported that there was a fluctuation in viscosity just before the abrupt viscosity increase, which was considered to be the result due to the phase separation of thermoplastic from the thermosets matrix.

In this study, the influences of molecular weight and content of phenolic hydroxyl-terminated PES on the cocuring conversions, morphologies, rheological behavior, and mechanical properties of phenolic hydroxyl-terminated PES modified blends of cyanate ester resin and epoxy resin during isothermal curing were investigated in detail. The results might be helpful to recognize the processing and properties of this system.

## EXPERIMENTAL

### Materials

The bisphenol-A dicyanate (BADCy) with a cyanate equivalent of 139 g/equiv was supplied by Shanghai Huifeng Technical and Business CO. (Shanghai, China). The epoxy resin, diglycidyl ether of bisphenol A (DGEBA) with an epoxide equivalent of 182–192 was supplied by Dow Chemical Co. Four kinds of phenolic hydroxyl-terminated PES, supplied by Jilin University (Jilin, China), were used [the intrinsic viscosities were 0.30, 0.36, 0.43, and 0.53 dL/g respectively]. The intrinsic viscosity was determined in *N,N*-dimethylformamide at 25°C. The PES was

designated as PES(*x*), where *x* represented the intrinsic viscosity (dL/g).

### Sample preparation

The modified blends were prepared by the procedure: PES was dissolved first in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), and then mixed with epoxy resin and cyanate ester resin at room temperature. The residual solvent was removed under vacuum at room temperature overnight after most of the solvent was evaporated at 40°C. The mixture was stirred continuously until a transparent blend was obtained. The molar ratio of BADCy and DGEBA was kept at 1 : 1. The samples for morphology and mechanical properties measurements were cured at 177°C for 2 h and postcured at 205°C for 4 h.

### Differential scanning calorimeter

The curing conversion was determined by Perkin-Elmer differential scanning calorimeter (DSC; Pyris 1). The DSC was calibrated with high-purity indium. The samples around 10 mg were weighed and loaded into small aluminum lid, then the temperature was increased from RT to 177°C at 200°C/min and kept at 177°C under a nitrogen flow of 20 mL/min and the heat flow curves were obtained. Curing conversions were calculated from the contrasting residual exotherms, which were observed in scans over the temperature range from 50 to 350°C at 10°C/min, with the total exotherms of uncured samples.

### Fourier transform infrared spectroscopy

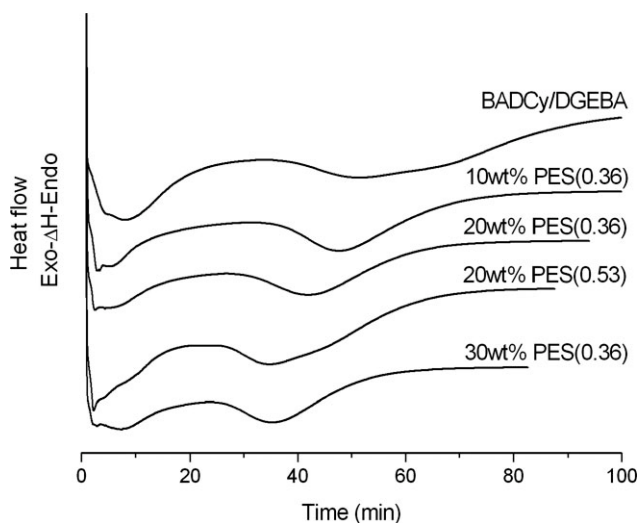
A Nicolet Nexus 440 Spectrometer equipped with a temperature-controlled sample holder in a N<sub>2</sub> atmosphere was used. The sample was put between NaCl and the curing reaction was preceded at 177°C in the Fourier transform infrared spectroscopy (FTIR) cell. The FTIR spectra *in situ* were obtained at constant temperature in an optical range of 600–4000 cm<sup>-1</sup>.

### Scanning electron microscopy

The morphology of the cured samples was observed by scanning electron microscopy (SEM; TS5136MM). The cured samples were fractured in liquid nitrogen and then the fracture surface was coated with a fine gold layer.

### Mechanical properties measurement

The mechanical properties testing were performed using an Instron tensile tester (model 1121) at a



**Figure 1** Isothermal DSC thermograms of BADCy/DGEBA, BADCy/DGEBA/20 wt % PES (0.53) and BADCy/DGEBA/PES (0.36) with various PES contents cured at 177°C.

constant temperature. A gauge length of 15 mm and a crosshead speed of 1 mm/min were used. All the reported results are averages of at least five specimens.

### Viscosity measurement

The melt viscosity variations of the blends during curing reaction were recorded on ARES-4A rheometer by TA Instruments. About 1 g of the blend was sandwiched between two round plates and the plate distance was then adjusted to about 1 mm. All the blends were tested under a parallel plate mode with a controlled strain of 1% to ensure that measurements were performed under linear viscoelastic conditions. The test frequency was set at 1 rad/s. The diameters of the plates used for testing were 25 mm.

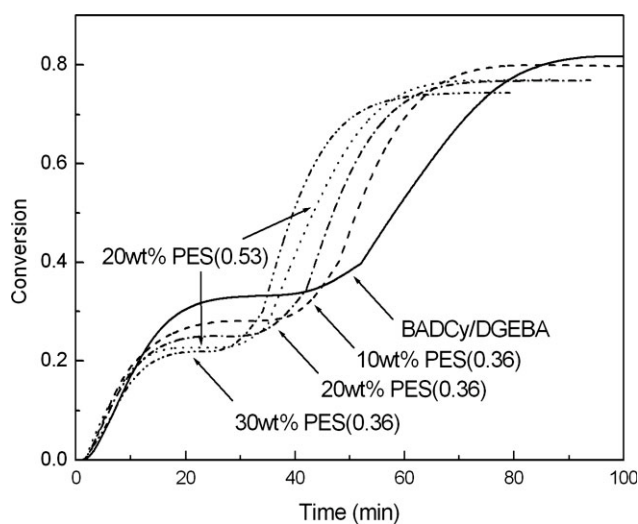
## RESULTS AND DISCUSSION

### Effects of PES on curing reaction

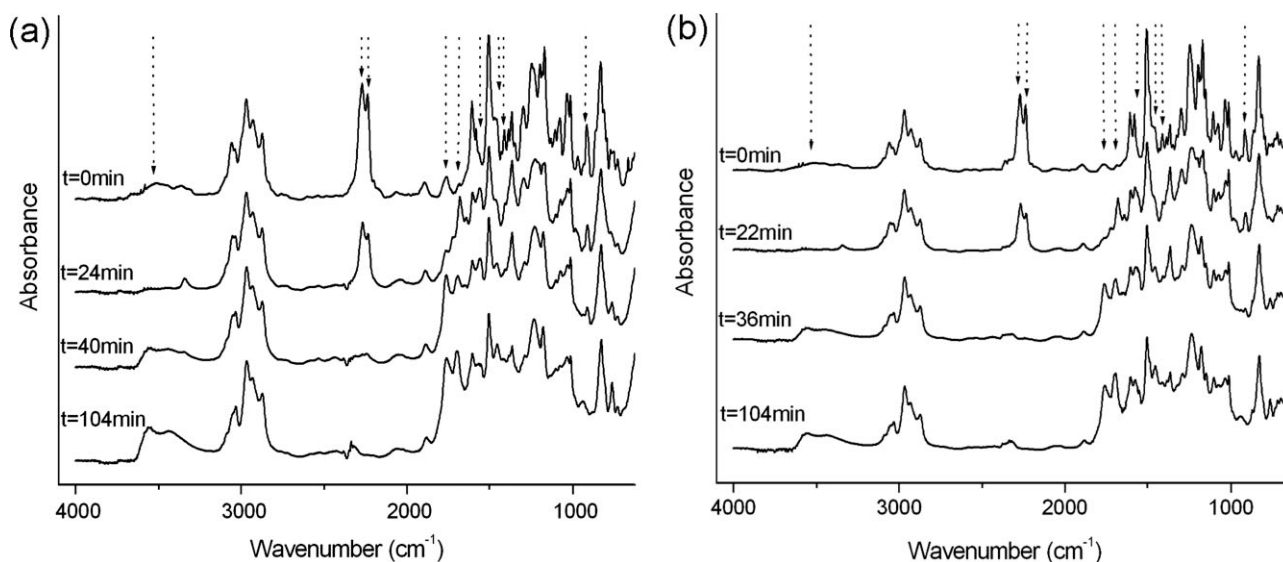
The curing processes of cyanate ester/epoxy and the blends modified with PES were studied by DSC and FTIR. Figure 1 shows the isothermal DSC thermograms for the blends of BADCy/DGEBA, BADCy/DGEBA/20 wt % PES (0.53) and BADCy/DGEBA/PES (0.36) with various PES contents cured at 177°C as examples. The higher molecular weight and concentration of PES shifted the exothermic peak of the blends to the shorter curing times. Two obviously separated exothermic peaks can be seen for all the blends, Grenier-Loustalot and Lartigau<sup>28</sup> reported the similar results of the cyanate ester/epoxy blend containing imidazole and AcAcCu, the first exothermic peak mainly corresponded to the formation of

triazine ring from cyanate ester and the second exothermic peak attributed to triazine-epoxy cocuring reactions. Moreover, the onset time of the second exothermic peak decreased with increasing of PES content. In addition, the onset time of the second exothermic peak of the modified blend with 20 wt % PES (0.53) is shorter than that of the modified blend with 20 wt % PES (0.36), which may be induced by higher concentration of cyanate ester/epoxy because the phase separation of the modified blend with 20 wt % PES (0.53) was earlier than that of the modified blend with 20 wt % PES (0.36).

The curing conversions of BADCy/DGEBA, BADCy/DGEBA/20 wt % PES(0.53) and BADCy/DGEBA/PES (0.36) with various PES contents cured at 177°C isothermally are shown in Figure 2. It's worth noticing that the curing conversion versus time curves of the samples showed sigmoidal trends, which could to be a result of interaction between the curing promoted by phenolic hydroxyl groups of PES and concentration fluctuation induced by phase separation. At the initial curing stage of about 10 min, the curing conversions of the PES modified blends were higher than that without PES, which could be attribute to the phenol hydroxyl groups that promoted the polycyclotrimerization reactions and consequently increased curing rates. However, the curing conversions of the PES modified blends were lower than that without PES during the curing stage corresponding to the range of conversion versus time curve around from the first turning point to the second turning point, which could be the result of lower concentration of BADCy/DGEBA (i.e., epoxide group, cyanate, and triazine ring) before complete phase separation and higher viscosity in



**Figure 2** Curing conversion versus the curing time for BADCy/DGEBA, BADCy/DGEBA/20 wt % PES (0.53) and BADCy/DGEBA/PES (0.36) with various PES contents cured at 177°C isothermally.



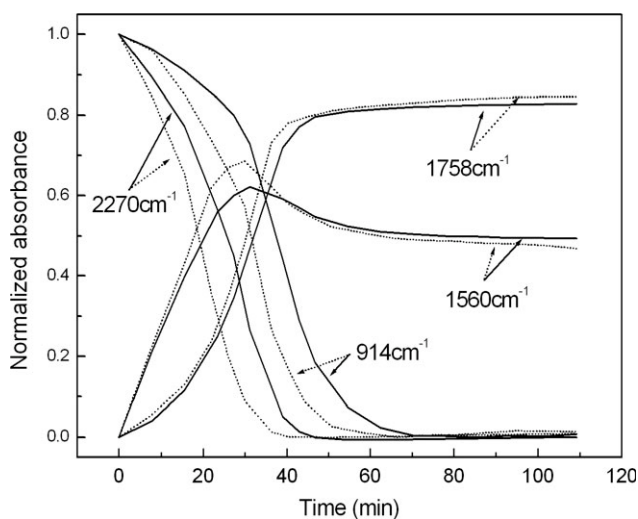
**Figure 3** FTIR spectra of (a) BADCy/DGEBA and (b) BADCy/DGEBA/10 wt % PES (0.36) cured at 177°C isothermally.

the modified blends with PES, in addition, a descending of the curing conversions of the PES modified blends during the curing stage could be seen with increase of PES content. However, with increasing of BADCy/DGEBA concentration as a result of phase separation process, the curing conversions of the PES modified blends were higher than that without PES reappeared at the curing stage after the second turning point of conversion versus time curve, which mainly corresponded triazine-epoxy curing reactions and suggested that the phenolic hydroxyl groups of PES acted as catalyst of the modified blends, that is, the addition of PES accelerated the polycyclotrimerization reaction and the curing processes between cyanate ester and epoxy of modified blends. It is well-known that the hydroxyl of epoxy resin could catalyze the curing reaction of cyanate ester and enhance the curing rate of the cyanate ester/epoxy blend.<sup>9</sup> Similarly, in our studied systems, the curing rates of PES modified blends showed increase compared with the neat BADCy/DGEBA resin due to the existence of phenolic hydroxyl groups of PES. However, the fully cured conversions of modified blends with PES were lower than that of the BADCy/DGEBA, it could be attributed to the dilution effect and viscosity increase because of the addition of PES. Obviously, molecular weight and content of PES affected remarkably the curing behavior of the modified blends mentioned earlier, as shown in Figures 1 and 2.

Fourier transform infrared spectroscopy was used to monitor the curing reaction of the modified blends. FTIR spectra of BADCy/DGEBA and BADCy/DGEBA/10 wt % PES (0.36) cured at 177°C isothermally are shown in Figure 3. The consumption of the cyanate (2270 and 2235  $\text{cm}^{-1}$ ) is accompa-

nied with the increase of triazine ring (1560  $\text{cm}^{-1}$ ), which suggested that cyanate ester reacted and converted into polycyanurate. Meanwhile, the increasing absorption of isocyanurate (1453 and 1694  $\text{cm}^{-1}$ ) and oxazolidinone (1758  $\text{cm}^{-1}$ ) accompanied with the decreasing absorption of triazine ring (1560  $\text{cm}^{-1}$ ) and epoxide group (914  $\text{cm}^{-1}$ ). In addition, the absorption of hydroxyl group (3300–3600  $\text{cm}^{-1}$ ) decreased with the consumption of the cyanate groups and then increased after the cyanate groups converted to triazine rings, which indicated there were some proportion of hydroxyl group consumed during the polycyclotrimerization reaction of cyanate ester and then the hydroxyl group increased as the result of ring-opening of epoxide group reacted with triazine rings. From Figure 3(a,b), it was found that the consumption of cyanate group of the modified blends is faster than BADCy/DGEBA blend owing to the catalytic effect of phenolic hydroxyl groups of PES for polycyclotrimerization reaction of cyanate ester, which was in agreement with DSC results.

To understand the evolution of cure reaction of the modified blends, the normalized absorbance of the characteristic peaks was shown in Figure 4 used 2970  $\text{cm}^{-1}$  as internal reference. It's observed that the consumption of cyanate (2270  $\text{cm}^{-1}$ ) and epoxide group (914  $\text{cm}^{-1}$ ) of PES modified blend were sooner than that of the blend without PES, meanwhile, the increase of absorbance of triazine ring (1560  $\text{cm}^{-1}$ ) and oxazolidinone (1758  $\text{cm}^{-1}$ ) at initial curing stage was faster in the modified blends with PES, which indicated that the presence of PES could accelerate both polycyclotrimerization reaction of cyanate ester and curing process between cyanate ester and epoxy of the modified blends. In addition, it could be seen that at the later curing stage, the



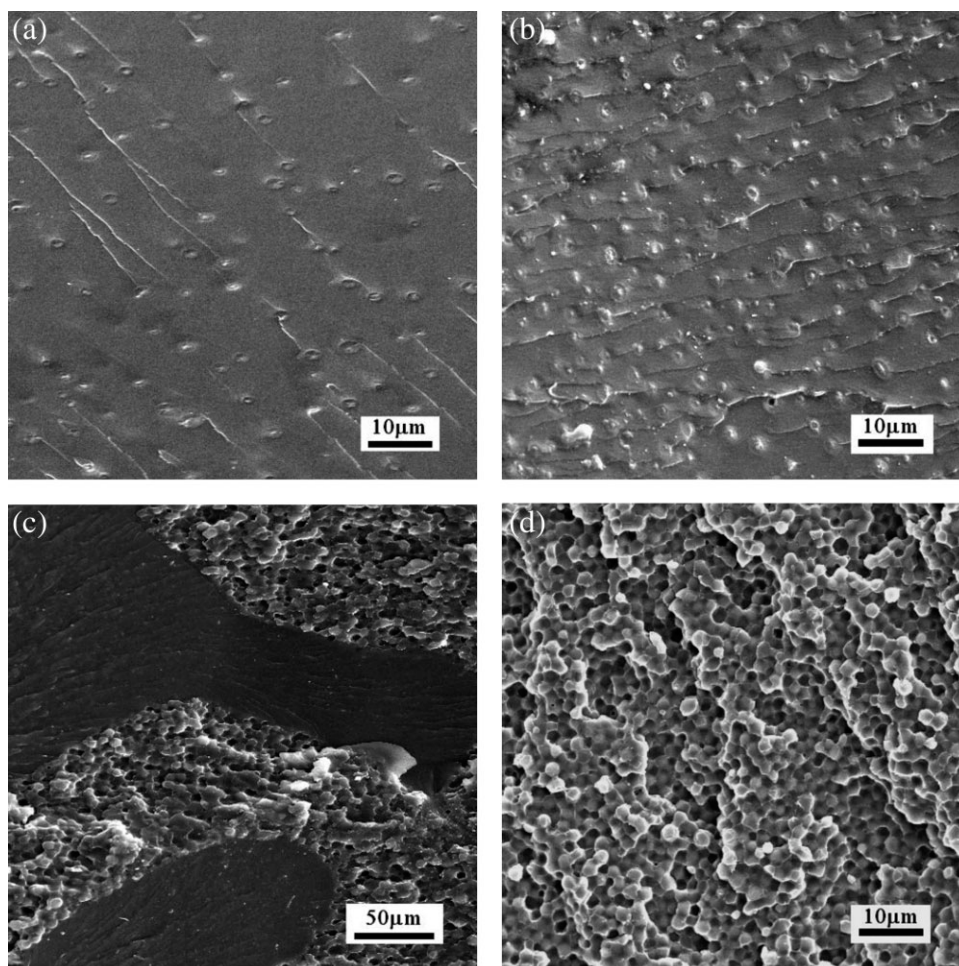
**Figure 4** Normalized absorbance of the different characteristic peaks versus time cured at 177°C isothermally. Solid lines corresponding to the data of BADCy/DGEBA and dots corresponding to the data of BADCy/DGEBA/10 wt % PES (0.36).

absorbance of triazine ring ( $1560\text{ cm}^{-1}$ ) was lower and that of the oxazolidinone ( $1758\text{ cm}^{-1}$ ) of PES modified blend was higher than that of the blend without PES, which suggested further that there were more triazine ring converted to oxazolidinone owing to phenolic hydroxyl groups of PES.

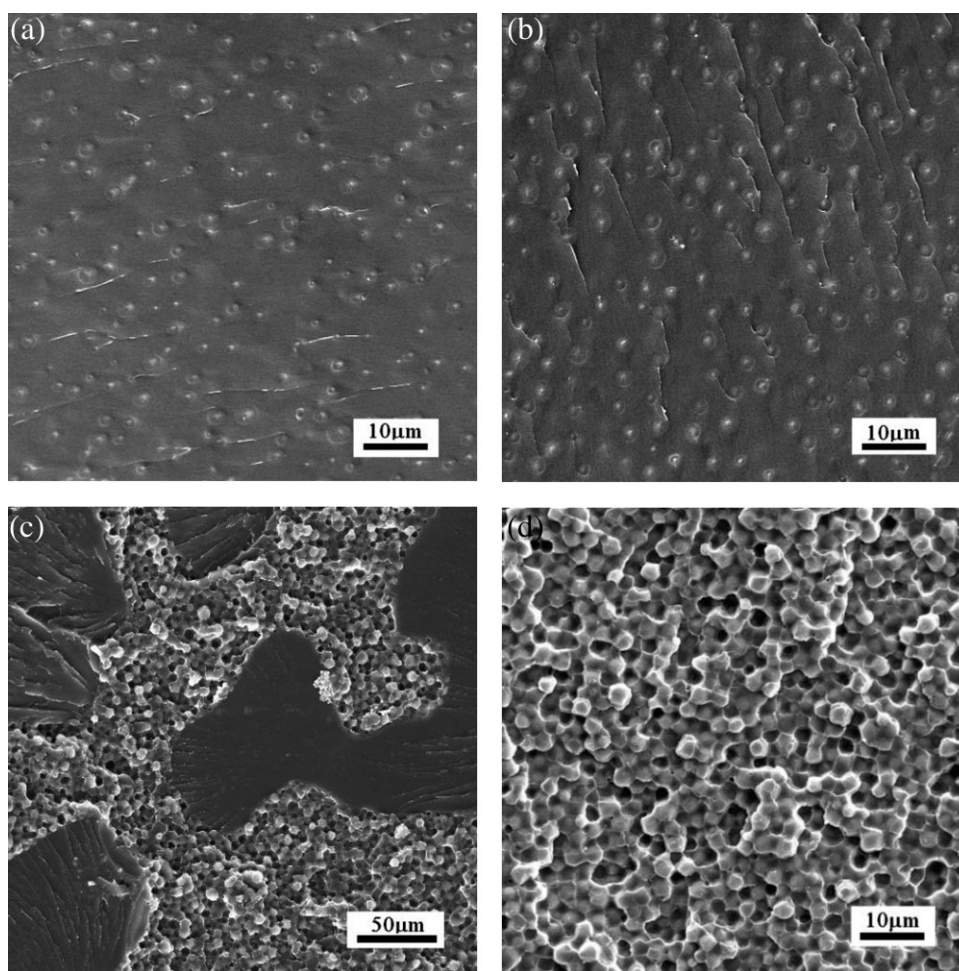
### Morphologies

According to phase separation theories, the morphologies of modified blends were related to their composition and molecular weight of the system. As shown in Figures 5–8, the morphologies of the blends changed dramatically with PES content and molecular weight.

Figures 5 and 6 showed the morphologies of the blends of BADCy/DGEBA/PES (0.30, 0.36) with various PES contents cured at 177°C for 2 h and post-cured at 205°C for 4 h. The blends with 10 wt % and 15 wt % PES showed spherical domains around 1–4 micron in diameter dispersed in the BADCy/



**Figure 5** Morphologies of the BADCy/DGEBA/PES (0.30) blends cured at 177°C for 2 h and postcured at 205°C for 4 h with various PES contents: (a) 10 wt %, (b) 15 wt %, (c) 20 wt %, (d) 30 wt %.



**Figure 6** Morphologies of the BADCy/DGEBA/PES (0.36) blends cured at 177°C for 2 h and postcured at 205°C for 4 h with various PES contents: (a) 10 wt %, (b) 15 wt %, (c) 20 wt %, (d) 30 wt %.

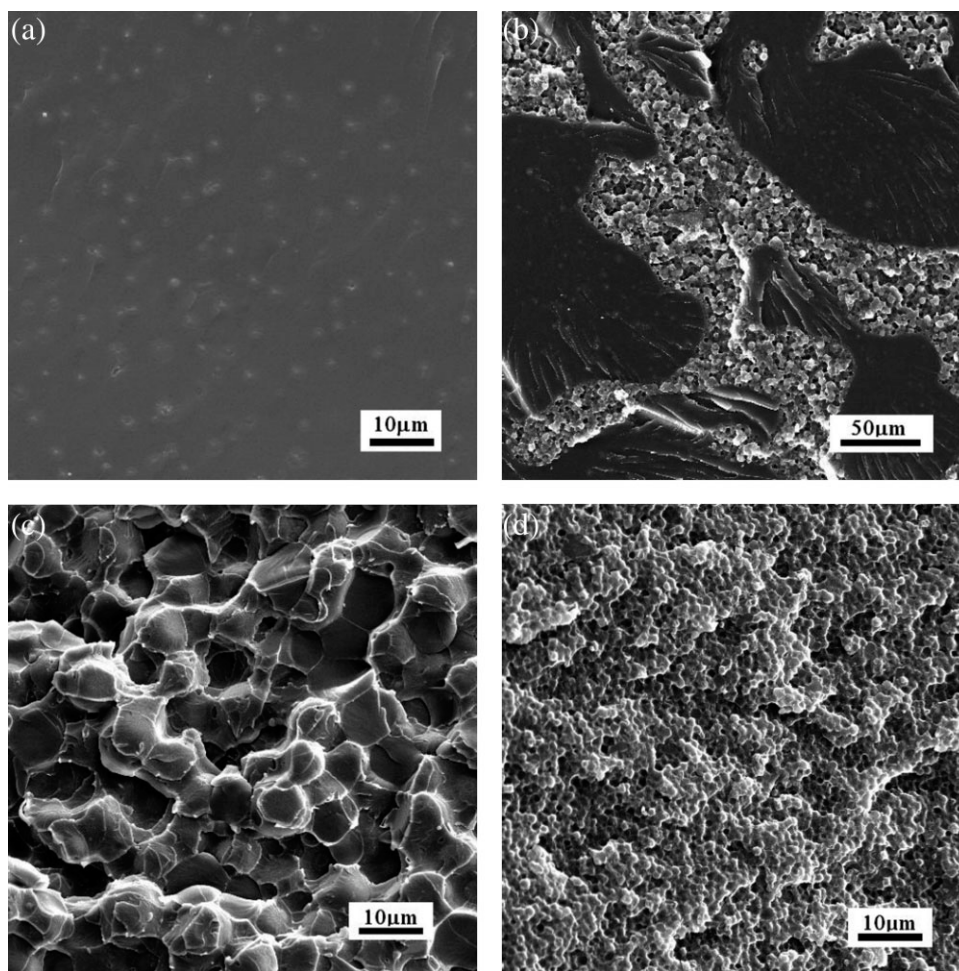
DGEBA-rich matrix. Compared with the blend with 10 wt % PES, there were more spherical domains could be seen in the blend with 15 wt % PES. When the PES contents increased to 20 wt %, the morphologies of the blends showed bicontinuous phase structures, in which small PES particles were dispersed in the BADCy/DGEBA continuous phase and spherical BADCy/DGEBA particles were dispersed in the PES continuous phase, which was induced by secondary phase separation as we have reported.<sup>29</sup> The modified blends with 30 wt % PES showed phase inversion structures, the PES phase formed the matrix and the BADCy/DGEBA appeared as uniformly interconnected spherical particles of around 2 micron in diameter.

However, as shown in Figures 7 and 8, the blends of BADCy/DGEBA/PES (0.43, 0.53) have different morphologies from that of BADCy/DGEBA/PES (0.30, 0.36). In the blends of BADCy/DGEBA/PES (0.43, 0.53), the PES spherical domains dispersed in the BADCy/DGEBA-rich matrix could be seen when the PES contents were 10 wt %, the blends with 15

wt % PES showed bicontinuous phase structures and the blends with 20 wt % PES showed phase inversion structures with interconnected spherical BADCy/DGEBA-rich particles in diameter around 8–10 micron.

In light of the comparison of Figures 5–8, it shows clearly that the effects of the PES molecular weight on the morphology of the modified blends. The morphologies of all the modified blends containing 10 wt % PES with different molecular weights showed dispersed phase structures, whereas phase inversion structures could be observed in all the blends containing 30 wt % PES with different molecular weights. However, the blends containing 15 wt % and 20 wt % PES showed different morphologies related to the molecular weights of PES.

Based on the above experimental results and Flory-Huggens theory, we can give the following explanation of molecular weight of PES on the phase separation and final morphologies. The final morphologies of the PES modified blends induced by phase separation depended primarily on the location



**Figure 7** Morphologies of the BADCy/DGEBA/PES (0.43) blends cured at 177°C for 2 h and postcured at 205°C for 4 h with various PES contents: (a) 10 wt %, (b) 15 wt %, (c) 20 wt %, (d) 30 wt %.

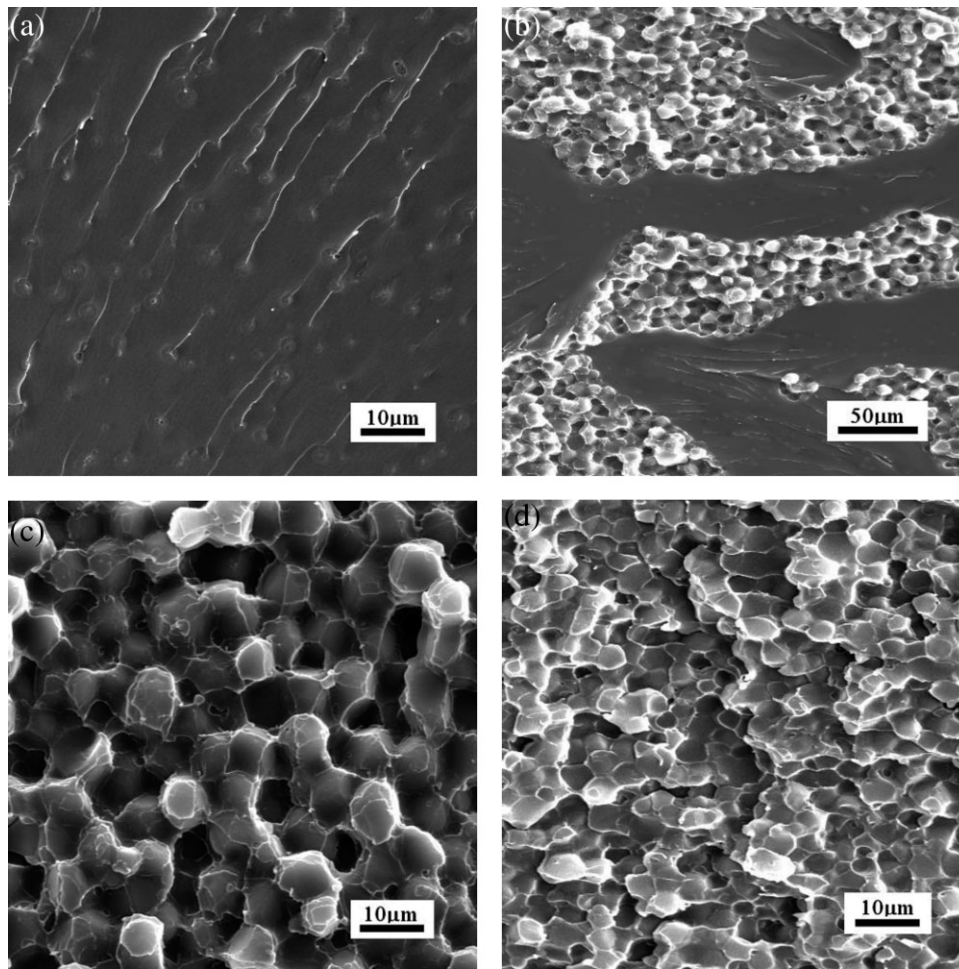
of the trajectory in the conversion versus composition transform diagram. When the initial PES content was located in the off-critical region and on the left of the critical PES content, the final morphology was a dispersion of thermoplastic-rich particles in thermoset-rich matrix. When the initial PES content was located in the off-critical region and on the right of the critical PES content, phase inversion structure could be obtained. In a composition region close to the critical point, a variety of morphologies, including bicontinuous phase structure, double-phase morphology, and ribbon-like structure, may form.<sup>30</sup> Furthermore, the similar bicontinuous phase structure could be observed in the blends with 20 wt % PES (0.30) and 15 wt % PES (0.53), which suggested that the critical point could shifted down to left with increasing of the PES molecular weight, as shown in Figure 9.

### Mechanical properties

To understand the effect of phase morphologies on the mechanical properties of the modified blends,

the tensile properties of BADCy/DGEBA and modified blends with PES were investigated. As shown in Table I, combined with SEM results, the tensile strength of the blends increased with increasing of PES content for a given PES molecular weight, especially, the tensile strength of the blends with 15 wt % PES (0.53) and 20 wt % PES (0.36, 0.43, and 0.53) increased obviously, it increased remarkably when the phase morphology changed from dispersed phase structure to bicontinuous or phase inversion structure. Whereas, the tensile strength of the blend with 20 wt % PES (0.30) increased a little, which could be due to the larger scale phase structures of PES-rich phase and BADCy/DGEBA-rich phase.

The elongation at break of BADCy/DGEBA/PES blends with 10 wt % PES was close to that of BADCy/DGEBA blend, it was reasonable that the dispersed phase structure contributed little to the elongation at break of blends because of BADCy/DGEBA matrix of the modified blends. The elongation at break of blends with 15 wt % PES increased slightly for different PES molecular weights. Whereas, there was an obvious enhance of the



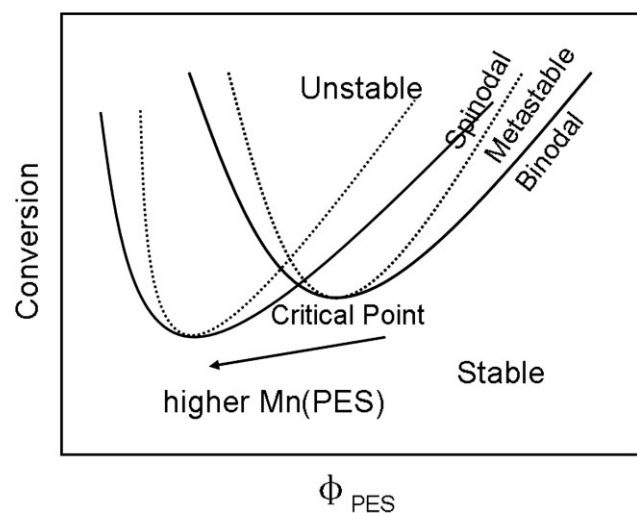
**Figure 8** Morphologies of the BADCy/DGEBA/PES (0.53) blends cured at 177°C for 2 h and postcured at 205°C for 4 h with various PES contents: (a) 10 wt %, (b) 15 wt %, (c) 20 wt %, (d) 30 wt %.

elongation at break of blends with 20 wt % PES regardless of the PES molecular weight, which indicates that the elongation at break of the blends could increase remarkably for bicontinuous and phase inversion structures.

### Rheological behavior

Figure 10 shows the evolution of complex viscosities of BADCy/DGEBA/PES (0.36) blends with various PES contents cured at 177°C. Obviously, there is an induction period<sup>31</sup> (where the increase in viscosity is modest and gradual, followed by a rapid exponential increase in viscosity) existed for each sample, as shown in Figure 10(a). The induction period of the BADCy/DGEBA blend was around 1250 s, and the induction periods of the modified blends varied with various PES contents, as shown in Figure 10(a), which were around 720 s, 440 s, and 260 s for the BADCy/DGEBA/PES (0.36) blends with 10 wt %, 20 wt %, and 30 wt % PES, respectively. The results revealed that the addition of PES could shorten the induction periods of the modified blends for the

BADCy/DGEBA/PES (0.36) blends, which could be the result of the hastening of phenolic hydroxyl group to the curing rates and the phase separation



**Figure 9** Schematic diagram of the conversion versus composition transformation curves of the BADCy/DGEBA/PES blends changing with PES molecular weight.



**TABLE I**  
**Tensile Properties of BADCy/DGEBA/PES**  
**Blends Cured at 177°C for 2 h, and Postcured**  
**at 205°C for 4 h (Error: 8%)**

Intrinsic viscosity (dm <sup>3</sup> /kg)	Composition	Tensile strength (MPa)	Elongation at break (%)
—	BADCy/DGEBA	45	4.2
0.30	10 wt % PES	48	3.9
	15 wt % PES	48	4.6
	20 wt % PES	49	5.9
0.36	10 wt % PES	51	4.3
	15 wt % PES	52	4.9
	20 wt % PES	71	7.5
0.43	10 wt % PES	50	4.2
	15 wt % PES	55	4.6
	20 wt % PES	64	6.1
0.53	10 wt % PES	49	4.6
	15 wt % PES	60	5.0
	20 wt % PES	67	7.2

affected by PES contents. From the logarithmic Figure 10(b), an abrupt decrease of complex viscosity in the blend with 10 wt % PES was observed, which shown the occurrence of the phase separation of PES from the continuous BADCy/DGEBA and that would be occurred through a nucleation and growth mechanism, as Varley has reported.<sup>31</sup> The complex viscosities of the blends with 20 wt % and 30 wt % PES increased quickly with increasing curing time, combining the morphologies of the blends, which would be occurred by a spinodal decomposition mechanism.

Furthermore, the evolution of complex viscosities of the modified blends during the early stage of phase separation showed an exponential growth, as found in our previous work.<sup>32</sup> Figure 11 shows the

evolution of complex viscosity during the early stage of phase separation of the BADCy/DGEBA/PES (0.36) blends with various PES contents and BADCy/DGEBA/20 wt % PES blends with different molecular weights cured at 177°C. The experimental results of  $\eta^*$  were simulated by an exponential growth eq. (1):

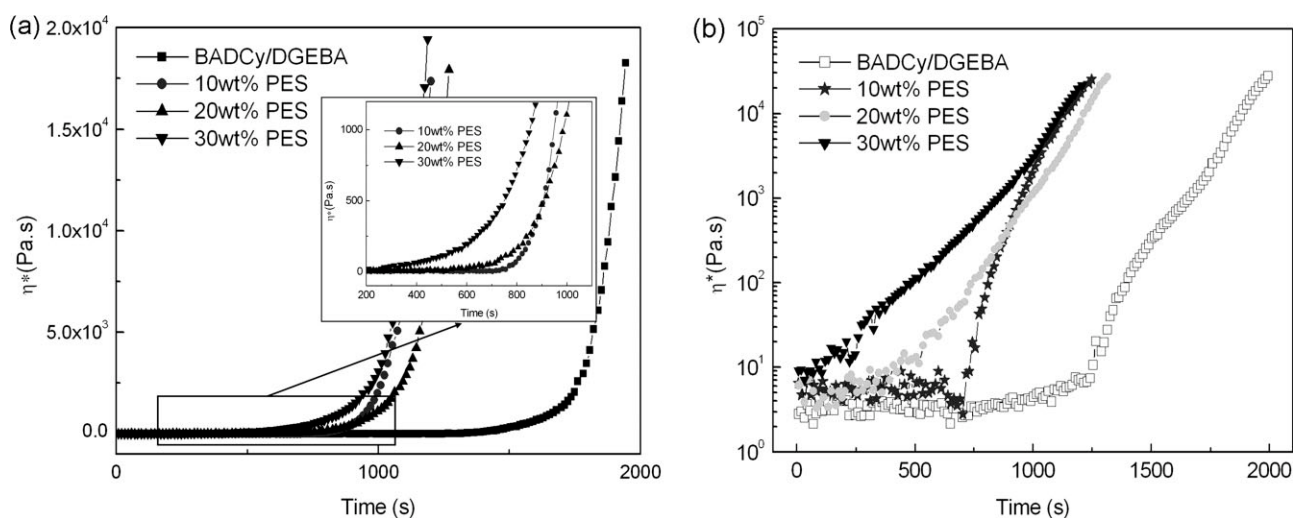
$$\eta^*(t) = \eta_0^* + A_\eta \exp(t/\tau_\eta), \quad (1)$$

where  $A_0$  is magnifier and  $\tau_\eta$  is the relaxation time.

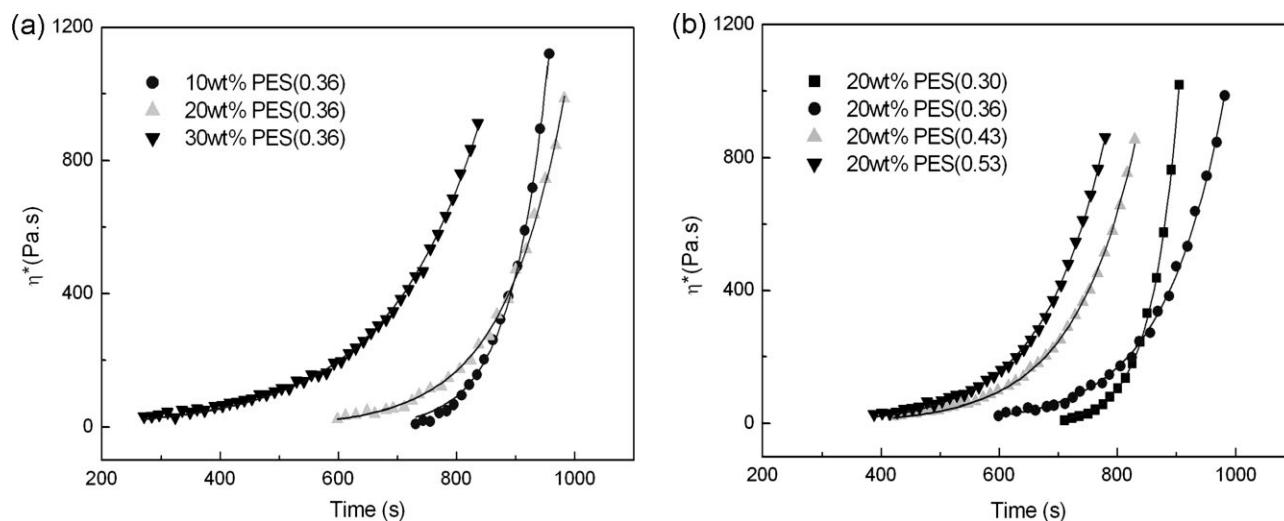
For these systems mentioned earlier, the relaxation times of rheological behavior were obtained by simulation of all complex viscosity patterns from eq. (1) (Table II), and the results indicated that the development of complex viscosities of the modified blends during the early stage of phase separation fitted exponential growth quite well. It demonstrated experimentally that the coarsening processes of droplets of BADCy and DGEBA and the final morphologies obtained in the blends modified with PES were affected by viscoelastic behavior, as reported in our previous works.<sup>33</sup>

## CONCLUSIONS

The blends of cyanate ester resin and epoxy resin were modified with phenolic hydroxyl-terminated PES of different molecular weights. It was found that there were two exothermic peaks corresponding to the formation of triazine ring from cyanate ester and triazine-epoxy cocuring reactions, respectively, and the addition of PES could accelerate the polycyclotrimerization reaction of cyanate ester and cocuring processes between cyanate ester and epoxy of modified blends. The morphologies of the modified blends were related to content and molecular weight



**Figure 10** The evolution of complex viscosities of BADCy/DGEBA and BADCy/DGEBA/PES (0.36) with various PES contents cured at 177°C.



**Figure 11** The evolution of complex viscosities during the early stage of phase separation of BADCy/DGEBA/PES (0.36) blends with various PES contents (a) and BADCy/DGEBA/PES blends with 20 wt % PES of different molecular weights (b) cured at 177°C. Dots corresponding to the experimental data and lines corresponding to the results simulated by  $\eta^*(t) = \eta_0^* + A_1 \exp(t/\tau_1)$ .

of PES. Bicontinuous and phase inversion structures could be obtained at lower PES content of higher molecular weight PES, which could be attribute to the shift of the critical point of phase diagram to lower PES concentration with increasing of PES molecular weight. The mechanical properties of the modified blends were correlated with the corresponding morphologies. In addition, the addition of PES could shorten the time at which the complex viscosity began to increase during the isothermal curing of the BADCy/DGEBA/PES blends. The evolution of complex viscosities of modified blends fitted exponential growth quite well during the early stage of phase separation, which demonstrated experimentally further that the phase separation of the blends modified with PES are affected by viscoelastic behavior.

**TABLE II**

**Relaxation Times Obtained in Evolution of Complex Viscosities During the Early Stage of Phase Separation of BADCy/DGEBA/PES (0.36) Blends with Various PES Contents and BADCy/DGEBA/PES Blends with 20 wt % PES of Different Molecular Weights Cured at 177°C**

Composition	$\tau_1$ (s)	$R^2$
10 wt % PES (0.36)	62	0.998
20 wt % PES (0.36)	102	0.998
30 wt % PES (0.36)	156	0.999
20 wt % PES (0.30)	46	0.999
20 wt % PES (0.43)	106	0.999
20 wt % PES (0.53)	105	0.999

$R^2$ : Correlation coefficient.

## REFERENCES

- Nair, C. P. R.; Mathew, D.; Ninan, K. N. *Adv Polym Sci* 2001, 155, 1.
- Fang, T.; Shimp, D. A. *Prog Polym Sci* 1995, 20, 61.
- Recalde, I. B.; Recalde, D.; García-Lopera, R.; Gómez, C. M. *Eur Polym J* 2005, 41, 2635.
- Hwang, J. W.; Cho, K.; Yoon, T. H.; Park, C. E. *J Appl Polym Sci* 2000, 77, 921.
- Harismendy, I.; Río, M. D.; Eceiza, A.; Gavalda, J.; Gómez, C. M.; Mondragon, I. *J Appl Polym Sci* 2000, 76, 1037.
- Harismendy, I.; Río, M. D.; Marieta, C.; Gavalda, J.; Gómez, C. M.; Mondragon, I. *J Appl Polym Sci* 2001, 80, 2759.
- Chang, J. Y.; Hong, J. L. *Polymer* 2000, 41, 4513.
- Chang, J. Y.; Hong, J. L. *Polymer* 2001, 42, 1525.
- Hamerton, I. *Chemistry and Technology of Cyanate Ester Resins*; Blackie Academic and Professional: London, 1994.
- Shimp, D. A.; Wentworth, J. E. In the 37th Int SAMPE Symposium; 1992; vol. 37, p. 293.
- Martinez, I.; Martin, M. D.; Eceiza, A.; Oyanguren, P.; Mondragon, I. *Polymer* 2000, 41, 1027.
- Riccardi, C. C.; Borrajo, J.; Williams, R. J. J.; Girard Reydet, E.; Sautereau, H.; Pascault, J. P. *J Polym Sci Part B: Polym Phys* 1996, 34, 349.
- Francis, B.; Thomas, S.; Jose, J.; Ramaswamy, R.; Rao, V. L. *Polymer* 2005, 46, 12372.
- Poncet, S.; Boiteux, G.; Pascault, J. P.; Sautereau, H.; Seytre, G.; Rogozinski, J.; Kranbuehl, D. *Polymer* 1999, 40, 6811.
- Prolongo, S. G.; Cabanelas, J. C.; Fine, T.; Pascault, J. P. *J Appl Polym Sci* 2004, 93, 2678.
- Van Overbeke, E.; Devaux, J.; Legras, R.; Carter, J. T.; McGrail, P. T.; Carlier, V. *Polymer* 2003, 44, 4899.
- Yu, Y. F.; Wang, M. H.; Gan, W. J.; Li, S. J. *J Phys Chem B* 2004, 108, 6208.
- Girard-Reydet, E.; Sautereau, H.; Pascault, J. P.; Keates, P.; Navard, P.; Thollet, G.; Vigier, G. *Polymer* 1998, 39, 2269.
- Tao, Q. S.; Gan, W. J.; Yu, Y. F.; Wang, M. H.; Tang, X. L.; Li, S. J. *Polymer* 2004, 45, 3505.
- Zhan, G. Z.; Yu, Y. F.; Tang, X. L.; Tao, Q. S.; Li, S. J. *J Polym Sci Part B: Polym Phys* 2006, 44, 517.

21. Zheng, S. X.; Wang, J.; Guo, Q. P.; Wei, J.; Li, J. *Polymer* 1996, 37, 4667.
22. Harismendy, I.; Gomez, C. M.; Del Rio, M.; Mondragon, I. *Polym Int* 2000, 49, 735.
23. Mortimer, S.; Ryan, A. J.; Stanford, J. L. *Macromolecules* 2001, 34, 2973.
24. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: New York, 1967.
25. Tribut, L.; Fenouillot, F.; Carrot, C.; Pascault, J. P. *Polymer* 2007, 48, 6639.
26. Cicala, G.; La Spina, R.; Recca, A.; Sturiale, S. *J Appl Polym Sci* 2006, 101, 250.
27. Kim, H.; Char, K. *Ind Eng Chem Res* 2000, 39, 955.
28. Grenier-Loustalot, M. F.; Lartigau, C. *J Polym Sci Part A: Polym Chem* 1997, 35, 3101.
29. Tang, X. L.; Zhang, L. X.; Wang, T.; Yu, Y. F.; Gan, W. J.; Li, S. J. *Macromol Rapid Commun* 2004, 25, 1419.
30. Pascault, J. P.; Williams, R. J. J. In *Polymer Blends*; Paul, D. R.; Bucknull, C. B., Eds.; Wiley: New York, 2000; vol. 1, chapter 13.
31. Varley, R. J. *Macromol Mater Eng* 2007, 292, 46.
32. Gan, W. J.; Zhan, G. Z.; Wang, M. H.; Yu, Y. F.; Xu, Y. Z.; Li, S. J. *Colloid Polym Sci* 2007, 285, 1727.
33. Gan, W. J.; Yu, Y. F.; Wang, M. H.; Tao, Q. S.; Li, S. J. *Macromolecules* 2003, 36, 7746.