

# Different Parameters Controlling the Initial Solubility of Two Thermoplastics in Epoxy Reactive Solvents

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**ABSTRACT:** The influence of different factors on the miscibility of diglycidyl ether of bisphenol A (DGEBA)/thermoplastic blends was studied. DGEBA/poly(ether imide) (PEI) blends exhibited upper critical solution temperature behavior. The addition of a trifunctional epoxy [triglycidyl *para*-amino phenol (TGpAP)] increased the miscibility window. The addition of diamines as hardeners could also increase [4,4'-methylene-bis(3-chloro-2,6-diethylaniline) (MCDEA)] or decrease (4,4'-diaminodiphenylsulfone) the miscibility window. DGEBA/poly(ether sulfone) (PES) blends showed lower critical solution temperature behavior. The addition of TGpAP had an effect similar to that for PEI blends, but the presence of MCDEA as a hardener decreased the miscibility of epoxy/PES blends. The modeling of the cloud-point curves was performed with the Flory–Huggins equation (Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 672) according to the procedure developed by K. Kamide, S. Matsuada, and H. Shirataki (*Eur Polym J* 1990, 26, 379), with the interaction parameter used as the fitting parameter. A phenomenological model that takes into account the molar mass of DGEBA and the amount of TGpAP is proposed and is found to predict the cloud-point temperature of any TGpAP/DGEBA/PEI blend. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1385–1396, 2002

**Key words:** phase diagrams; thermoplastic-modified epoxies; poly(ether imides); poly(ether sulfones); Flory–Huggins equation; phase separation

## INTRODUCTION

Thermosetting polymers such as epoxy resins are widely used as structural materials in the aerospace and electronic industries for their high strength, high elastic modulus, and good heat and solvent resistance. However, an undesirable feature is their low fracture toughness relative to that of other polymer families. Therefore, they

need to be toughened to increase their range of possible applications. Studies have demonstrated that thermoplastics (TPs) such as polysulfones, poly(ether imide)s (PEIs), polyimides, and poly(phenylene ether)s can enhance fracture toughness without the glass-transition temperature ( $T_g$ ) or other desirable properties of thermosets (TSs) being sacrificed.<sup>1–6</sup> The TPs have to be initially miscible with the epoxy monomers, but at a particular conversion, depending on the composition and reaction temperature, phase separation occurs.<sup>7</sup> Depending on the initial composition, the resulting TP-toughened epoxies may exist as particulate, bicontinuous, or phase-inverted morphologies.<sup>7</sup> This work deals with the study of the

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initial miscibility of TPs in TS precursors. Two types of behavior can be observed: upper critical solution temperature (UCST) behavior, in which full miscibility is obtained with an increase of temperature,<sup>8</sup> and lower critical solution temperature (LCST) behavior, in which full miscibility is obtained with a decrease in the temperature.<sup>9–11</sup>

The aim of this work is an analysis of the effect of various TS precursor/TP blends on the initial miscibility before reaction. Two amorphous TPs have been studied: nonfunctional PEI and poly(ether sulfone) (PES) with a phenol end-capped chain. The influence of the addition of a trifunctional epoxy [triglycidyl *para*-amino phenol (TGpAP)] on a diglycidyl ether of bisphenol A (DGEBA)/TP blend has been investigated.

The influence of the addition of an amine hardener on epoxy/TP blend miscibility before reaction has also been reported. Experimental cloud-point temperatures ( $T_{cp}$ 's) were fitted to a thermodynamic model based on the Flory–Huggins (FH) approach,<sup>12</sup> which considers the polydispersity of each blend component (TP and TS precursors). A phenomenological model has been proposed to predict the TS precursor/TP blend miscibility over the entire compositional range.

## EXPERIMENTAL

### Materials

The epoxy prepolymers used were DGEBA, with average degrees of polymerization ( $\bar{n}$ ) ranging from 0.03 to 2.32 (Dow [Midland, MI] and Ciba Geigy [Basel, Switzerland] products), and TGpAP (Ciba Geigy). The hardeners used were the aromatic diamines 4,4'-methylene-bis(3-chloro-2,6-diethylaniline) (MCDEA; Lonza, Basel, Switzerland) and 4,4'-diaminodiphenylsulfone (DDS; Fluka, Buchs, Switzerland). Two amorphous TPs were used: PEI (Ultem 1000, General Electric) and PES (5003P, Sumitomo, Chiva, Japan). The chemical structures and characteristics of all species are reported in Table I. The discontinuous molecular weight distributions of the different DGEBA epoxy resins are shown in Table II. In contrast, the TP distribution is continuous, and the TP molar mass distribution is obtained with a Schulz–Zimm (SZ) equation [see eq. (2)].<sup>13</sup>

### Techniques

#### Size Exclusion Chromatography (SEC)

SEC with epoxy standards for calibration was used to obtain the molar mass distribution of

DGEBA prepolymers. SEC was performed with 10<sup>3</sup>-, 500-, and 100-Å columns of PL gel (Polymer Laboratories). The solvent was tetrahydrofuran at a 1.5 mL min<sup>-1</sup> flow rate and a pressure of 5 × 10<sup>6</sup> Pa. The chromatogram was monitored with a refractive-index detector.

#### Cloud-Point Curves (CPCs)

$T_{cp}$ 's of nonreactive blends and PEI–DGEBA/hardener unreacted mixtures containing different TP concentrations were determined with a light transmission device described elsewhere.<sup>14</sup> For PEI blends, the temperature was increased until a homogeneous solution was obtained, kept constant for several minutes, and then decreased at a cooling rate of about 1 K min<sup>-1</sup>.  $T_{cp}$  was determined at the onset time of the light transmission decrease. For PES blends, PES was first mixed with the epoxy precursor and then dissolved in a solution of dichloromethane that was 10 vol % methanol.<sup>9–11</sup> When the blend became miscible, the solvent was driven off under primary vacuum, and if necessary, the diamine hardener was added. To obtain experimental cloud points, we increased the temperature at different heating rates of 1, 5, and 10 K min<sup>-1</sup> from room temperature to 220°C (which was the limit of the apparatus).  $T_{cp}$  was determined by extrapolation to a zero heating rate.

#### Calorimetric Measurements

$T_g$ 's of blends were obtained with a differential scanning calorimeter from Mettler at a heating rate of 10°C/min from –50 to 250°C (the onset temperature). To check the reproducibility, we repeated the procedure two more times.

## BACKGROUND

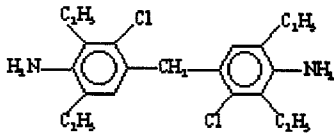
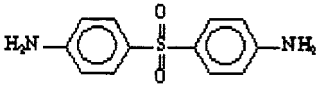
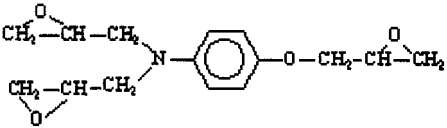
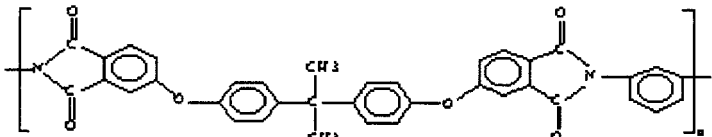
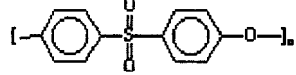
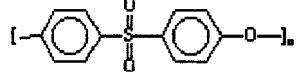
### Tools for Modeling

A pseudobinary phase diagram is composed of two curves: the vitrification curve, which separate the liquid-phase and vitreous-phase areas, and the CPC, which delimits the one-phase and two-phase areas in the liquid state (Fig. 1).

The vitrification curve is calculated with the Couchman equation:<sup>15</sup>

$$\ln T_g = \frac{M_1 \Delta C_{p1} \ln T_{g1} + (1 - M_1) \Delta C_{p2} \ln T_{g2}}{M_1 \Delta C_{p1} + M_2 \Delta C_{p2}} \quad (1)$$

**Table I Characteristics of the Blend Components**

Materials				
Reactant	Formula			Supplier
MCDEA		$M = 380 \text{ g mol}$	$V_m = 333 \text{ cm}^3/\text{mol}$	Lonza
DDS		$M = 238 \text{ g mol}$	$V_m = 179.7 \text{ cm}^3/\text{mol}$	Fluka
DGEBA $\bar{n}$ from 0.03–2.32		$M_{n=0} = 340 \text{ g mol}$ $M_{Mu} = 284 \text{ g mol}$	$V_{m(n=0)} = 296.6 \text{ cm}^3 \text{ mol}$ $V_{m_{Mu}} = 242.7 \text{ cm}^3 \text{ mol}$	Ciba Geigy
TGpAP		$M = 300 \text{ g mol}$	$V_m = 245.9 \text{ cm}^3/\text{mol}$	Ciba Geigy MY0510
PEI		$M_n = 26,000 \text{ g mol}$ $M_w = 50,000 \text{ g mol}$	$V_m = 466 \text{ cm}^3/\text{mol}$	General Electric Ultem 1000
PES		$M_n = 21,900 \text{ g mol}$ $M_w = 45,990 \text{ g mol}$	$V_m = 169 \text{ cm}^3/\text{mol}$	Sumitomo 5003P

$V_m$  = the component molar volume;  $V_{m_{Mu}}$  represents DGEBA repetitive unit molar volume.

where the subscript 1 indicates the TS precursor and the subscript 2 indicates the TP.  $M_i$  is the weight ratio of  $i$  in the mixture, and  $T_{gi}$  and  $\Delta C_{pi}$  are the glass-transition temperature and heat capacity change at  $T_g$  of component  $i$ .

The vitrification curve can also be determined experimentally with calorimetric measurements. In the UCST case, the vitrification curve crosses the CPC at a certain TP concentration (Bergham

point), whereas in the LCST case, it never crosses the CPC (Fig. 1).<sup>4</sup>

Different approaches exist for modeling the CPCs of blends, and they are described in a previous article.<sup>8</sup> We decided to calculate the CPCs from the FH energy equation, following the procedure developed by Kamide et al.,<sup>16</sup> in which the polydispersities of both the TP and TS blend components are considered. The TP is assumed to

**Table II** Mass Fraction of the *n*-Mer [ $\omega(n)$ ] Versus Polymerization Degree (*n*) for Different DGEBA Resins

$\bar{n}$	<i>n</i>					
	0	1	2	4	6	8
0.03	0.95	0.05	—	—	—	—
0.15	0.76	0.21	0.02	—	—	—
0.49	0.58	0.03	0.20	0.13	0.06	—
2.32	0.12	0.01	0.20	0.21	0.16	0.30

have a continuous molar mass distribution obtained with the SZ equation [Fig. 2 and eq. (2)], whereas the TS DGEBA precursors have a discontinuous distribution calculated from the SEC chromatogram (Fig. 2).

For TP,

$$\omega(i) = \lfloor g^{h+1}/\Gamma(h + 1) \rfloor \cdot i^h \exp(-g \cdot i) \quad (2)$$

where  $\omega(i)$  is the mass fraction of macromolecules with a polymerization degree *i*,  $\Gamma$  is the gamma function, and  $m_i = M_u i$ :

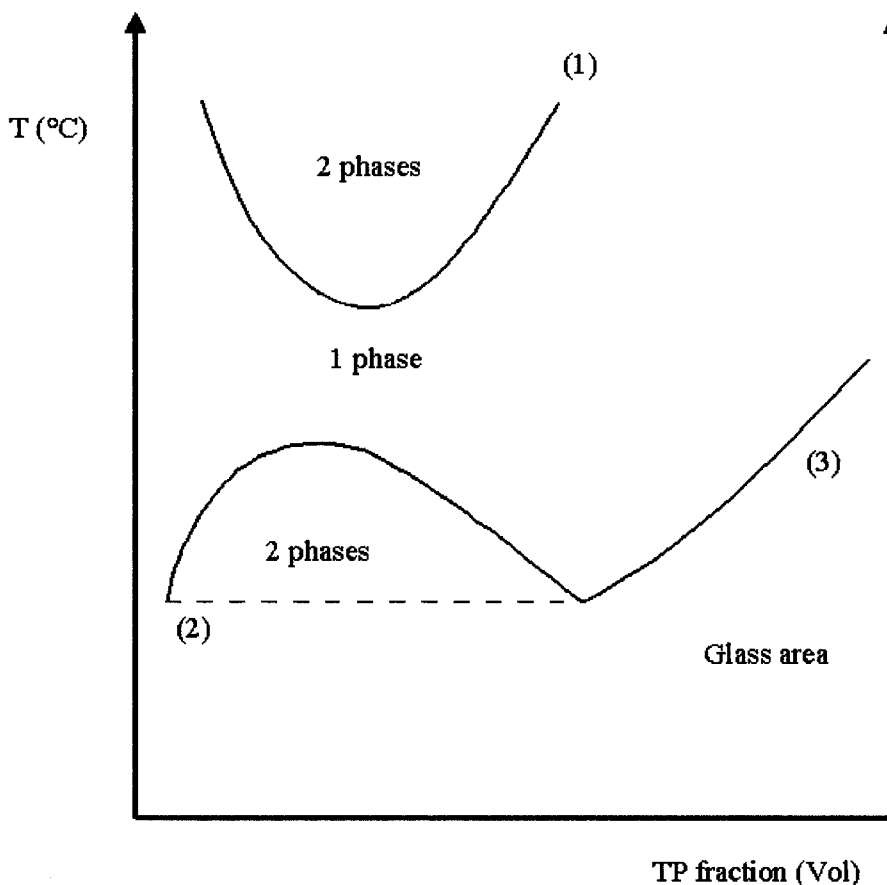
$$h = \left[ \left( \frac{\bar{X}_w}{\bar{X}_n} \right) - 1 \right]^{-1} \quad (3)$$

$$g = \frac{h}{\bar{X}_n} \quad (4)$$

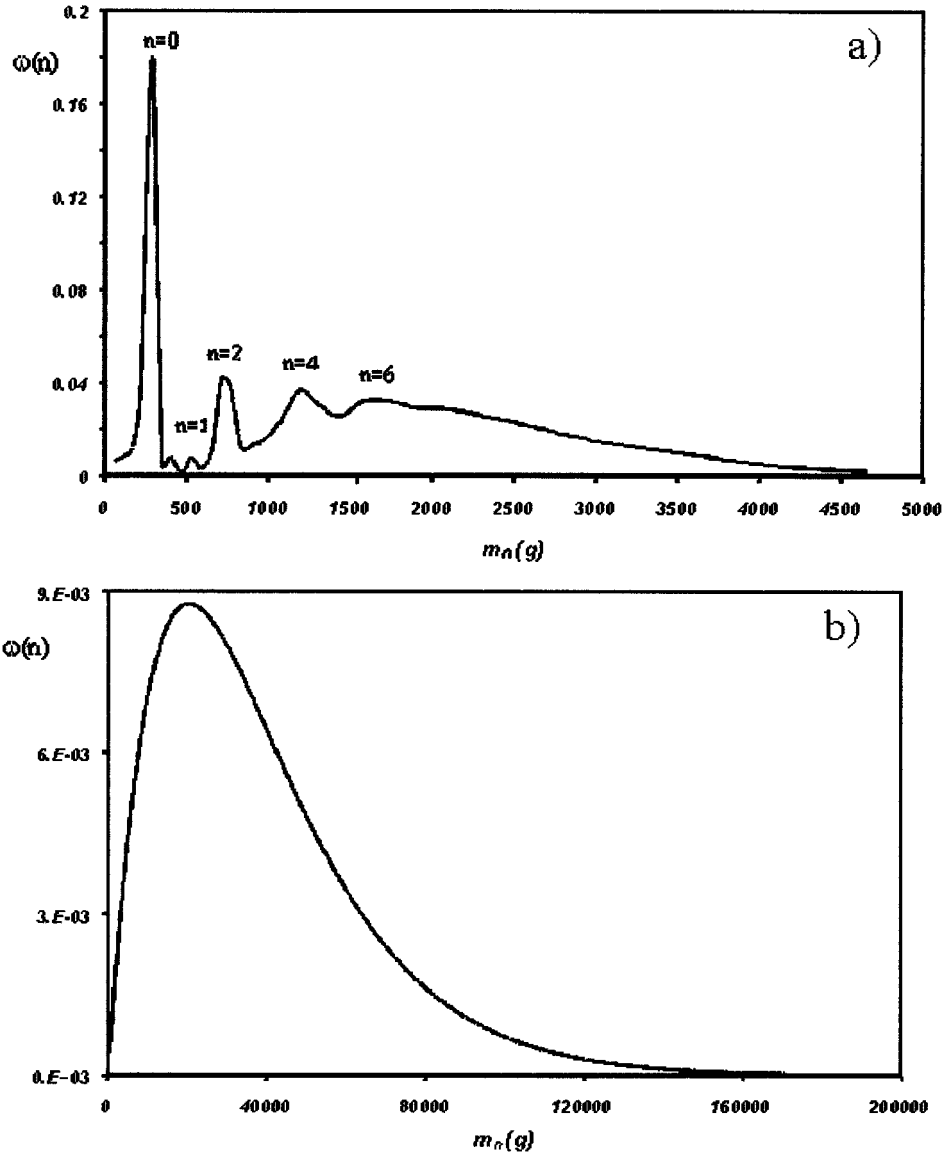
$$\bar{X}_n = \frac{\sum \Phi_i}{\sum \frac{\Phi_i}{i}}; \quad \bar{X}_w = \frac{\sum \Phi_i i}{\sum \Phi_i}; \quad \bar{X}_z = \frac{\sum \Phi_i i^2}{\sum \Phi_i i} \quad (5)$$

where  $\Phi_i$  is the volume fraction of species *i* and  $\bar{X}_n, \bar{X}_w$ , and  $\bar{X}_z$  characterize the TP polydispersity.

The FH equation, written in terms of Gibb's free energy of mixing per mole of unit cells ( $\Delta G$ ), is given by



**Figure 1** Schematic view of the phase diagram: (1) LCST behavior, (2) UCST behavior, and (3) vitrification curve.



**Figure 2** Discontinuous mass distribution of a 50 wt % DGEBA<sub>n=0.03</sub>/50 wt % DGEBA<sub>n=2.32</sub> blend and continuous mass distribution of PEI.  $m_n$  represents the  $n$ -mer mass.

$$\frac{\Delta G}{RT} = \frac{1}{Z_1} \sum \frac{\Phi_i}{i} \ln \Phi_i + \frac{1}{Z_2} \sum \frac{\Phi_j}{j} \ln \Phi_j + \chi(T)\Phi_1\Phi_2 \quad (6)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature (K),  $Z_1 = V_1/V_r$  and  $Z_2 = V_2/V_r$ ,  $V_r$  is the reference volume taken as the smallest species volume,  $V_{1,2}$  is the species molar volume,  $\Phi_{1,2}$  is the volume fraction of species 1 (TP) and 2 (TS),  $\Phi_1 = \sum \Phi_i$  and  $\Phi_2 = \sum \Phi_j$ , and  $\chi$  is the temperature-dependent interaction parameter.

As explained in a previous article,<sup>8</sup> the interaction parameter  $\chi$  is selected to fit experimental CPCs. Through the derivation of Gibbs's free energy, it is now possible to calculate the  $\chi$  parameter for each temperature and composition:

$$\Delta\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \quad (7)$$

where  $n_i$  is the species molar number:

$$\frac{\Delta\mu_1}{RT} = 1 + \ln \phi_1 - Z_1 \left[ \left( \frac{\phi_2}{Z_2} + \frac{\phi_1}{Z_1} \right) - \chi\phi_2^2 \right] \quad (8)$$

and

$$\frac{\Delta\mu_2}{RT} = 1 + \ln \phi_2 - Z_2 \left[ \left( \frac{\phi_2}{Z_2} + \frac{\phi_1}{Z_1} \right) - \chi \phi_1^2 \right] \quad (9)$$

At the equilibrium of the  $\alpha$  and  $\beta$  phases,

$$\Delta\mu_1^\alpha = \Delta\mu_1^\beta \quad (10)$$

and

$$\Delta\mu_2^\alpha = \Delta\mu_2^\beta \quad (11)$$

By applying eq. (10), we obtain

$$\begin{aligned} 1 + \ln \phi_1^\alpha - Z_1 \left( \frac{\phi_2^\alpha}{Z_2} + \frac{\phi_1^\alpha}{Z_1} \right) + Z_1 \chi \phi_2^{\alpha^2} \\ = 1 + \ln \phi_1^\beta - Z_1 \left( \frac{\phi_2^\beta}{Z_2} + \frac{\phi_1^\beta}{Z_1} \right) + Z_1 \chi \phi_2^{\beta^2} \end{aligned} \quad (12)$$

Also, by applying eq. (11), we obtain

$$\begin{aligned} 1 + \ln \phi_2^\alpha - Z_2 \left( \frac{\phi_2^\alpha}{Z_2} + \frac{\phi_1^\alpha}{Z_1} \right) + Z_2 \chi \phi_1^{\alpha^2} \\ = 1 + \ln \phi_2^\beta - Z_2 \left( \frac{\phi_2^\beta}{Z_2} + \frac{\phi_1^\beta}{Z_1} \right) + Z_2 \chi \phi_1^{\beta^2} \end{aligned} \quad (13)$$

Working with this equality, we obtain the following equations:

$$\sigma_1 = \left( \frac{\phi_2^\beta}{Z_2} + \frac{\phi_1^\beta}{Z_1} \right) - \left( \frac{\phi_2^\alpha}{Z_2} + \frac{\phi_1^\alpha}{Z_1} \right) + \chi(\phi_2^{\alpha^2} - \phi_2^{\beta^2}) \quad (14)$$

and

$$\sigma_2 = \left( \frac{\phi_2^\beta}{Z_2} + \frac{\phi_1^\beta}{Z_1} \right) - \left( \frac{\phi_2^\alpha}{Z_2} + \frac{\phi_1^\alpha}{Z_1} \right) + \chi(\phi_1^{\alpha^2} - \phi_1^{\beta^2}) \quad (15)$$

By subtracting eq. (14) from eq. (15), we obtain

$$\sigma_1 - \sigma_2 = \chi [(\phi_2^{\alpha^2} - \phi_2^{\beta^2}) - (\phi_1^{\alpha^2} - \phi_1^{\beta^2})] \quad (16)$$

This implies

$$\chi = \frac{(\sigma_1 - \sigma_2)}{2(\phi_2^\alpha - \phi_2^\beta)} \quad (17)$$

By introducing eq. (17) into eq. (14), we find

$$\begin{aligned} \sigma_1 = \left( \frac{\phi_2^\beta}{Z_2} + \frac{\phi_1^\beta}{Z_1} \right) - \left( \frac{\phi_2^\alpha}{Z_2} + \frac{\phi_1^\alpha}{Z_1} \right) \\ + \frac{(\sigma_1 - \sigma_2)}{2(\phi_2^\alpha - \phi_2^\beta)} (\phi_2^{\alpha^2} - \phi_2^{\beta^2}) \end{aligned} \quad (18)$$

knowing that

$$\sigma_1 = \frac{1}{Z_1} \ln \frac{\phi_1^\beta}{\phi_1^\alpha} \quad (19)$$

and

$$\sigma_2 = \frac{1}{Z_2} \ln \frac{\phi_2^\beta}{\phi_2^\alpha} \quad (20)$$

and with the mass balance

$$\phi_1^\alpha + \phi_2^\alpha = 1 \quad \text{and} \quad \phi_1^\beta + \phi_2^\beta = 1 \quad (21)$$

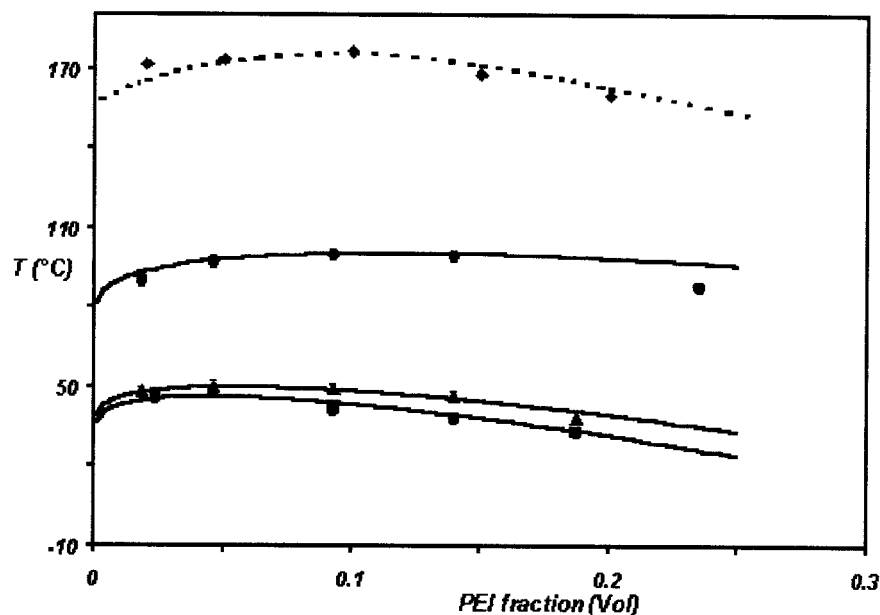
Working with eq. (18), we obtain

$$\begin{aligned} \frac{\phi_2^\beta}{Z_2} + \frac{\phi_1^\beta}{Z_1} - \frac{\phi_2^\alpha}{Z_2} - \frac{\phi_1^\alpha}{Z_1} - \frac{\sigma_2}{2} (\phi_2^\alpha + \phi_2^\beta) \\ - \frac{\sigma_1}{2} (\phi_1^\alpha + \phi_1^\beta) = 0 \end{aligned} \quad (22)$$

Introducing eqs. (19) and (20) into eqs. (21) and (22) and considering that, at the beginning of the phase-separation process,  $\phi_1^\alpha = \phi_1^0$  and  $\phi_2^\alpha = \phi_2^0$  (the initial composition), we obtain a system of two nonlinear equations:

$$\begin{aligned} F1 = \phi_1^0 \left( \sum_j \frac{\omega(j) e^{\sigma_1 Z_j}}{Z_j} - \sum_j \frac{\omega(j)}{Z_j} \right) \\ + \phi_2^0 \left( \sum_i \frac{\omega(i) e^{\sigma_2 Z_i}}{Z_i} - \sum_j \frac{\omega(i)}{Z_i} \right) \\ - \frac{\ln \phi_j}{2} \phi_1^0 \left( 1 + \sum_j \omega(j) e^{\sigma_1 Z_j} \right) \\ - \frac{\ln \phi_i}{2} \phi_2^0 \left( 1 + \sum_i \omega(i) e^{\sigma_2 Z_i} \right) = 0 \end{aligned} \quad (23)$$

$$F2 = \phi_1^0 \sum_j \omega(j) e^{\sigma_1 Z_j} + \phi_2^0 \sum_i \omega(i) e^{\sigma_2 Z_i} = 0 \quad (24)$$



**Figure 3** Experimental CPCs of nonreactive PEI/DGEBA blends with different molar masses: (■)  $\bar{n} = 0.03$ , (▲)  $\bar{n} = 0.15$ , and (●)  $\bar{n} = 0.49$ . Also shown are (◆) the experimental CPC for a 50 wt % DGEBA $_{\bar{n}=0.03}$ /50 wt % DGEBA $_{\bar{n}=2.32}$  blend, (—) the modeling of the experimental CPC, and (---) the predicted CPC for a 50 wt % DGEBA $_{\bar{n}=0.03}$ /50 wt % DGEBA $_{\bar{n}=2.32}$  blend.

The resolution of this system of two nonlinear equations is done with the numerical method of Newton Raphson. This numerical method is described in the literature.<sup>16</sup>

With the  $\sigma_1$  and  $\sigma_2$  values for which F1 and F2 are close to 0, we can calculate a value for  $\chi$ . The  $\chi$  calculation includes the entrance of  $V_r$ , which is defined as the molar volume of the smallest blend species. In PEI blends containing TGpAP, the TGpAP molar volume is considered to be  $V_r$ , whereas for blends without TGpAP, the DGEBA $_{n=0}$  molar volume is the smallest species volume and is considered to be  $V_r$ . For a comparison of  $\chi$  values, the interaction parameter must be expressed per unit of volume, so the  $\chi/V_r$  ratio of each blend can be compared. For PES blends, the PES repetitive unit has the smallest volume and so is considered to be  $V_r$  for all PES blends; therefore,  $\chi$  values can be compared directly.

In this work,  $\chi$  is considered to have a temperature dependence:  $\chi = a + b/T$  for UCST behavior and  $\chi = a - b/T$  for LCST behavior.

## RESULTS AND DISCUSSION

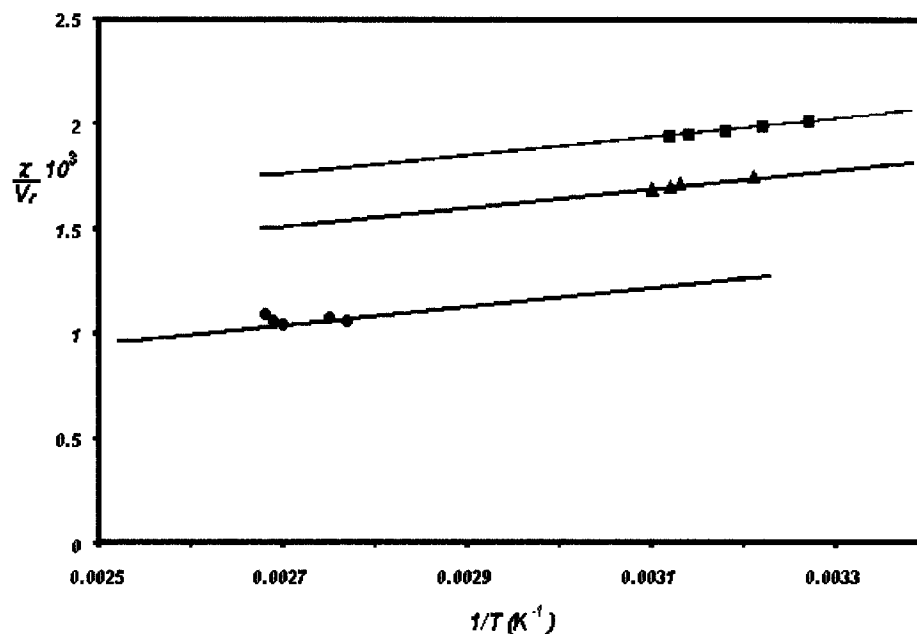
In this study, all of the PEI-based blends exhibited UCST behavior, whereas all of the PES blends exhibited LCST behavior.

### Blends Based on PEI

Experimental CPCs of PEI blends with DGEBA of different degrees of polymerization in the range of 0.03–0.49 are reported in Figure 3. Modeling based on the FH approach allows the calculation of an interaction parameter value for each composition and temperature. The molar volume of the monomer DGEBA $_{n=0}$  is considered to be the reference molar volume  $V_r$ . Figure 4 presents the plot of  $\chi/V_r$  versus  $1/T_{cp}$  for the different blends. Because  $\chi$  is expected to follow the relationship  $\chi = a + b/T$ , by choosing one  $b$  value for all the blends, we find the value of  $a$  varies with the average molar mass of the DGEBA prepolymer. In Figure 5, a relationship between  $a$  and  $\bar{n}$  is highlighted, leading to a simple phenomenological relation, giving  $\chi$  as a function of  $\bar{n}$  and  $T$  ( $K^{-1}$ ):

$$\frac{\chi}{V_r} 10^3 = -0.36 - 2.71\{\bar{n}(1 - \bar{n})\} + \frac{766}{T(K^{-1})} \quad (25)$$

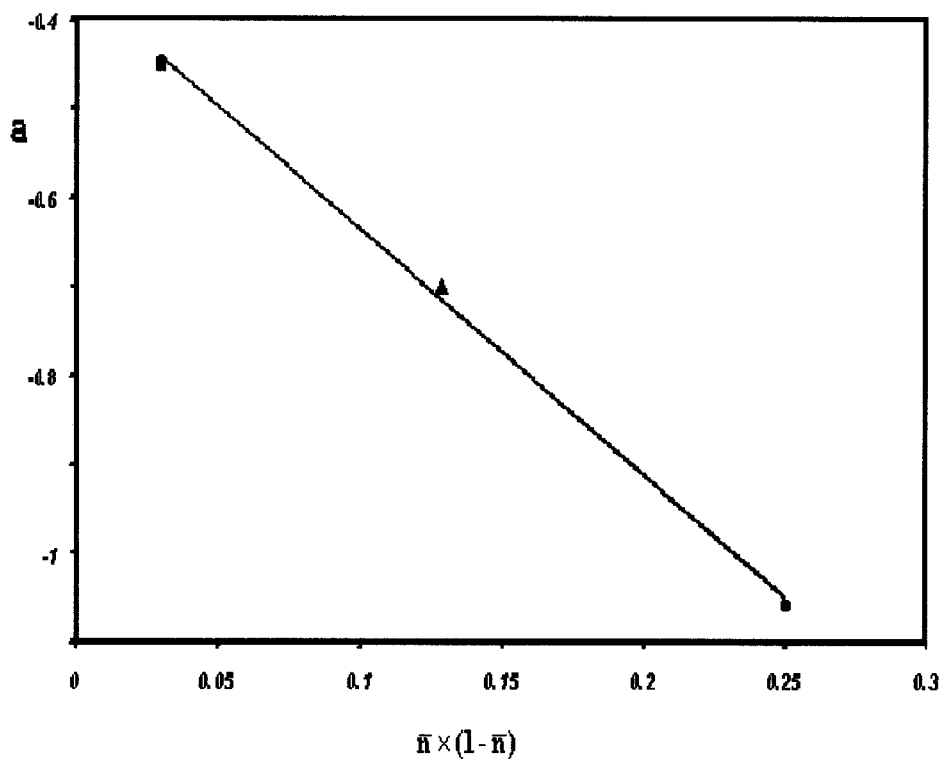
To test this relation, we can use it for a blend of PEI with a DGEBA monomer with a very broad molar mass distribution. A mixture of 50 wt % DGEBA $_{\bar{n}=0.03}$  and 50 wt % DGEBA $_{\bar{n}=2.32}$  was prepared. The molar mass distribution of this DGEBA mixture was characterized by SEC [Fig.



**Figure 4** Evolution of  $\chi/V_r$  as a function of  $1/T_{cp}$  for nonreactive PEI-DGEBA blends with different polymerization degrees: (■)  $\bar{n} = 0.03$ , (▲)  $\bar{n} = 0.15$ , and (●)  $\bar{n} = 0.49$ .

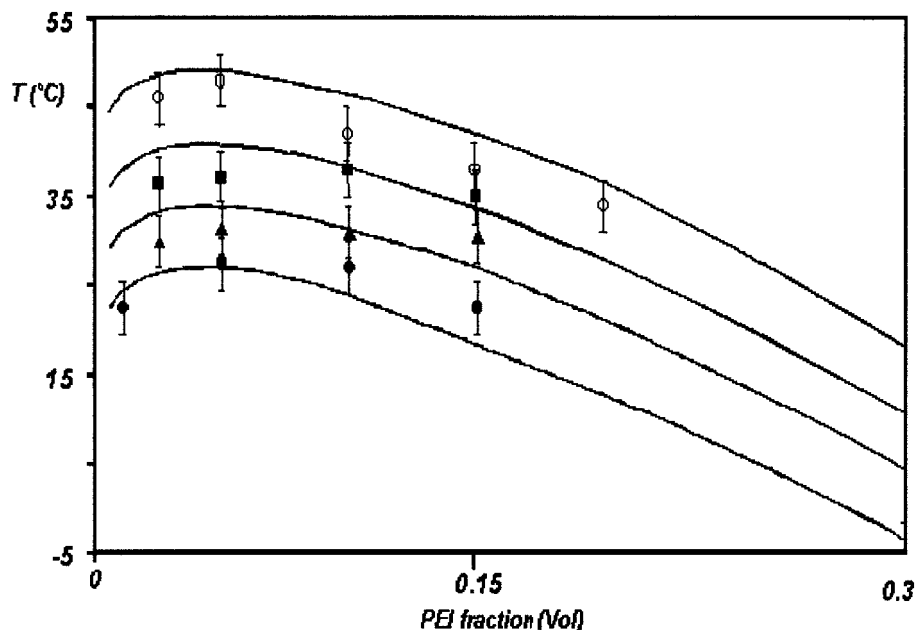
2(a)]. When this distribution is introduced to the model, it is possible to estimate the  $\chi$  value and, with the application of eq. (18), to estimate  $T_{cp}$  (see Fig. 3).

The predicted miscibility curve is in good agreement with the experimental results, and it validates the phenomenological equation. This modeling shows that for small values of  $\bar{n}$ , the



**Figure 5** Plot of a parameter from the equation  $\chi/V_r = a + b/T$  versus  $\bar{n} \times (1 - \bar{n})$ .





**Figure 6** Experimental CPCs of nonreactive TGpAP–DGEBA $_{\bar{n}=0.03}$ /PEI blends with different amounts of TGpAP: (○) 0 wt % TGpAP, (■) 10 wt % TGpAP, (▲) 20 wt % TGpAP, and (●) 25 wt % TGpAP. Also shown is (—) the modeling of the experimental CPC. The percentage is defined as the epoxy weight percentage by the whole epoxy weight.

increase in the molar mass leads to a favorable enthalpic effect, probably due to the hydroxyl groups present on the DGEBA molecule. However, for a certain value, this favorable effect is counterbalanced by an unfavorable entropic effect due to the mass increase.

#### Influence of the Epoxy Type in PEI Nonreactive Blends

Results reported in Figure 6 show that TGpAP addition to a DGEBA/PEI blend leads to an increase in the miscibility window. Modeling enables the prediction of  $\chi$  values for each composition and temperature. To compare  $\chi$  values, we use  $\chi/V_r$  values. For each blend, linear relations with the form  $\chi/V_r = a + b/T$  are found to fit, and they are presented as follows:

$$\text{DGEBA}_{\bar{n}=0.03}/\text{PEI} \quad \frac{\chi}{V_r} 10^3 = -0.45 + \frac{766}{T} \quad (26)$$

DGEBA $_{\bar{n}=0.03}$ , TGpAP (10 wt %)/PEI

$$\frac{\chi}{V_r} 10^3 = -0.47 + \frac{766}{T} \quad (27)$$

DGEBA $_{\bar{n}=0.03}$ , TGpAP (20 wt %)/PEI

$$\frac{\chi}{V_r} 10^3 = -0.49 + \frac{766}{T} \quad (28)$$

DGEBA $_{\bar{n}=0.03}$ , TGpAP (25 wt %)/PEI

$$\frac{\chi}{V_r} 10^3 = -0.53 + \frac{766}{T} \quad (29)$$

The TGpAP weight percentages are weight percentages from the whole epoxy weight (DGEBA + TGpAP).

With  $b$  a chosen constant, values of the parameter  $a$  are found to vary in a linear way with the TGpAP content, and a phenomenological relation, giving  $\chi$  as a function of the TGpAP weight percentage and  $T$ , can be written:

$$\frac{\chi}{V_r} 10^3 = -0.33 (\text{wt \% TGpAP}) - 0.44 + \frac{766}{T} \quad (30)$$

The established relationship allows the prediction of  $T_{cp}$  of any TGpAP/DGEBA/PEI composition.

**Table III Comparison Between Modeling Values and Experimental Values**

System	$T_p$ (°C)	
	Modeling	Experimental
DGEBA $_{\bar{n}=0.03}$ (70 wt %)-TGpAP (30 wt %)/PEI (5%)	24	23
DGEBA $_{\bar{n}=0.03}$ (70 wt %)-TGpAP (30 wt %)/PEI (10%)	21	24

For the validation of this relationship, two  $T_{cp}$ 's are checked and presented in Table III.

Because the  $b$  parameter has been given the same value for the two established phenomenological relations, eqs. (25) and (30), a global phenomenological relation can be deduced from these two equations if we consider that the TGpAP concentration and DGEBA degree of polymerization influences are additive:

$$\frac{\chi}{V_r} 10^3 = -2.71\{\bar{n}(1 - \bar{n})\} - 0.33 \text{ (wt \% TGpAP)} - 0.36 + \frac{766}{T} \quad (31)$$

It is now possible to validate this equation through a comparison of the predicted and experimental cloud points for two blends with two different DGEBA ( $\bar{n} = 0.03$  and  $\bar{n} = 0.15$ ) and the same amount of TGpAP (equal to 25 wt % of the total epoxy DGEBA plus the TGpAP content). In Figure 7, we can see that the modeling predicts an increase in the miscibility with an increase in the DGEBA molar mass from  $\bar{n} = 0.03$  to  $\bar{n} = 0.15$ . This fact is confirmed with experimentation, and predicted curves are in good agreement with experimental points.

#### Influence of the Hardener Type in Epoxy/Hardener/PEI Nonreacted Blends

Figure 8 presents the initial phase diagram obtained for PEI/epoxy precursor blends with a stoichiometric ratio of 1 mol of amino hydrogen group to 1 mol of epoxy function. The experimental miscibility window is modified differently by the introduction of hardeners with different structures. The blend based on DDS exhibits a lower miscibility than the initial DGEBA $_{\bar{n}=0.03}$ /PEI blend, contrary to the blend with MCDEA, which shows a larger miscibility window than the PEI/epoxy monomer blends.

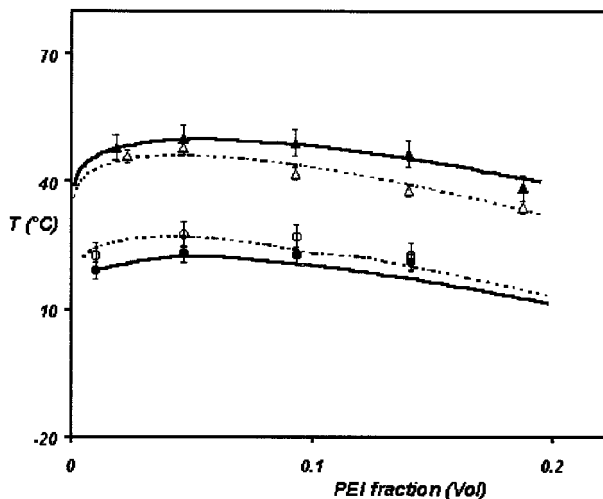
As noted previously, the modeling of these CPCs allows us to calculate the value of  $\chi$  for each blend:

$$\text{DGEBA}_{\bar{n}=0.03}\text{-MCDEA/PEI: } \frac{\chi}{V_r} 10^3 = 0.34 + \frac{480}{T} \quad (32)$$

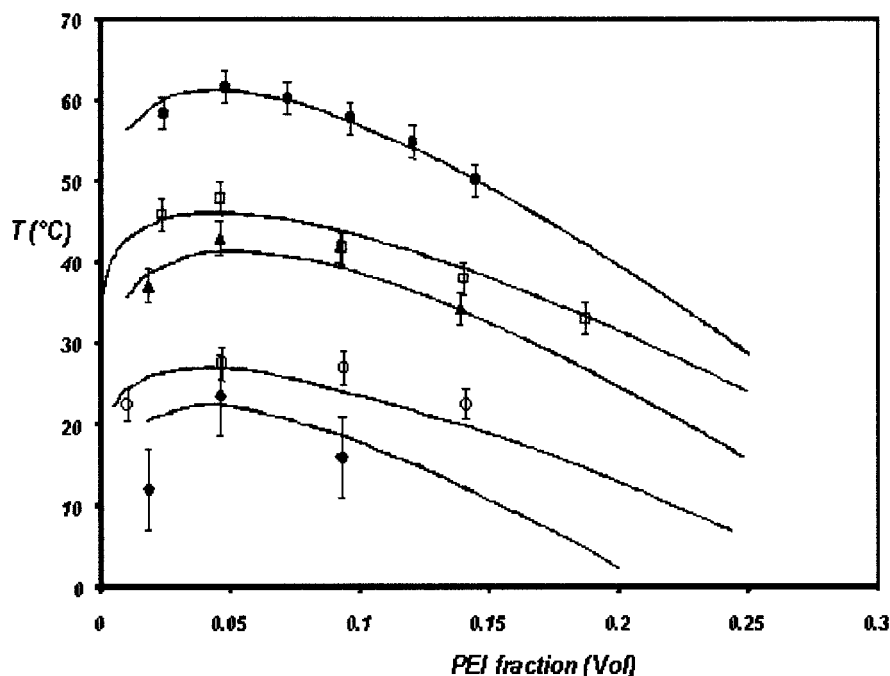
$$\text{DGEBA}_{\bar{n}=0.03}\text{-DDS/PEI: } \frac{\chi}{V_r} 10^3 = 0.34 + \frac{607}{T} \quad (33)$$

DGEBA $_{\bar{n}=0.03}$ , TGpAP (25 wt %)-MCDEA/PEI:

$$\frac{\chi}{V_r} 10^3 = 0.29 + \frac{480}{T} \quad (34)$$



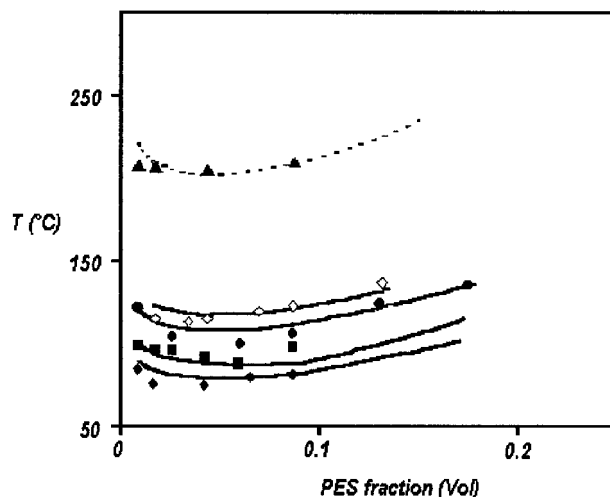
**Figure 7** (—, —) Predicted CPCs and ( $\Delta$ ,  $\blacktriangle$ ,  $\circ$ ,  $\bullet$ ) experimental CPCs of the following blends: ( $\Delta$ ) DGEBA $_{\bar{n}=0.15}$  (90 wt %)-TGpAP (10 wt %)/PEI, ( $\blacktriangle$ ) DGEBA $_{\bar{n}=0.03}$  (90 wt %)-TGpAP (10 wt %)/PEI, ( $\circ$ ) DGEBA $_{\bar{n}=0.03}$  (75 wt %)-TGpAP (25 wt %)/PEI, and ( $\bullet$ ) DGEBA $_{\bar{n}=0.15}$  (75 wt %)-TGpAP (25 wt %)/PEI. The percentage is defined as the epoxy weight percentage by the whole epoxy weight.



**Figure 8** Experimental CPCs of nonreacted blends of (●) DGEBA <sub>$\bar{n}=0.03$</sub> -DDS/PEI, (□) DGEBA <sub>$\bar{n}=0.03$</sub> /PEI, (▲) DGEBA <sub>$\bar{n}=0.03$</sub> -MCDEA/PEI, (○) DGEBA <sub>$\bar{n}=0.03$</sub>  (75 wt %)-TGpAP (25 wt %)/PEI, and (◆) DGEBA <sub>$\bar{n}=0.03$</sub>  (75 wt %)-TGpAP (25 wt %)-MCDEA/PEI. Also shown is (—) the modeling of the experimental CPC. The percentage is defined as the epoxy weight percentage by the whole epoxy weight.

### Blends Based on PES

Experimentally, the CPCs of the whole PES blends exhibited LCST behavior. Experimental  $T_{cp}$ 's of nonreacted TGpAP-DGEBA <sub>$\bar{n}=0.03$</sub> /diamine/PES blends were obtained via changes in the amounts of monomer and TP (Fig. 9). The diamine was always added in a stoichiometric ratio of 1 mol of amino hydrogen function to 1 mol of epoxy function. The influence of the trifunctional epoxy (TGpAP) and a diamine (MCDEA) on the miscibility of nonreacted DGEBA/PES blends was studied via variations in the TGpAP and MCDEA contents. Figure 9 shows that TGpAP addition to DGEBA/PES blends leads to an increase in the blend miscibility, whereas MCDEA addition to epoxy/PES blends leads to a decrease in the blend miscibility. Modeling allows one to estimate  $\chi$  values for each composition and temperature. Because  $V_r$  is the same for all PES blends (i.e., repetitive PES unit molar volume), the  $\chi$  values can be compared directly. Linear relationships between  $\chi$  and  $1/T_{cp}$  for all the TGpAP and MCDEA formulations, with the same  $b$  parameter, are established:



**Figure 9** Experimental CPCs of nonreacted TGpAP-DGEBA <sub>$\bar{n}=0.03$</sub> -MCDEA/PES blends with different amounts of TGpAP and MCDEA: (◆) 0 wt % TGpAP and 35 wt % MCDEA, (■) 6 wt % TGpAP and 37 wt % MCDEA, (●) 15 wt % TGpAP and 39 wt % MCDEA, (◇) 0 wt % TGpAP and 0 wt % MCDEA, and (▲) 100 wt % TGpAP and 44 wt % MCDEA. Also shown are (—) the modeling of the experimental CPC and (---) the predicted CPC. The percentage is defined as the component weight percentage by the whole blend weight.

DGEBA $_{\bar{n}=0.03}$  (65 wt %)-MCDEA

$$(35 \text{ wt \%})/\text{PES}: \frac{\chi}{V_r} 10^3 = 0.5500 - \frac{80}{T} \quad (35)$$

DGEBA $_{\bar{n}=0.03}$  (57 wt %), TGpAP

(6 wt %)-MCDEA (37 wt %)/PES:

$$\frac{\chi}{V_r} 10^3 = 0.5425 - \frac{80}{T} \quad (36)$$

DGEBA $_{\bar{n}=0.03}$  (46 wt %), TGpAP

(15 wt %)-MCDEA (39 wt %)/PES:

$$\frac{\chi}{V_r} 10^3 = 0.5400 - \frac{80}{T} \quad (37)$$

DGEBA $_{\bar{n}=0.03}$  (100 wt %)/PES:

$$\frac{\chi}{V_r} 10^3 = 0.5375 - \frac{80}{T} \quad (38)$$

The component percentages considered in these equations are weight percentages for all blends.

Parameter  $a$  is supposed to follow the relation  $a = a_1$  (MCDEA weight percentage)  $- a_2$  (TGpAP weight percentage)  $+ a_3$ , with the  $a_1$ ,  $a_2$ , and  $a_3$  constants to be determined.  $a_1$  leads to an increase in  $\chi$  because MCDEA has a negative enthalpic contribution to miscibility, and  $-a_2$  leads to a decrease in  $\chi$ . A simple relation can be written:

$$\chi = -[0.032 \cdot (\text{wt \% MCDEA}) - 0.072 \cdot (\text{wt \% TGpAP}) + 0.54] - \frac{80}{T} \quad (39)$$

This relation allows the prediction of  $T_{cp}$  of any TGpAP/DGEBA/MCDEA/PES blend composition.

## CONCLUSION

In this work, the initial miscibility of epoxy TS/TP blends was studied. Phase-separation behavior was shown to depend on the TP type.

For TS precursor/PEI blends, UCST behavior was observed, whereas for TS/PES blends, LCST behavior was observed. Introducing a given TGpAP concentration in DGEBA/TP blends led to an increase in the miscibility window in both PEI and PES blends. In contrast, MCDEA addition

increased the miscibility window for PEI blends but decreased the miscibility window in PES blends.

Modeling the CPCs of these blends was performed with the FH equation according to Kamide et al.'s procedure. The interaction parameter was used as a fitting parameter for experimental data, from which phenomenological equations were derived. These equations allowed the prediction of  $T_{cp}$  as a function of the TGpAP and MCDEA contents with the DGEBA molecular weight taken into account.

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