

**DIFFERENT PARAMETERS CONTROLLING THE INITIAL
SOLUBILITY OF TWO THERMOPLASTICS IN EPOXY REACTIVE
SOLVENTS**

L. Bonnaud¹, A. Bonnet¹ J.P. Pascault¹, H. Sautereau¹,
C.C. Riccardi^{2*}.

¹ Laboratoire des Matériaux Macromoléculaires, UMR-CNRS 5627, Bât. 403, INSA, 69621
Villeurbanne Cedex, France.

² Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and
National Research Council (CONICET), J.B. Justo 4302, (7600) Mar del Plata, Argentina.

(*) : To whom correspondence should be addressed.

DIFFERENT PARAMETERS CONTROLLING THE INITIAL SOLUBILITY OF TWO THERMOPLASTICS IN EPOXY REACTIVE SOLVENTS

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C.C. Riccardi^{2*}.

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² Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and
National Research Council (CONICET), J.B. Justo 4302, (7600) Mar del Plata, Argentina.

ABSTRACT

The influence of different factors on diglycidyl ether of bisphenol A (DGEBA)/thermoplastic (TP) blend miscibility has been studied. DGEBA/polyetherimide (PEI) blends exhibit an upper critical solution temperature, UCST behavior. Addition of a trifunctional epoxy (triglycidyl para amino phenol TGpAP) is found to increase the miscibility window. The addition of diamines as hardeners can also increase (4,4' methylene-bis (3-chloro-2,6-diethylaniline), MCDEA) or decrease (4,4' diaminodiphenylsulfone, DDS) the miscibility window.

DGEBA/polyethersulfone (PES) blends show a lower critical solution temperature, LCST behavior. Addition of TGpAP has a similar effect than for PEI blends but presence of MCDEA as hardener decreases the miscibility of epoxy/PES blends.

Modeling of cloud point curves was performed from the Flory – Huggins equation (Ithaca: Cornell University Press, p672, (1953)) following the procedure developed by Kamide et al (Eur. Polym. J., **26**, p379, (1990)) using the interaction parameter as the fitting parameter. A phenomenological model that takes into account DGEBA molar mass and TGpAP amount was proposed and was found to predict the cloud point temperature of any TGpAP/DGEBA/PEI blends.

Keywords : phase diagram / thermoplastic - modified epoxies / polyetherimide / polyethersulfone / Flory–Huggins equation.

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 other families of polymers. Therefore, they need to be toughened in order increase their range of possible applications. Studies have demonstrated that thermoplastics (TP) such as polysulfones, polyetherimides, polyimides or polyphenylene ether can enhance fracture toughness without sacrificing glass temperature (T_g) or other desirable properties of thermosets (TS) [1-6]. The thermoplastic has to be initially miscible with the epoxy monomers but at a particular conversion depending on composition and reaction temperature, phase separation occurs [7]. Depending on the initial composition, the resulting thermoplastic-toughened epoxies may exist as a particulate, bicontinuous or phase inverted morphologies [7]. This work deals with the study of the initial miscibility of TP in TS precursors. Two types of behavior can be observed: an upper critical solution temperature (UCST) behavior where full miscibility is obtained by an increase of temperature [8] and a lower critical solution temperature (LCST) behavior where full miscibility is obtained by decreasing temperature [9-11].

The aim of this work is to analyze the effect of varying TS precursors / TP blends on the initial miscibility before reaction. Two amorphous thermoplastics have been studied: a non functional polyetherimide (PEI) and a polyethersulfone (PES) with a phenol end-capped chain. The influence of the addition of a trifunctional epoxy (triglycidylparaaminophenol TGpAP) on a diglycidyl ether of bisphenol A (DGEBA)/thermoplastic blend has been investigated.

The influence of the addition of an amine hardener on the epoxy/thermoplastic blend miscibility before reaction has been also reported. Experimental cloud point temperatures were fitted to a thermodynamic model based on the Flory – Huggins (FH) approach [12] considering the polydispersity of each blend components (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 i) diglycidyl ether of bisphenol A (DGEBA), with different average degrees of polymerisation \bar{n} ranging from 0.03 to 2.32 (Dow and Ciba Geigy products), ii) triglycidyl para amino phenol (TGpAP, Ciba Geigy). The hardeners used were the aromatic diamines i) 4,4' methylene-bis (3-chloro-2,6-diethylaniline), MCDEA supplied by Lonza and ii) the 4,4'-diaminodiphenylsulfone (DDS) supplied by Fluka. Two amorphous thermoplastics are used, a polyetherimide, PEI (Ultem 1000, General Electric) and a polyethersulfone, PES (5003P, Sumitomo). The chemical structures and characteristics of all species are reported in Table I. The discontinuous molecular weight distribution of the different DGEBA epoxy resins is shown in Table II. In contrast TP distribution is continuous and the TP molar mass distribution is obtained by using a Schulz – Zimm (SZ) equation (see Eq. 2) [13].

Techniques:

Size exclusion chromatography (SEC) :

SEC using epoxy standards for calibration is used to obtain the molar mass distribution of DGEBA prepolymers. SEC was performed with columns of PL gel (Polymer Laboratories) 10^3 Å, 500 Å, 100 Å and 100 Å. The solvent was THF at a $1.5 \text{ ml}\cdot\text{min}^{-1}$ flow rate and a pressure of $5\cdot 10^6$ Pa. The chromatogram was monitored using a refractive index detector.

Cloud points curves (CPC's) :

Cloud points temperatures (T_{cp}) of non reactive blends and of PEI - DGEBA / hardener unreacted mixtures containing different TP concentrations, were determined using a light transmission device described elsewhere [14]. For PEI blends, the temperature was increased until a homogeneous solution is obtained, kept constant during several minutes and then decreased at a cooling rate in the order of $1 \text{ K}\cdot\text{min}^{-1}$. The T_{cp} value is determined at the onset time of the light transmission decrease. In the case of PES blends, the PES is firstly

mixed with the epoxy precursor, then, dissolved in a solution of dichloromethane with 10% in volume of methanol [9-11]. When the blend becomes miscible, the solvent is driven off under primary vacuum and if necessary the diamine hardener is added. To obtain experimental cloud points, the temperature is increased at different heating rates of 1, 5 and 10 K.min⁻¹ from room temperature to 220°C (which is the limit of the apparatus). The cloud point temperature was determined by extrapolating to a zero heating rate.

Calorimetric measurements:

The glass transition temperature T_g of blends is obtained using a differential scanning calorimeter (DSC) from METTLER at a heating rate of 10°C/min, from -50°C to 250°C (onset temperature). In order to check the reproductibility the procedure was repeated a further two times.

BACKGROUND :

Tools for modeling

A pseudo-binary phase diagram is composed of two curves i) the vitrification curve, separating the liquid and the vitreous phase areas, ii) the cloud points curve, delimiting between the one phase and the two phase areas in the liquid state (Figure 1).

i) The vitrification curve is calculated using the Couchman equation [15] :

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

where subscript 1 indicates the thermoset precursor, subscript 2 the thermoplastic ; M_i is the weight ratio of i in the mixture ; T_{gi} and ΔC_{pi} , are the glass transition temperature and the heat capacity change at T_g of component i .

The vitrification curve can also be determined experimentally using calorimetric measurements. In UCST case, vitrification curve crosses cloud point curve at a certain TP concentration (Bergham point) whereas in LCST case it never crosses it (Figure 1) [4].

ii) Different approaches exist to model cloud points curve of blends and are described in a previous paper [8]. We decided to calculate the cloud point curves from the Flory Huggins (FH) energy equation following the procedure developed by Kamide et al [16], where the polydispersities of both TP and TS blend components are considered. The TP is assumed to have a continuous molar mass distribution obtained using the Schulz – Zimm equation (Figure 2 and eq 2), while the TS DGEBA precursors have a discontinuous distribution calculated from the SEC chromatogram (Figure 2).

For TP:

$$\omega(i) = \left[g^{h+1} / \Gamma(h+1) \right] \cdot i^h \exp(-g \cdot i) \quad \text{Eq.2}$$

with $\omega(i)$: mass fraction of macromolecules with a polymerization degree i .

Γ : gamma function.

$$m_i = M_u \cdot i$$

$$h = \left[\left(\frac{\overline{X_w}}{\overline{X_n}} \right) - 1 \right]^{-1} \quad \text{Eq.3}$$

$$g = \frac{h}{\overline{X_n}} \quad \text{Eq.4}$$

$$\overline{X_n} = \frac{\sum \Phi_i}{\sum \frac{\Phi_i}{i}} ; \overline{X_w} = \frac{\sum \Phi_i \cdot i}{\sum \Phi_i} ; \overline{X_z} = \frac{\sum \Phi_i \cdot i^2}{\sum \Phi_i \cdot i} \quad \text{Eq.5}$$

with Φ_i , the volume fraction of species i . $\overline{X_n}$, $\overline{X_w}$ and $\overline{X_z}$ characterise the TP polydispersity.

The FH equation written in terms of Gibb free energy of mixing per mol of unit cells ΔG is given by:

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

Where R: gas constant

T: absolute temperature (K)

$$Z_1 = V_1/V_r \text{ and } Z_2 = V_2/V_r$$

V_r : reference volume taken as the smallest species volume.

$V_{1,2}$: species molar volume

$\Phi_{1,2}$: volume fraction of species 1 (TP) and 2 (TS)

$\Phi_1 = \sum \Phi_i$ and $\Phi_2 = \sum \Phi_j$

χ : temperature dependent interaction parameter

As explained in a previous paper [8], the interaction parameter χ is selected to fit experimental cloud – point curves. By derivating the Gibb's free energy (eq 6), it is now possible to calculate the χ parameter for each temperature and composition:

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

with n_i the specie mole number

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

and

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

At equilibrium of α and β phases

$$\Delta\mu_1^\alpha = \Delta\mu_1^\beta \quad \text{Eq.10}$$

and

$$\Delta\mu_2^\alpha = \Delta\mu_2^\beta \quad \text{Eq.11}$$

By applying equation 10, we obtain:

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

And by applying equation 11:

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

By working with this equality the following equations are obtained

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

and

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

By subtracting equation 14 from equation 15

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

This implies

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

By introducing equation 17 into equation 14, we find

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

Knowing that:

$$\sigma_1 = \frac{1}{Z_1} \ln \frac{\phi_1^\beta}{\phi_1^\alpha} \quad \text{Eq.19}$$

and

$$\sigma_2 = \frac{1}{Z_2} \ln \frac{\phi_2^\beta}{\phi_2^\alpha} \quad \text{Eq.20}$$

and using the mass balance:

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

Working with equation 18, we obtain:

$$\frac{\phi_2^\beta}{Z_2} + \frac{\phi_1^\beta}{Z_1} - \frac{\phi_2^\alpha}{Z_2} - \frac{\phi_1^\alpha}{Z_1} - \frac{\sigma_2}{2} (\phi_2^\alpha + \phi_2^\beta) - \frac{\sigma_1}{2} (\phi_1^\alpha + \phi_1^\beta) = 0 \quad \text{Eq.22}$$

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

$$F2 = \phi_2^0 \left(\sum_j^n \frac{\omega(j) \cdot \phi_j^{Z_j}}{Z_j} - \sum_j^f \frac{\omega(j)}{Z_j} \right) + \phi_1^0 \left(\sum_i^n \frac{\omega(i) \cdot \phi_i^{Z_i}}{Z_i} - \sum_i^f \frac{\omega(i)}{Z_i} \right) - \frac{\ln \phi_2}{2} \phi_2^0 \left(1 + \sum_j^f \omega(j) \cdot \phi_j^{Z_j} \right) - \frac{\ln \phi_1}{2} \phi_1^0 \left(1 + \sum_i^n \omega(i) \cdot \phi_i^{Z_i} \right) = 0 \quad \text{Eq.23}$$

$$F1 = \phi_1^0 \sum_i^n \omega(i) \cdot \phi_i^{Z_i} + \phi_2^0 \sum_j^f \omega(j) \cdot \phi_j^{Z_j} - 1 = 0 \quad \text{Eq.24}$$

Resolution of this system of two non-linear equations is done using the numerical method of Newton Raphson. This numerical method is described in the literature [16].

With the σ_1 and σ_2 values for which F1 and F2 are close to 0, we can calculate a value for χ . The χ calculation includes the entrance of a reference volume, V_r , which is defined as the molar volume of the smallest blend specie. In PEI blends containing TGpAP, the TGpAP molar volume is considered to be the reference volume, whereas for blends without TGpAP, the DGEBA_{n=0} molar volume is the smallest specie volume and is considered as V_r . To compare χ values, the interaction parameter must be expressed per unit of volume, so the $\frac{\chi}{V_r}$ ratio of each blend can be compared. In the case of PES blends, the PES repetitive unit has the smallest volume and so is considered to be V_r for all PES blends so that χ values can be compared directly.

In this work, χ is considered to have a temperature dependence : $\chi = a + \frac{b}{T}$ in the case of a UCST behavior and $\chi = a - \frac{b}{T}$ in the case of a LCST behavior.

RESULTS AND DISCUSSION

In this study all of the PEI based blends exhibited UCST behavior while all of the PES blends exhibited LCST behavior.

Blends based on PEI.

Experimental cloud point curves of PEI blends with DGEBA of different degrees of polymerization in the range of 0.03 to 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 as reference molar volume, V_r . Figure 4 presents the plot of χ/V_r versus $1/T_{CP}$ for the different blends. Since χ is expected to follow the relation $\chi = a + \frac{b}{T}$, by choosing equal b value for all blends, the value of a is found to vary with the average molar mass of the DGEBA prepolymer. In Figure 5, a relation between a and \bar{n} is highlighted, leading to a simple phenomenological relation, giving χ as a function of \bar{n} and T (K^{-1}):

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

To test this relation, it can be used for a blend of PEI with a DGEBA monomer with a very broad molar mass distribution. A mixture of 50 wt% of DGEBA $\bar{n}=0.03$ with 50 wt% of DGEBA $\bar{n}=2.32$ was prepared. The molar mass distribution of this DGEBA mixtures is characterised by SEC (Figure 2 a). While introducing this distribution in the model, it is possible to estimate the χ value and by applying equation 18, to estimate the cloud point temperatures (example in Figure 3).

The predicted miscibility curve is in good agreement with the experimental results and it validates the phenomenological equation. This modeling shows that for the small values of \bar{n} , the increase of the molar mass leads to a favorable enthalpic effect, probably due to the hydroxyl groups which are present on the DGEBA molecule. But 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 non reactive blends

Results reported in Figure 6 show that TGpAP addition to a DGEBA/PEI blend leads to an increase of the miscibility window. Modeling enables the prediction of χ values for each composition and temperature. To compare χ values, $\frac{\chi}{V_r}$ values are used. For each blend,

linear relations having the form $\frac{\chi}{V_r} = a + \frac{b}{T}$ were found to fit and they are presented below :

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

$$\text{DGEBA } \bar{n} = 0.03, \text{ TGpAP (10 wt\%)/ PEI} \quad \frac{\chi}{V_r} 10^3 = -0.47 + \frac{766}{T} \quad \text{Eq.27}$$

$$\text{DGEBA } \bar{n} = 0.03, \text{ TGpAP (20 wt\%)/ PEI} \quad \frac{\chi}{V_r} 10^3 = -0.49 + \frac{766}{T} \quad \text{Eq.28}$$

$$\text{DGEBA } \bar{n} = 0.03, \text{ TGpAP (25 wt\%)/ PEI} \quad \frac{\chi}{V_r} 10^3 = -0.53 + \frac{766}{T} \quad \text{Eq.29}$$

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

With b chosen constant, values of parameter a are found to vary in a linear way with TGpAP content and a phenomenological relation, giving χ as a function of TGpAP wt% and T can be written:

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

The established relationship allows the prediction of the cloud point temperatures of any TGpAP/DGEBA/PEI composition. In order to validate this relationship, two cloud points temperatures are checked and presented in Table III.

As b parameter has been chosen to have the same value for the two established phenomenological relations, equations 25 and 30, a global phenomenological relation can be deduced from these two equations, considering that the TGpAP concentration and DGEBA degree of polymerization influences are additive.

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

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

Influence of the hardener type in epoxy/hardener/PEI non reacted blends

Figure 8 presents the initial phase diagram obtained for PEI/epoxy precursor blends with a stoichiometric ratio 1 mol of amino hydrogen group for 1 mole of epoxy function. The experimental miscibility window is differently modified 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 PEI/epoxy monomer blends.

As previously, modeling of these cloud points curves allows us to calculate the value of χ for each blend :

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

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

$$\text{DGEBA } \bar{n}=0.03, \text{ TGpAP (25 wt\%)} - \text{MCDEA} / \text{PEI} : \frac{\chi}{V_r} 10^3 = 0.29 + \frac{480}{T} \quad \text{Eq.34}$$

Blends based on PES

Experimentally, the cloud point curves of the whole PES blends exhibited a LCST behavior. Experimental cloud point temperatures of non reacted TGpAP, DGEBA $\bar{n}=0.03$ /diamine/PES blend were obtained by changing monomers and TP amounts (Figure 9). The diamine is always added in a stoichiometric ratio: 1 mole of amino hydrogen function for 1 mole of epoxy function. The influence of the trifunctional epoxy (TGpAP) and of a diamine (MCDEA) on the miscibility of non reacted DGEBA/PES blends were studied by varying the TGpAP and MCDEA content. Figure 9 shows that TGpAP addition to DGEBA/PES blends leads to an increase of the blend miscibility whereas MCDEA addition to epoxy/PES blends leads a decrease of the blend miscibility. Modeling allows one to estimate χ values for each compositions and temperature. Since the reference volume, V_r is the same for all PES blends (i.e. PES repetitive unit molar volume), the χ values can be compared directly. Linear relationships between χ and $1/T_{CP}$ for all the TGpAP and MCDEA formulations, with the same b parameter are established.

DGEBA $\bar{n}=0.03$ (65 wt%)- MCDEA (35 wt%)/ PES :

$$\frac{\chi}{V_r} 10^3 = 0.5500 - \frac{80}{T} \quad \text{Eq.35}$$

DGEBA $\bar{n}=0.03$ (57 wt%), TGpAP (6 wt%) - MCDEA (37 wt%)/ PES :

$$\frac{\chi}{V_r} 10^3 = 0.5425 - \frac{80}{T} \quad \text{Eq.36}$$

DGEBA $\bar{n} = 0.03$ (46 wt%), TGpAP (15 wt%) - MCDEA (39 wt%)/ PES :

$$\frac{\chi}{V_r} 10^3 = 0.5400 - \frac{80}{T} \quad \text{Eq.37}$$

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

$$\frac{\chi}{V_r} 10^3 = 0.5375 - \frac{80}{T} \quad \text{Eq.38}$$

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

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

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

This relationship (Eq.39) allows the prediction of the cloud point temperature of any TGpAP/DGEBA/MCDEA/PES blend composition.

CONCLUSION

In this work, the initial miscibility of epoxy thermoset/thermoplastic blends were studied. Phase separation behavior has been shown to depend upon thermoplastic type.

For thermoset precursor /PEI blends, an UCST behavior was observed whereas for thermoset/PES blends, a LCST behavior was observed. Introducing a given concentration of TGpAP in DGEBA/TP blends leads to an increase of the miscibility window in both: PEI and PES blends. In contrast, MCDEA addition increases the miscibility window in the case of PEI blends whereas it decreases the miscibility window in PES blends.

Modeling of cloud point curves of these blends was performed using the FH equation and following the Kamide procedure. The interaction parameter is used as a fitting parameter

for experimental data, from which, phenomenological equations was derived. These equations allowed the prediction of the cloud point temperature as a function of TGpAP and MCDEA content as well as taking into account the DGEBA molecular weight.

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CAPTIONS AND FIGURES

Table I: Characteristics of the blend components.

Table II: Mass fraction of the n-mer ($\omega(n)$) versus polymerization degree (n) for different DGEBA resins.

Table III : Comparison between modeling values and experimental ones

Figure 1: Schematic view of phase diagram. LCST behavior (1); UCST behavior (2); vitrification curve (3).

Figure 2: discontinuous mass distribution of a blend 50 wt % of DGEBA $\bar{n} = 0.03$ / 50 wt % of DGEBA $\bar{n} = 2.32$ and continuous mass distribution of PEI. m_n represents the n-mer mass.

Figure 3: Experimental cloud point curves of non-reactive blends PEI/DGEBA with different molar mass. (■) $\bar{n} = 0.03$; (♦) $\bar{n} = 0.15$; (●) $\bar{n} = 0.49$; (◆) 50 wt % of DGEBA $\bar{n} = 0.03$ / 50 wt % of DGEBA $\bar{n} = 2.32$ blend; (—) modeling of the experimental CPC and; (----) predicted cloud point curve for a 50 wt % of DGEBA $\bar{n} = 0.03$ / 50 wt % of DGEBA $\bar{n} = 2.32$ blend.

Figure 4: Evolution of χ/V_r as a function of $1/T_{cp}$ for non-reactive blends PEI - DGEBA with different polymerization degree. (■) $\bar{n} = 0.03$; (♦) $\bar{n} = 0.15$; (●) $\bar{n} = 0.49$.

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

Figure 6: Experimental cloud point curves of non reactive TGpAP - DGEBA $\bar{n}=0.03$ /PEI blends with different amount of TGpAP. (○) 0wt% TGpAP; (■) 10wt% TGpAP; (♦) 20wt% TGpAP; (●) 25wt% TGpAP; modeling (—) of the experimental CPC.

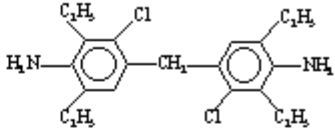
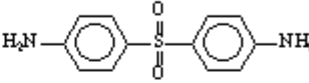
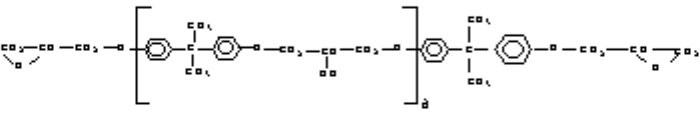
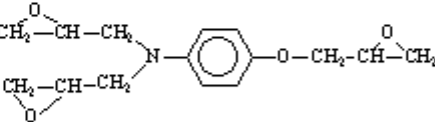
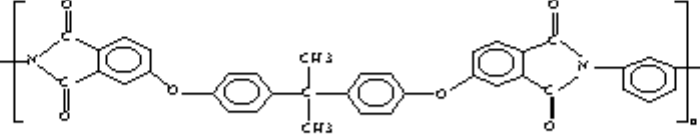
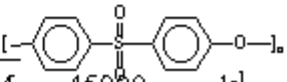
Percentage is defined as epoxy weight percentage by the whole epoxy weight.

Figure 7: Predicted (—, ---) and experimental cloud point curves of blends DGEBA $\bar{n}=0.15$ (90 wt%)- TGpAP (10 wt%)/PEI (Δ); DGEBA $\bar{n}=0.03$ (90 wt%) - TGpAP (10 wt%)/PEI (♦); DGEBA $\bar{n}=0.03$ (75 wt%) - TGpAP (25 wt%)/PEI (○); DGEBA $\bar{n}=0.15$ (75 wt%) - TGpAP (25 wt%)/PEI (●). Percentage is defined as epoxy weight percentage by the whole epoxy weight.

Figure 8: Experimental cloud point curves of non reacted blends of: DGEBA $\bar{n}=0.03$ - DDS/PEI (●); DGEBA $\bar{n}=0.03$ /PEI (\square) and DGEBA $\bar{n}=0.03$ - MCDEA/PEI (♦); DGEBA $\bar{n}=0.03$ (75 wt%) - TGpAP (25 wt%)/PEI (○) and DGEBA $\bar{n}=0.03$ (75 wt%) - TGpAP (25 wt%) - MCDEA/PEI (\curvearrowright); modeling (—) of the experimental CPC. Percentage is defined as epoxy weight percentage by the whole epoxy weight.

Figure 9: Experimental cloud point curves of non reacted blends TGpAP - DGEBA $\bar{n}=0.03$ - MCDEA/PES with different amount 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 (\updownarrow); 100 wt% TGpAP and 44 wt% MCDEA (♦); modeling (—) of the experimental CPC and; predicted cloud point curve (----). Percentage is defined as component weight percentage by the whole blend weight.

Materials

Reactant	Formula	Supplier
4,4' - methylene-bis [3 - chloro-2,6- diethylaniline] MCDEA	 $M = 380 \text{ g mol}^{-1}$ $V_m = 333 \text{ cm}^3/\text{mol}$	Lonza
4,4' - diamino diphenyl sulfone DDS	 $M = 238 \text{ g mol}^{-1}$ $V_m = 179.7 \text{ cm}^3/\text{mol}$	Fluka
Diglycidyl ether of bisphenol A DGEBA \bar{n} from 0.03 to 2.32	 $M_{n=0} = 340 \text{ g mol}^{-1}$ $V_{m(n=0)} = 290.6 \text{ cm}^3/\text{mol}$ $M_{Mn} = 284 \text{ g mol}^{-1}$ $V_{m_{Mn}} = 242.7 \text{ cm}^3/\text{mol}$	Ciba Geigy
Triglycidyl para amino phenol TGpAP	 $M = 300 \text{ g mol}^{-1}$ $V_m = 245.9 \text{ cm}^3/\text{mol}$	Ciba Geigy MY0510
Polyetherimide PEI	 $\bar{M}_n = 26000 \text{ g mol}^{-1}$ $\bar{M}_w = 50000 \text{ g mol}^{-1}$ $V_m = 466 \text{ cm}^3/\text{mol}$	General Electric Ultem 1000
Polyethersulfone PES	 $\bar{M}_n = 21900 \text{ g mol}^{-1}$ $\bar{M}_w = 45990 \text{ g mol}^{-1}$ $V_m = 169 \text{ cm}^3/\text{mol}$	Sumitomo 5003P

V_m is the component molar volume

$V_{m_{Mn}}$ represents the DGEBA repetitive unit molar volume

Table I

\bar{n}	n=0	n=1	n=2	n=4	n=6	n=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

Table II

System	T_{CP} (modelling) °C	T_{CP} (experimental) °C
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

Table III

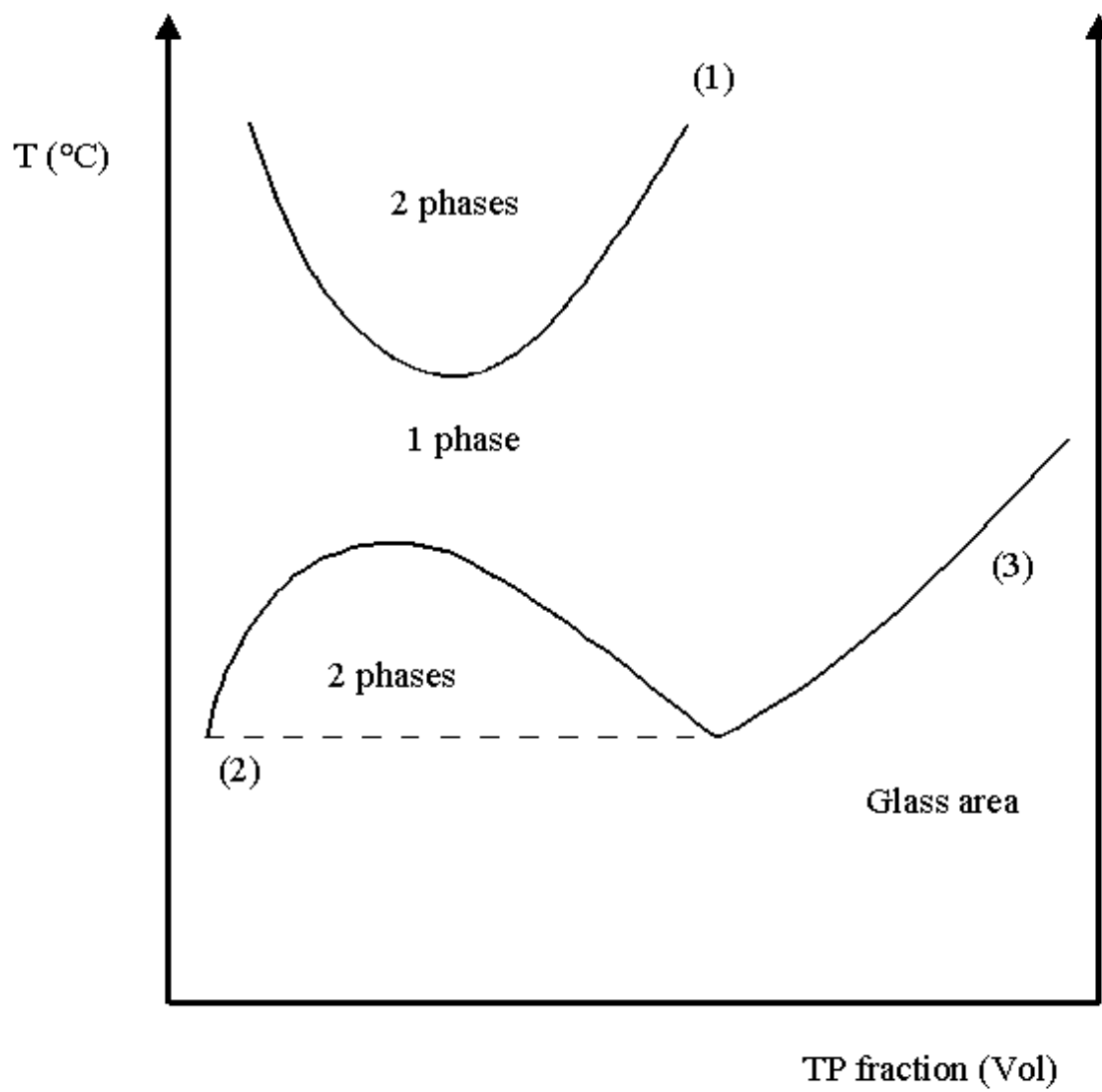


Figure 1

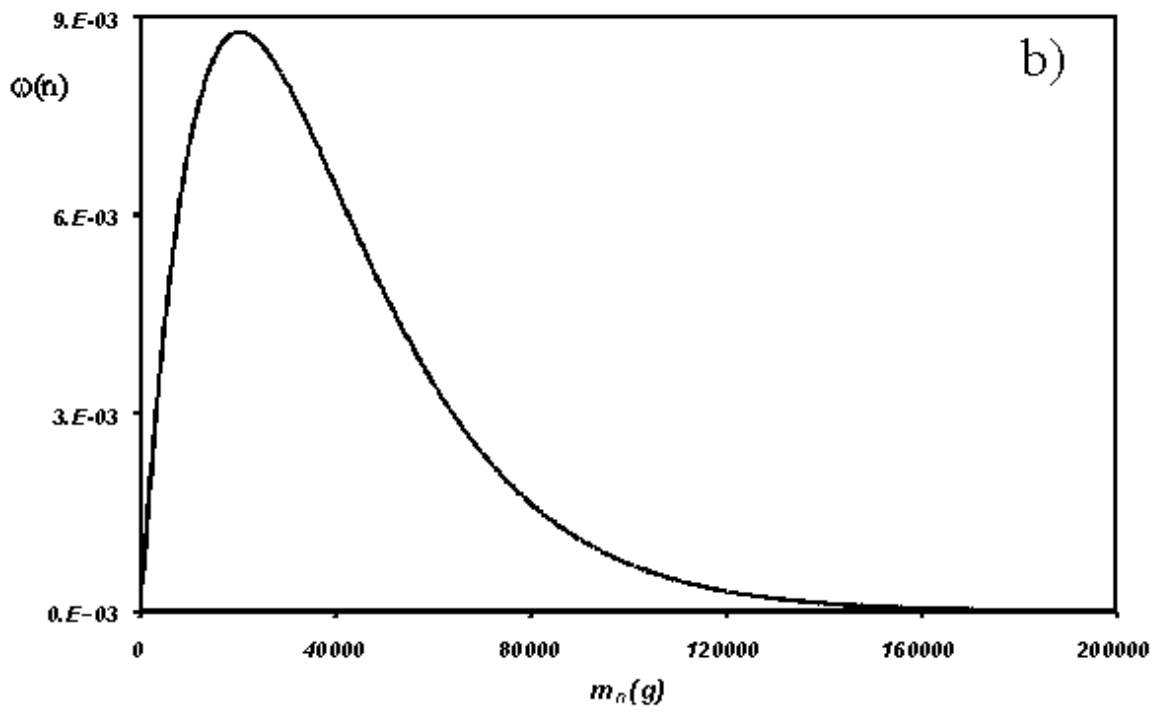
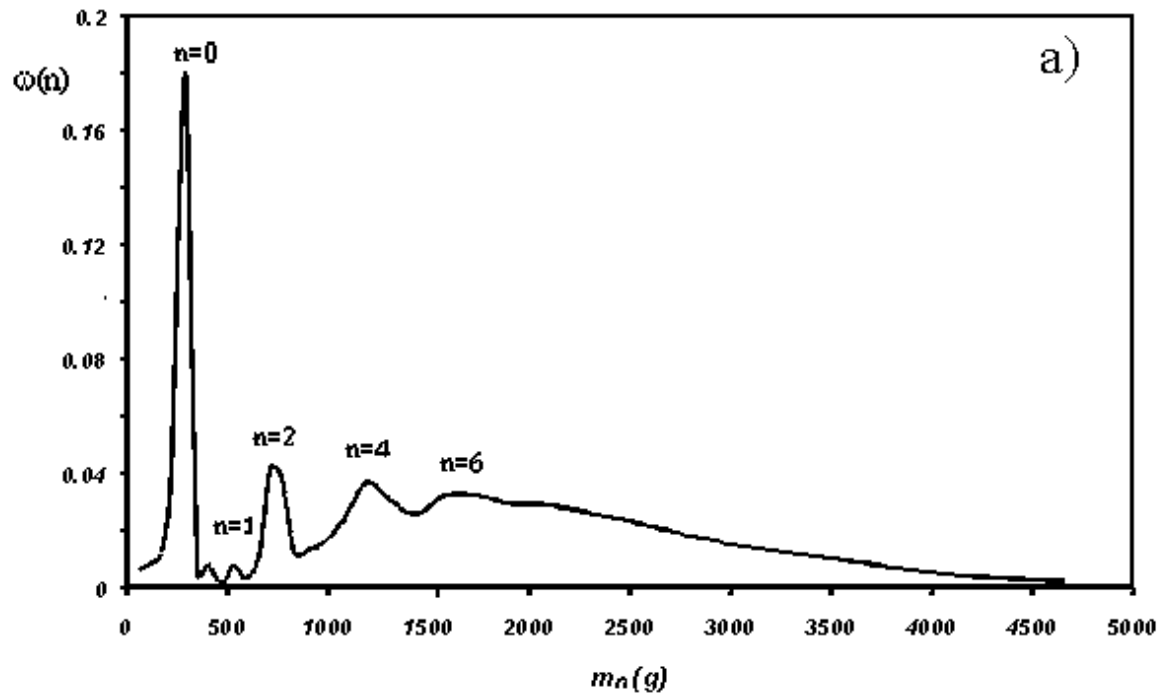


Figure 2

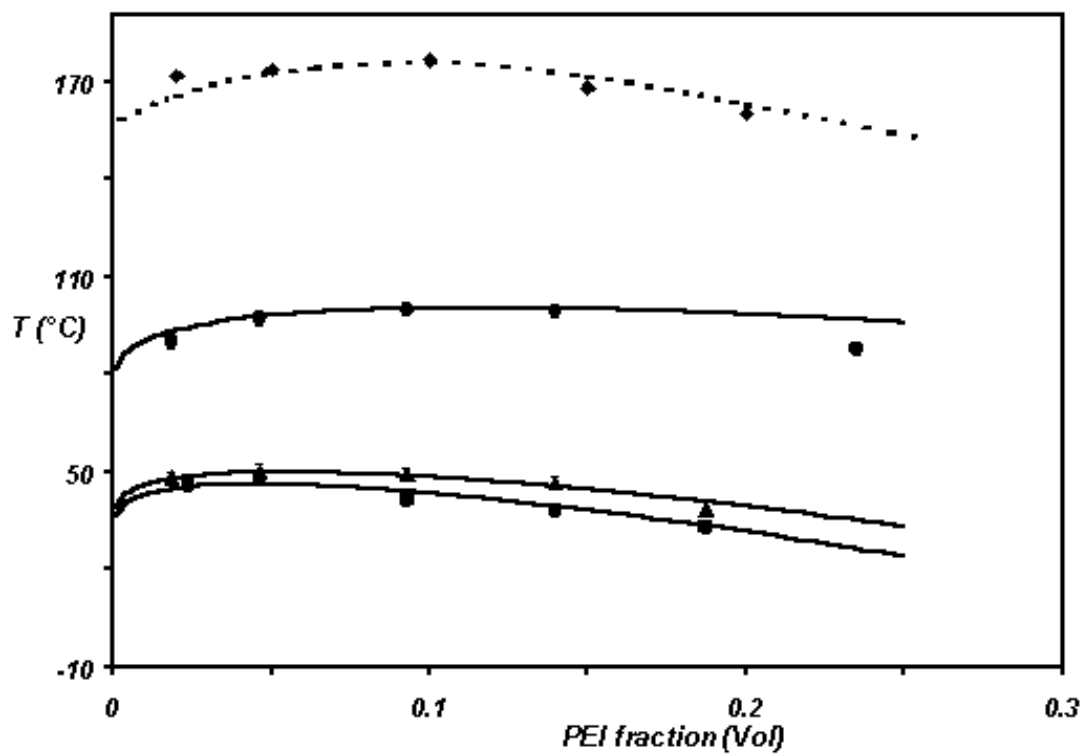


Figure 3

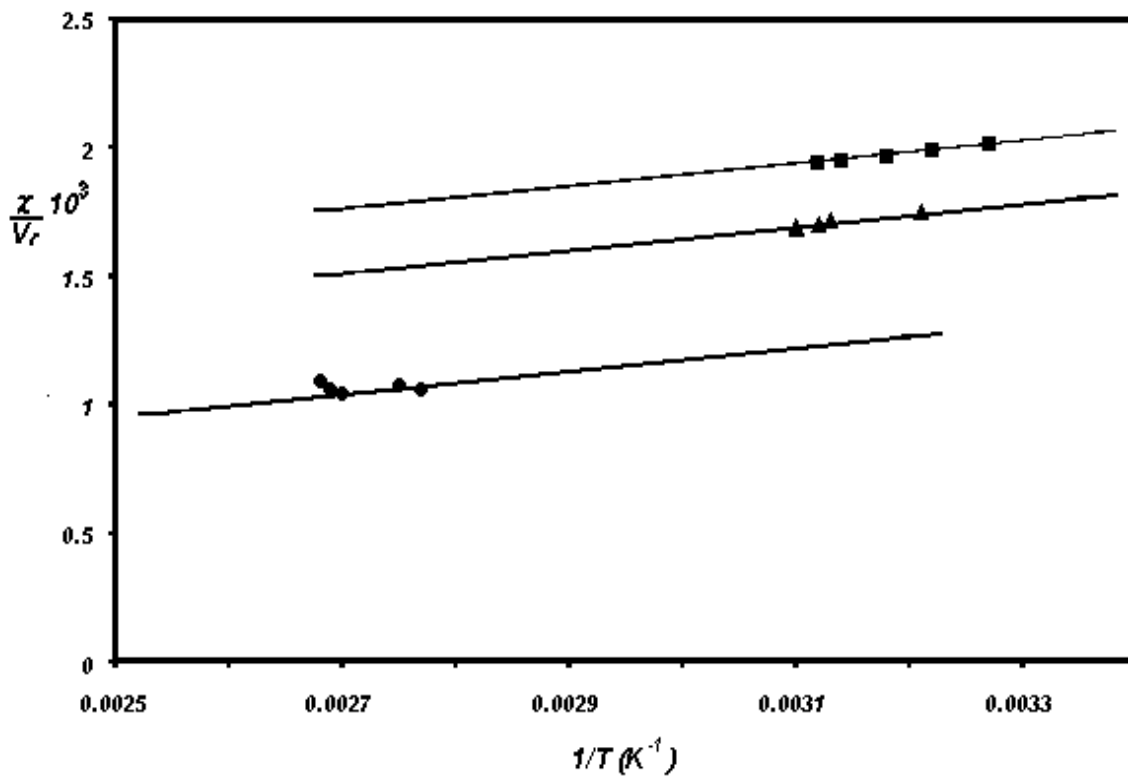


Figure 4

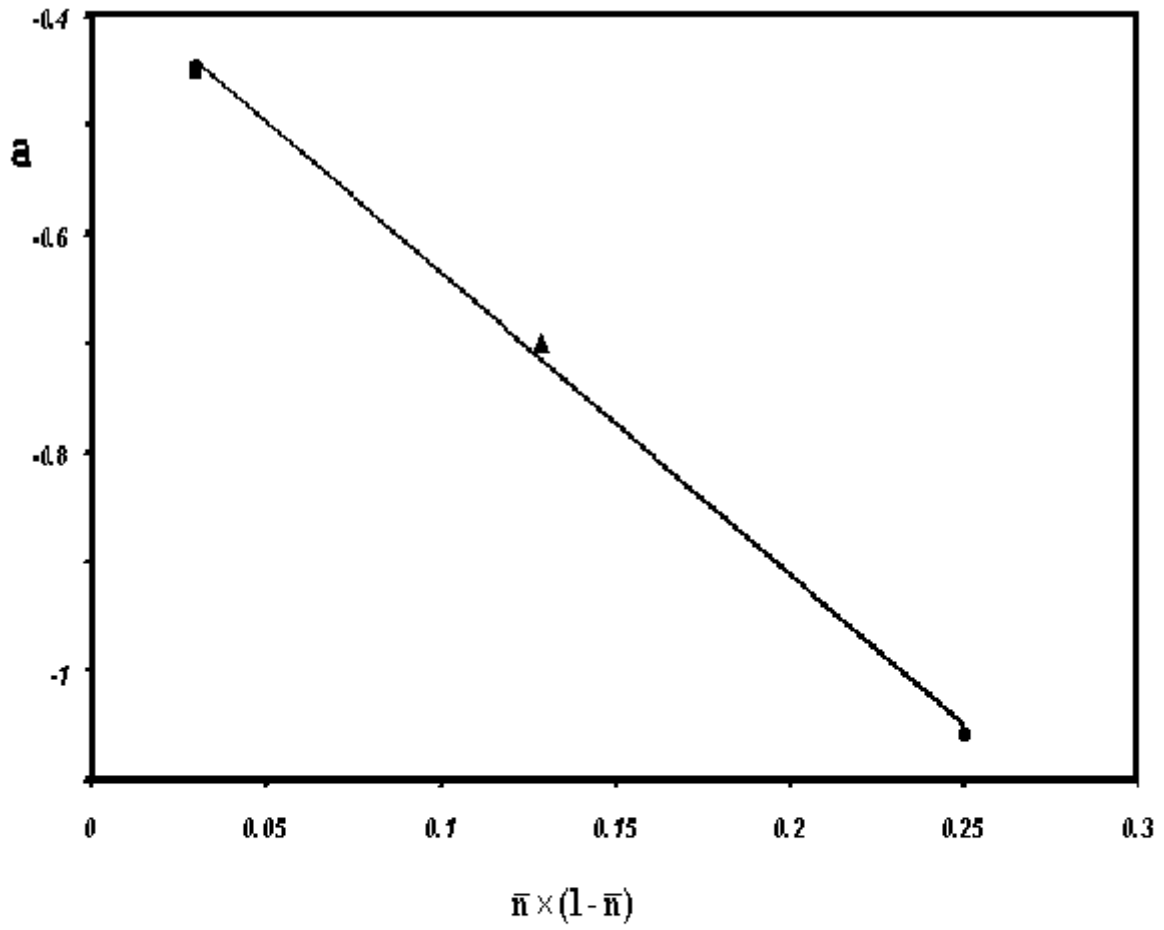


Figure 5

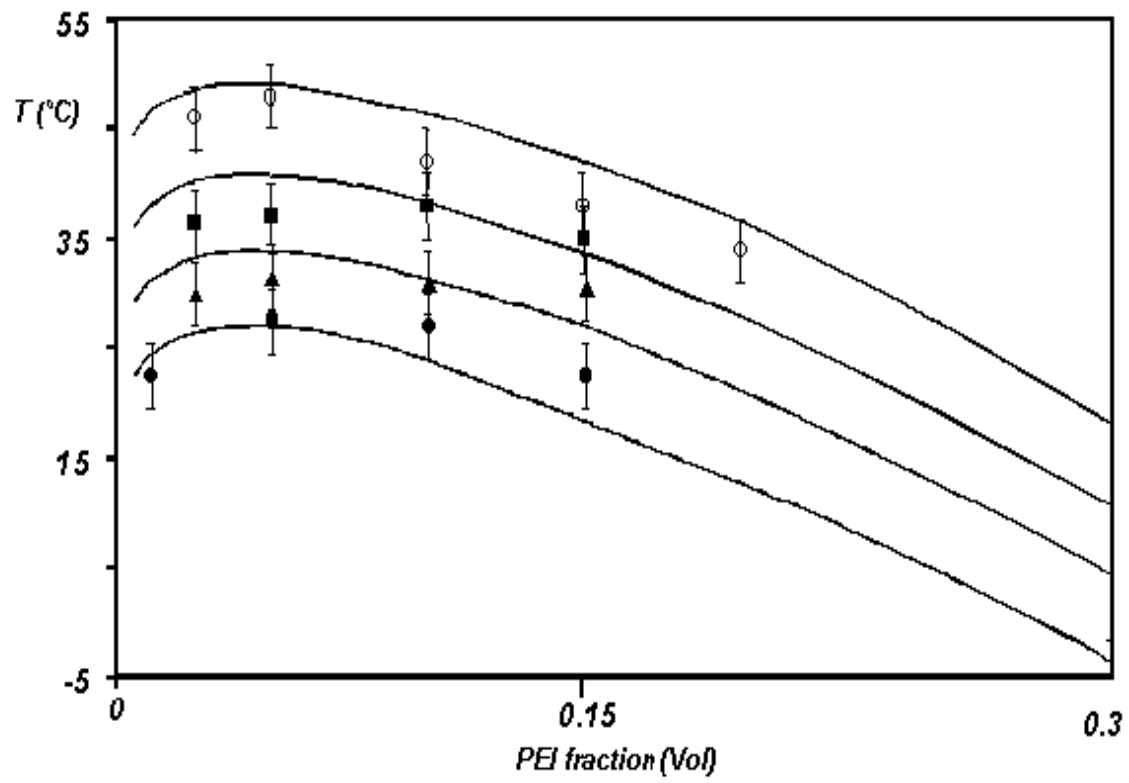


Figure 6

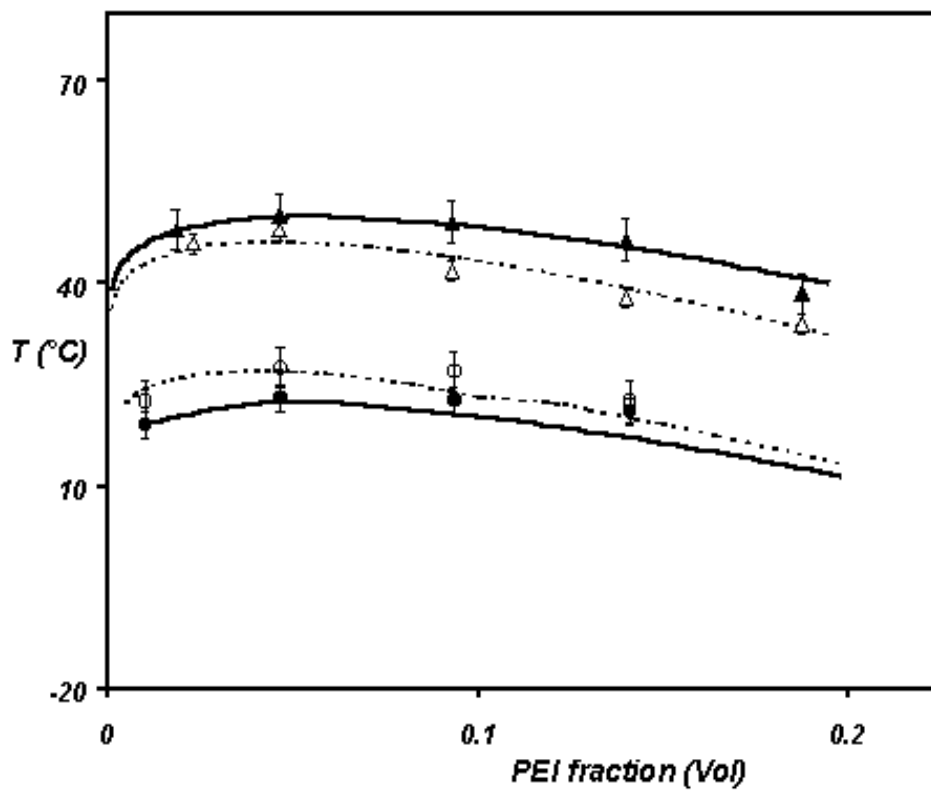


Figure 7

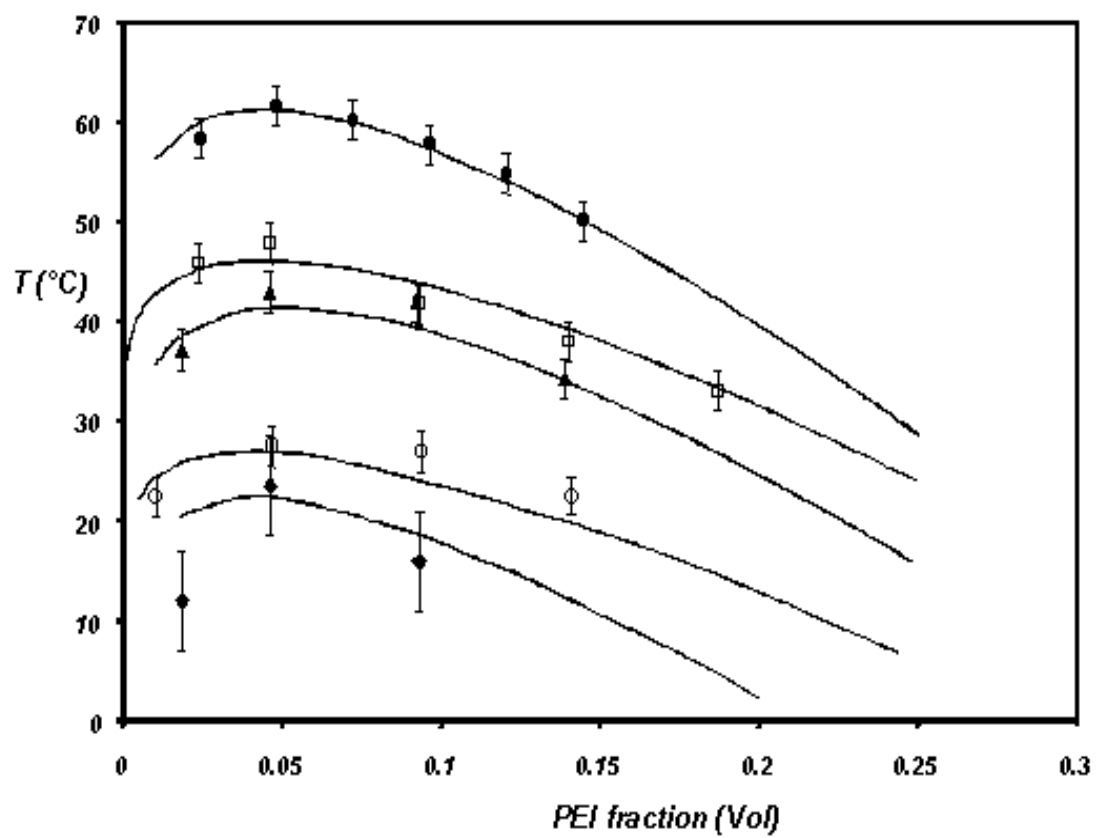


Figure 8

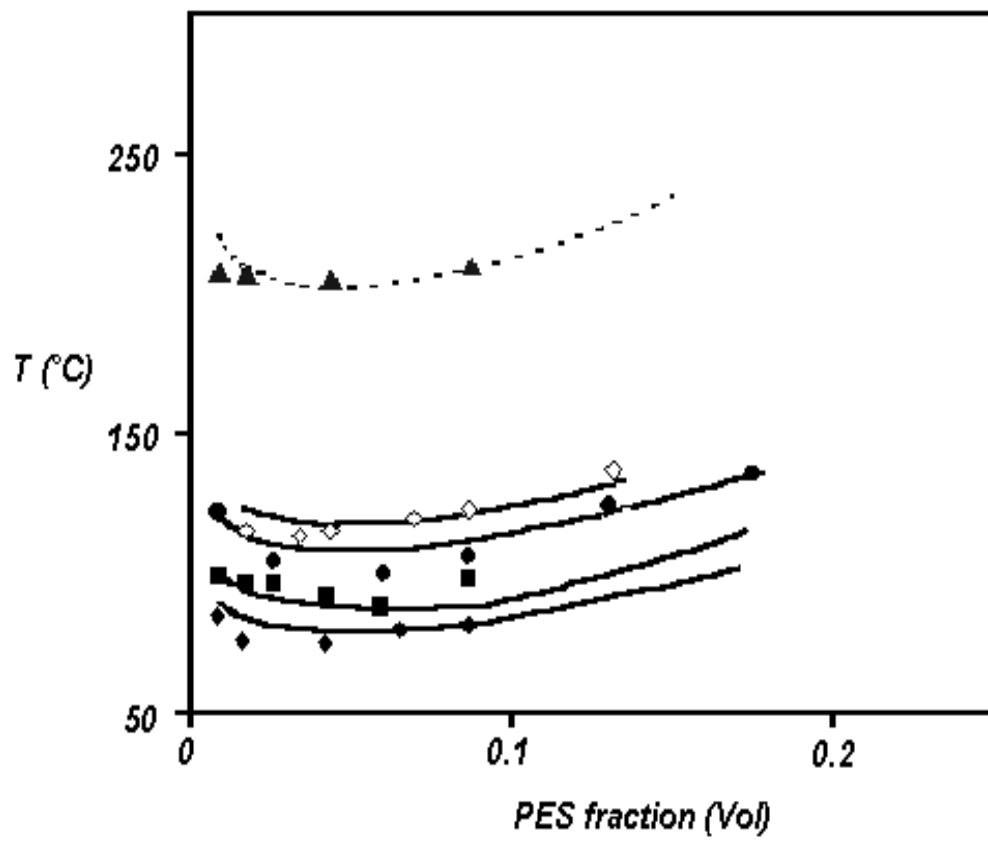


Figure 9