

Thermodynamic Analysis of the Reaction-Induced Phase Separation in Model Systems Based on Blends of a Rubber in Diepoxide / Monoamine Precursors

*Ileana A. Zucchi, María J. Galante, Julio Borrajo, Roberto J.J. Williams**

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

Summary: The reaction-induced phase separation in blends based on a carboxyl-terminated poly(butadiene-*co*-acrylonitrile) rubber (CTBN), dissolved in diglycidyl ether of bisphenol A (DGEBA) – benzylamine (BA) monomers, was studied. The polymerization kinetics was followed by size exclusion chromatography, for both the neat DGEBA-BA system and for blends containing 10 wt % CTBN. No effect of CTBN addition on the polymerization rate was observed within experimental error. The kinetics could be fitted with a model based on the presence of non-catalytic and OH-catalyzed reactions and assuming equal reactivity of primary and secondary amine hydrogens. Cloud-point conversions were determined at 60, 70 and 80 °C. The Flory-Huggins model provided a reasonable fitting of experimental data using an interaction parameter depending exclusively on temperature, and taking polydispersities of both linear polymers into account. Linear epoxy/amine systems may be used to test the reliability of thermodynamic theories in more complex situations (e.g., modifiers with a broad distribution of molar masses or mixtures of several modifiers).

Keywords: cloud point conversion, kinetics, phase separation

Introduction

Morphologies generated by reaction-induced phase separation in initially homogeneous blends of a modifier in thermoset precursors, are the resultant of both thermodynamic and kinetic factors.^[1,2] A correct qualitative description of the phase separation process was obtained with the use of the Flory-Huggins thermodynamic model, assuming a blend of two monodisperse pseudocomponents, and using an interaction parameter depending exclusively on temperature.^[3-5] Further refinements of the model were to consider the molar mass distribution of the thermosetting polymer as a function of conversion,^[6-9] and the fact that the interaction parameter could vary with conversion due to the change in the chemical structure of the thermosetting polymer along reaction.^[10,11] A quantitative fitting of experimental results required to take into account the polydispersities of both components and the fact that the

interaction parameter had to be described as a function of both conversion and temperature.^[12-14] At conversions close to the gel point, the mathematical solution becomes increasingly difficult due to the large number of terms necessary to describe the distribution of the thermosetting polymer. After gelation it is necessary to take into account the distribution of finite species present in the sol, and to include the elastic contribution to the free energy.^[15,16] Therefore, the modeling of formulations including modifiers that become phase separated at high conversions is relatively complex.

In order to avoid the problems introduced by gelation, the reaction-induced phase separation in the course of a linear polymerization may be conveniently analyzed. These model systems can be used to test the usual assumptions of thermodynamic theories employed to describe the reaction-induced phase separation process. A blend of a carboxyl-terminated poly(butadiene-*co*-acrylonitrile) (CTBN) rubber in a stoichiometric mixture of diglycidyl ether of bisphenol A (DGEBA) / benzylamine (BA) monomers, was selected for this study. The DGEBA/BA polymerization follows an ideal path when using stoichiometric proportions of both monomers or when employing a BA excess.^[17] With a DGEBA excess, a polyetherification of epoxy groups was observed after completion of the epoxy/amine reaction.^[17] The reliability of the Flory-Huggins model, with an interaction parameter depending exclusively on temperature, to fit cloud-point conversions in CTBN-stoichiometric DGEBA/BA blends, will be the focus of the present analysis.

Experimental

Materials

The chemical structures of the diepoxide, monoamine and rubber are shown in Figure 1. The epoxy monomer (Der 332, Dow), was based on diglycidylether of bisphenol A (DGEBA, mass per mole of epoxy groups = 174.3 g/mol, mass density = 1.17 g/cm³). Its initial content of secondary hydroxyls was equal to 0.015 per mole of epoxy groups. Benzylamine (BA, Riedel-De Haën, mass density = 0.981 g/cm³), was used in stoichiometric proportion with respect to DGEBA.

The selected rubber was a carboxyl-terminated poly(butadiene-*co*-acrylonitrile) copolymer (CTBN), containing 26 wt % acrylonitrile (Hycar 1300x13, BF Goodrich, mass density = 0.960 g/cm³). Its number-average molar mass was $M_n = 3200$ g/mol and the polydispersity index was $M_w/M_n = 2.13$.^[18]

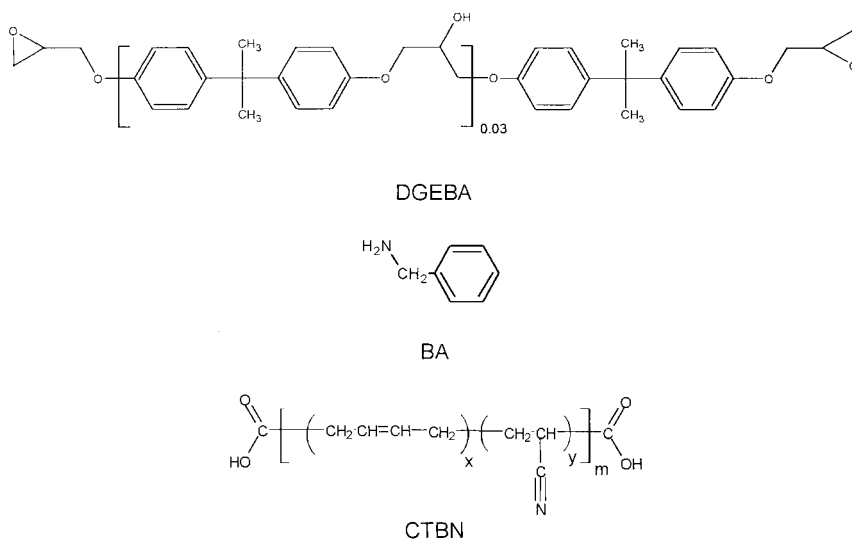


Fig. 1. Chemical structures of the diepoxide (DGEBA), monoamine (BA) and rubber (CTBN).

Blends containing 5, 10 and 15 wt % CTBN in DGEBA/BA, were prepared by first dissolving the corresponding CTBN amount in DGEBA at about 80 °C, cooling to room temperature and adding the stoichiometric amount of BA. Blends were homogeneous at room temperature.

Techniques

Transmission optical microscopy (TOM) was employed to determine cloud-point times during polymerization at constant temperature. A Leica DMLB microscope provided with a video camera (LEICA DC 100) and a hot stage (Linkam THMS 600), was used for these purposes. Samples were placed between two glasses using a 0.5 mm stainless-steel spacer. The small average size of the generated dispersed domains, made it difficult to precise the cloud-point time by focusing on one plane of the sample through the microscope. The value could, however, be obtained by visual observation of the sample placed in the hot stage (it became opalescent at the cloud-point time).

Differential scanning calorimetry (DSC, Perkin-Elmer Pyris 1), was used to determine the total reaction heat of the neat DGEBA/BA system and the blends with CTBN. Runs were carried out at 10 °C/min under a nitrogen atmosphere. Glass transition temperatures of materials cured to complete conversion were determined during a subsequent heating scan at 10 °C/min. They were defined at the onset value of the change in the specific heat.

The polymerization kinetics was determined following the height of the DGEBA peak in size exclusion chromatograms, as a function of reaction time. A set of glass tubes containing known masses of the reacting mixture, in the range of 8–25 mg, were placed in a thermostat at the desired temperature. Tubes were removed at pre-determined times, their contents dissolved in 5 ml tetrahydrofuran (THF), and 25 μL of the resulting solution injected in the size exclusion chromatograph (SEC, Waters 510 with HR 0.5, 1 and 3 ultrastyrigel columns, UV detector at 254 nm, and a THF flow rate of 1 ml/min). The height of the peak corresponding to the DGEBA monomer was measured and expressed per unit mass of the initial mixture. Assuming that both epoxy groups have equal reactivity and there are no substitution effects, the fraction of unreacted DGEBA at a particular epoxy conversion, p , is given by the simultaneous probability that both epoxy groups remain unreacted.^[19]

$$c/c_0 = h/h_0 = (1 - p)^2 \quad (1)$$

where h/h_0 is the ratio of the actual height of the peak with respect to the initial one (both expressed per unit mass of sample). The conversion is then given by:

$$p = 1 - (h/h_0)^{1/2} \quad (2)$$

CTBN-DGEBA/BA blends were also polymerized at constant temperatures in aluminum molds. The resulting plaques, of about 5 mm thickness, were fractured after immersion in liquid air. Fracture surfaces were coated with a fine gold layer and observed by scanning electron microscopy (SEM, Jeol JSM 35CF).

Results and Discussion

Polymerization Kinetics

The effect of the CTBN addition on the polymerization kinetics was first studied. Figure 2a shows DSC thermograms for the neat epoxy and for a blend containing 10 wt % CTBN. The reaction heat was 96.3 kJ/mol for the neat epoxy system and 100.7 kJ/mol for the CTBN-modified epoxy. These values are within the range of reported reaction heats for epoxy-amine formulations. The peak temperature is the same for both systems, meaning that no significant effect of CTBN addition on reaction rate may be expected (the dilution effect of a 10 wt % CTBN addition is not relevant).

Glass transition temperatures obtained in the course of second scans were 54 °C for the neat epoxy/amine system and 46 °C for the CTBN-modified epoxy (Figure 2b). The decrease in the glass transition temperature is ascribed to the CTBN fraction that remained dissolved in the epoxy/amine matrix at the end of the polymerization.

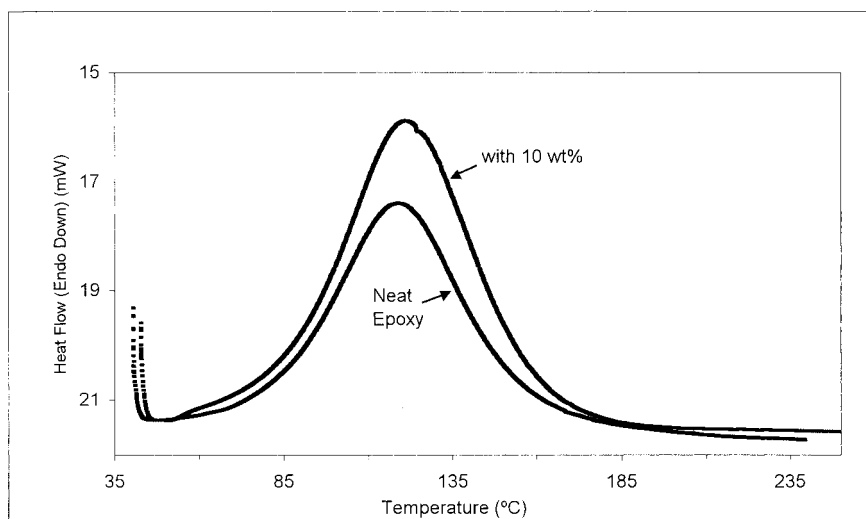


Fig. 2a. DSC scans for the neat epoxy and for the blend containing 10 wt % CTBN.

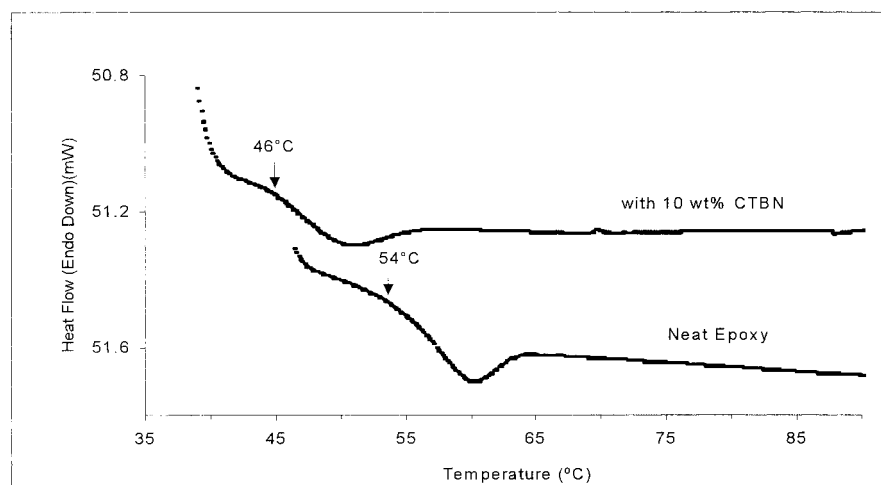


Fig. 2b. Glass transition temperatures of the neat epoxy reacted to complete conversion and of the epoxy-rich phase of the blend with 10 wt % CTBN, after polymerization.

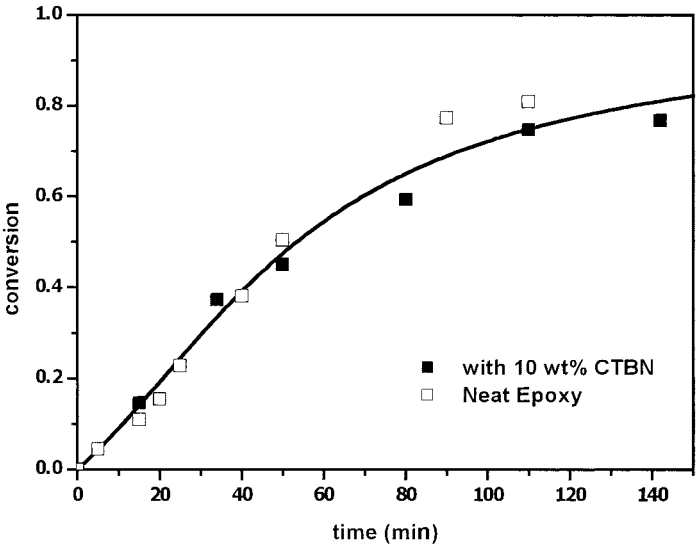


Fig. 3a. Conversion vs. time curves at 60 °C.

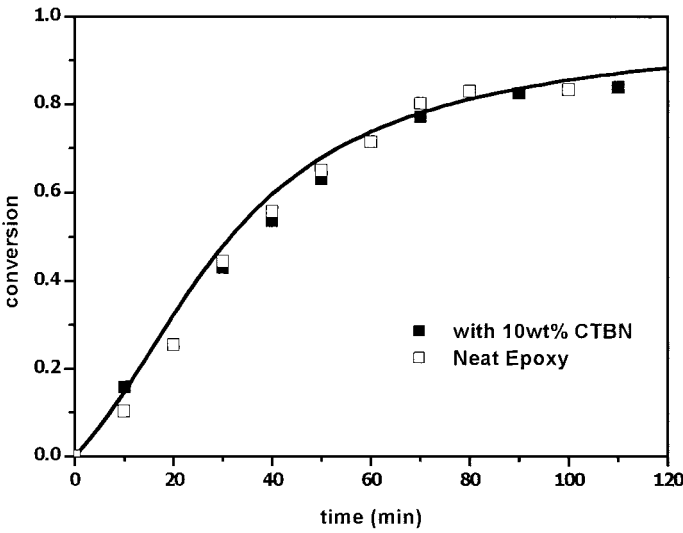


Fig. 3b. Conversion vs. time curves at 70 °C.

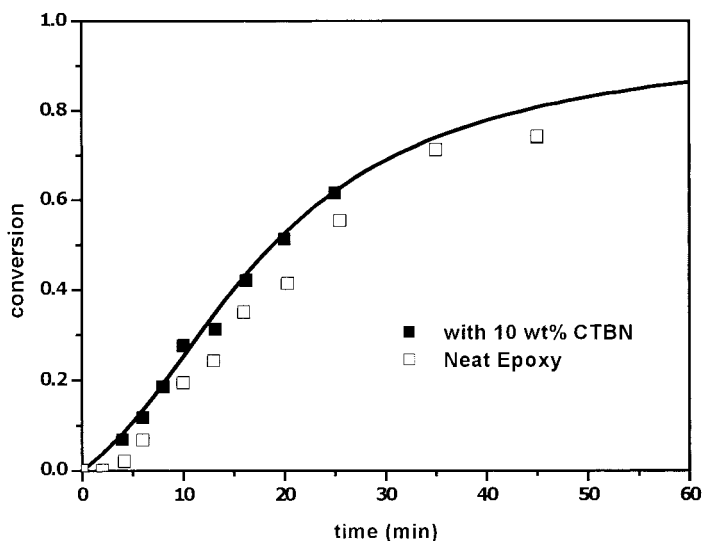


Fig. 3c. Conversion vs. time curves at 80 °C.

Conversion vs. time curves, arising from the determination of the residual DGEBA monomer by SEC, were obtained at 60, 70 and 80 °C, for both the neat epoxy/amine system and for a blend containing 10 wt % CTBN. Results are shown in Figures 3a-c. Within the experimental error of this determination there was no influence of the CTBN addition on the polymerization kinetics.

The following rate equation was used to fit the experimental results:

$$\frac{dx}{dt} = [k_A + k_B (p + 0.015)](1 - p)^2 \quad (3)$$

This rate equation results from a mechanistic model assuming the presence of a non-catalytic path (rate k_A), and a path catalyzed by the OH groups initially present (0.015 per mole of epoxy groups), and those generated by reaction (rate k_B). Equal reactivities of primary and secondary amine hydrogens, was also assumed.

An excellent fitting of the proposed model with experimental results, shown by the curves plotted in Figures 3a-c, resulted from the following values of the specific rate constants:

$$k_A \text{ (min}^{-1}\text{)} = 7.733 \cdot 10^2 \exp(-3848.4/T) \quad (4)$$

$$k_B \text{ (min}^{-1}\text{)} = 3.465 \cdot 10^8 \exp(-7607.1/T) \quad (5)$$

The activation energy of the catalytic reaction ($E_B = 63.2$ kJ/mol), lies within the range of values reported in the literature for this type of mechanistic model.^[19-23]

Morphologies Generated

The initial CTBN-DGEBA/BA blends were homogeneous but phase separated in the course of polymerization. Figure 4 shows SEM micrographs of blends with 5, 10 and 15 wt % CTBN, polymerized at 70 °C to a high conversion ($p > 0.9$).

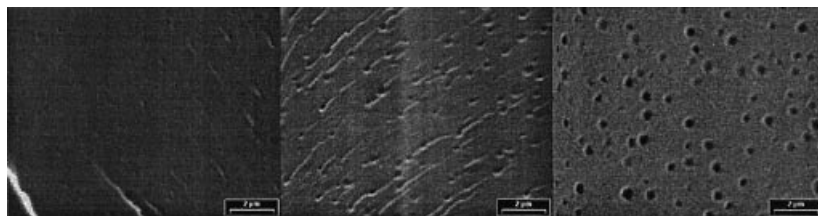


Fig. 4. SEM micrographs of blends containing, from left to right, 5, 10, and 15 wt % CTBN.

The blend modified with 5 wt % CTBN exhibits a small concentration of particles with sizes in the range of 100 – 200 nm. These blends were slightly opalescent and it was therefore not possible, to obtain cloud-point times with enough accuracy. Both the concentration and the average size of dispersed domains increased with the CTBN concentration, as expected.

Cloud-Point Conversions

Cloud-point times could be obtained for blends containing 10 and 15 wt % CTBN. These values were converted to cloud-point conversions using the kinetic model (it was assumed that the kinetics was the same for both concentrations). Table 1 shows the corresponding results.

Table 1. Cloud-point conversions for CTBN-DGEBA/BA blends.

wt % CTBN	Cloud-point conversion		
	60 °C	70 °C	80 °C
10	0.56	0.61	0.65
15	0.54	0.60	0.64

The selected CTBN rubber was very soluble in the epoxy/amine formulation and became phase separated at relatively high conversions. The cloud-point conversion increased with temperature, consistently with an upper-critical-solution-temperature (UCST) behavior. Cloud-point conversions decreased slightly by increasing the initial CTBN amount from 10 to 15 wt %.

Thermodynamic Analysis

The possibility of using the Flory-Huggins (FH) model to fit these experimental data will be now assessed. As the range of cloud-point conversions is relatively narrow, the interaction parameter, χ , will be considered as only dependent on temperature:

$$\chi = a + b/T \quad (6)$$

The search will be focused on the existence of such a function and on the ability of the FH model to predict a slight dependence of the cloud-point conversion with composition in the range of 10–15 wt % CTBN.

In order to state the FH equation it is necessary to define the volume of the unit cell. This will be taken as the average molar volume of the CTBN “monomer”. Taking into account the molar masses of butadiene (54 g/mol) and acrylonitrile (53 g/mol), and their mass fractions in the copolymer, the molar mass of the “monomer” is 53.74 g/mol, and the reference volume is $V_r = 53.74/0.96 = 55.98 \text{ cm}^3/\text{mol}$.

The molar-mass distribution of CTBN is described by the Schulz-Zimm (SZ) equation:^[24]

$$w_x = [g^{h+1}/\Gamma(h+1)] x^h \exp(-gx) \quad (7)$$

where w_x is the mass fraction of the x -mer, $h = [x_w/x_n - 1]^{-1} = 0.885$, $g = h/x_n = 0.01486$, and $\Gamma(h+1) = 0.9567$. The SZ equation for CTBN is finally written as:

$$w_x = 3.746 \cdot 10^{-4} x^{0.885} \exp(-0.01486 x) \quad (8)$$

The volume fraction of a generic x -mer is given by:

$$\phi_x = w_x \phi_{20} \quad (9)$$

where ϕ_{20} is the initial volume fraction of CTBN in the blend.

The molar-mass distribution of the epoxy/amine linear polymer may be calculated from the Stockmayer equation applied for a stoichiometric $A_2 + B_2$ polymerization, up to a conversion p of functional groups.^[24] The concentration of a generic species, $E_{m,n}$, containing m BA units and n DGEBA units, is given by:

$$E_{m,n} = 2 (BA)_0 (1-p)^2 p^{m+n-1} (m-n) \quad (10)$$

$$E_{m,n} = (BA)_0 (1-p)^2 p^{m+n-1} \quad (m = n+1 \text{ or } n = m+1) \quad (11)$$

where $(BA)_0 = (DGEBA)_0$, is the initial concentration of one of the monomers. The corresponding volume fractions of $E_{m,n}$ species in the reaction mixture, is obtained from:

$$\phi_{m,n} = E_{m,n} (m V_{BA} + n V_{DGEBA}) \phi_{10} / [(BA)_0 V_{BA} + (DGEBA)_0 V_{DGEBA}] \quad (12)$$

where $\phi_{10} = 1 - \phi_{20}$, is the initial volume fraction of the epoxy/amine polymer in the blend, and $V_{BA} = 109.2 \text{ cm}^3/\text{mol}$, $V_{DGEBA} = 297.9 \text{ cm}^3/\text{mol}$, are the molar volumes of both monomers.

A pseudocomponent with a generic degree of polymerization $y = m + n$, may be defined. Its concentration and volume fraction are given by:

$$E_y = 2 (BA)_0 (1-p)^2 p^{y-1} \quad (13)$$

$$\phi_y = y(1-p)^2 p^{y-1} \phi_{10} \quad (14)$$

The free energy of mixing per mol of unit cells is given by the FH equation:

$$\Delta G/RT = \sum (\phi_x/x) \ln \phi_x + (1/Z) \sum (\phi_y/y) \ln \phi_y + \chi \phi_1 \phi_2 \quad (15)$$

where $Z = (1/2)(V_{BA} + V_{DGEBA}) / V_r$.

Cloud-point curves were calculated from equation (15) following the procedure developed by Kamide et al.^[25] A detail of these calculations for the particular case of a monodisperse modifier is reported elsewhere.^[6] Continuous distributions were discretized using 40 species for CTBN and 30 species for the DGEBA/BA linear polymer. It was verified that average values (number, mass and zeta), were the same for the discrete and continuous distributions. The numerical solution was obtained using Mathcad 8.

Figure 5 shows the predicted cloud-point conversions plotted as a function of the initial rubber volume fraction, for the three reaction temperatures. The FH model provides a reasonable fitting of the experimental cloud-point conversions, with an interaction parameter depending exclusively on temperature:

$$\chi = -0.155 + 75.273/T(K) \quad (16)$$

The small decrease of the cloud-point conversion with composition in the range 10 – 15 wt % CTBN, is indeed predicted by the model.

Every couple of points located on both branches of a cloud-point curve, at a particular conversion, correspond to a particular blend with an associated cloud-point temperature vs. composition curve. Therefore, there is a different critical composition for any couple of points located at the same conversion. However, the minimum of each one of the curves represented in Figure 5, corresponds to a critical composition that pertains to the curve. These critical volume fractions are 0.241 at 60 °C, 0.251 at 70 °C and 0.263 at 80 °C. As the initial CTBN

volume fractions (0.115 and 0.171), are located in the off-critical region at the left of the cloud-point, the generated morphologies consisted of a dispersion of rubber particles in an epoxy/amine matrix, as expected.^[2]

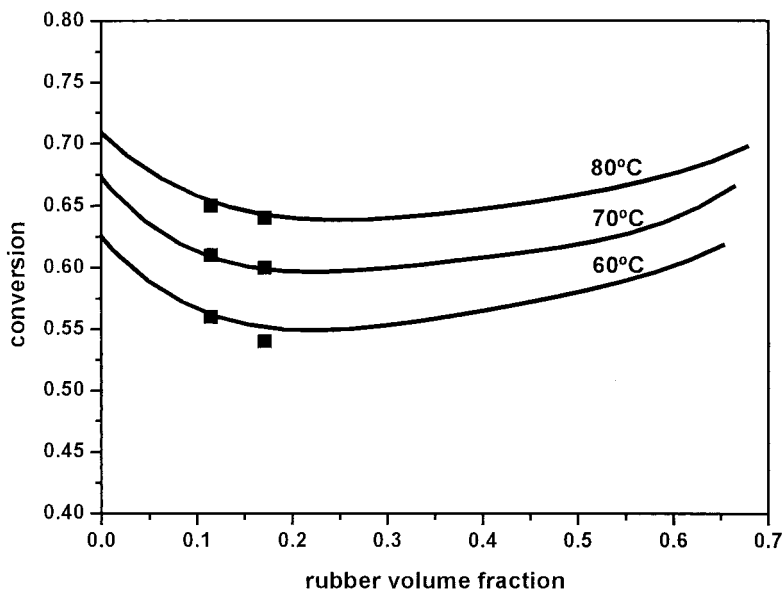


Fig. 5. Cloud-point conversion vs. the initial rubber volume fraction, for three reaction temperatures.

The location of the critical point can be calculated from expressions derived by Koningsveld and Kleintjens.^[26]

$$1/(1 - \phi_{2c}) = 1 + (Z^{1/2} y_w x_z^{1/2}) / (x_w y_z^{1/2}) \quad (17)$$

$$\chi_c = 0.5 [1/x_z^{1/2} + 1/(Z y_z^{1/2})] / [x_z^{1/2}/x_w + y_z^{1/2}/(Z^{1/2} y_w)] \quad (18)$$

For the initial formulation ($p = 0$), $y_w = y_z = 1$. The Schulz-Zimm distribution leads to the following average values for CTBN: $x_w = 126.83$ and $x_z = 194.12$. As $Z = 3.636$, equations (17) and (18) lead to the following critical values: $\phi_{2c} = 0.173$ and $\chi_c = 0.189$. From equation (16), $T_c = 218.8$ K. This means that the model predicts that no phase separation will occur in the initial blend above 218.8 K. This agrees with the fact that no phase separation was observed by keeping the initial formulations during prolonged times at 253 K.

Conclusions

The use of a model system consisting of a blend of a rubber in diepoxide /monoamine monomers (leading to a linear epoxy/amine polymer), enabled to test the reliability of the FH model to fit experimental data without the mathematical complexities introduced by gelation. This is particularly useful for modifiers (e.g. a rubber) that are very soluble in the mixture of monomers and, consequently, phase separate at high conversions as was the case of the blend selected for this study. Model systems may be used to test thermodynamic models in more complex situations, such as modifiers exhibiting a very broad distribution of molar-masses, or formulations including two different modifiers.

Acknowledgements

The financial support of CONICET, ANPCyT and University of Mar del Plata, is gratefully acknowledged.

- [1] R. J. J. Williams, B. A. Rozenberg, J. P. Pascault, *Adv. Polym. Sci.* **1997**, 128, 95.
- [2] J. P. Pascault, R. J. J. Williams, in: "*Polymer Blends, Vol. 1: Formulation*", D. R. Paul, C. B. Bucknall, Eds., J. Wiley & Sons, New York 2000, p.379.
- [3] R. J. J. Williams, J. Borrajo, H. E. Adabbo, A. J. Rojas, in: "*Rubber-Modified Thermoset Resins*", C. K. Riew, J. K. Gillham, Eds., *Adv. Chem. Ser.* 208, American Chemical Society, Washington DC 1984, p.195.
- [4] A. Vazquez., A. J. Rojas, H. E. Adabbo, J. Borrajo, R. J. J. Williams, *Polymer* **1987**, 28, 1156.
- [5] S. M. Moschiar, C. C. Riccardi, R. J. J. Williams, D. Verchère, H. Sautereau, J. P. Pascault, *J. Appl. Polym. Sci.* **1991**, 42, 717.
- [6] C. C. Riccardi, J. Borrajo, R. J. J. Williams, *Polymer* **1994**, 35, 5541.
- [7] N. Clarke, T. C. B. McLeish, S. D. Jenkins, *Macromolecules* **1995**, 28, 4650.
- [8] S. Elliniadis, J. S. Higgins, N. Clarke, T. C. B. McLeish, R. A. Choudhery, S. D. Jenkins, *Polymer* **1997**, 38, 4855.
- [9] C. J. G. Plummer, R. Mezzenga, L. Boogh, J. A. E. Manson, *Polym. Eng. Sci.* **2001**, 41, 43.
- [10] R. Mezzenga, L. Boogh, J. A. E. Manson, *J. Polym. Sci., B: Polym. Phys.* **2000**, 38, 1883.
- [11] R. Mezzenga, L. Boogh, J. A. E. Manson, *J. Polym. Sci., B: Polym. Phys.* **2000**, 38, 1893.
- [12] J. Borrajo, C. C. Riccardi, R. J. J. Williams, Z. Q. Cao, J. P. Pascault, *Polymer* **1995**, 36, 3541.
- [13] C. C. Riccardi, J. Borrajo, R. J. J. Williams, E. Girard-Reydet, H. Sautereau, J. P. Pascault, *J. Polym. Sci., B: Polym. Phys.* **1996**, 34, 349.
- [14] P. A. Oyanguren, C. C. Riccardi, R. J. J. Williams, I. Mondragon, *J. Polym. Sci., B: Polym. Phys.* **1998**, 36, 1349.
- [15] J. Borrajo, C. C. Riccardi, R. J. J. Williams, H. Masood Siddiqi, M. Dumon, J. P. Pascault, *Polymer* **1997**, 39, 845.
- [16] C. C. Riccardi, J. Borrajo, R. J. J. Williams, H. Masood Siddiqi, M. Dumon, J. P. Pascault, *Macromolecules* **1998**, 31, 1124.
- [17] J. Klee, H. H. Hörhold, W. Tänzer, in: "*Crosslinked Epoxies*", B. Sedláček, J. Kahovec, Eds., Walter de Gruyter, Berlin 1987, p. 47.
- [18] D. Verchère, H. Sautereau, J. P. Pascault, S. M. Moschiar, C. C. Riccardi, R. J. J. Williams, *Polymer* **1989**, 30, 107.
- [19] D. Verchère, H. Sautereau, J. P. Pascault, C. C. Riccardi, S. M. Moschiar, R. J. J. Williams, *Macromolecules* **1990**, 23, 725.
- [20] C. C. Riccardi, H. E. Adabbo, R. J. J. Williams, *J. Appl. Polym. Sci.* **1984**, 29, 2481.
- [21] G. Wisanrakkit, J. K. Gillham, *J. Appl. Polym. Sci.* **1990**, 41, 2885.
- [22] N. Galgo, A. Vazquez, R. J. J. Williams, *Polymer* **1994**, 35, 857.

- [23] C. W. Wise, W. D. Cook, A. A. Goodwin, *Polymer* **1997**, 38, 3251.
- [24] L. H. Peebles, "*Molecular Weight Distributions in Polymers*", Wiley-Interscience, New York 1971.
- [25] K. Kamide, S. Matsuda, H. Shirataki, *Eur. Polym. J.* **1990**, 26, 379.
- [26] R. Koningsveld, L. A. Kleintjens, *J. Polym. Sci., Polym. Symp.* **1977**, 61, 221.