Rubber-modified epoxies: *in situ* detection of the phase separation by differential scanning calorimetry

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The phase separation of a rubber in the course of a thermosetting polymerization is associated with heat release. Mixing is endothermic as revealed by the positive value of the interaction parameter while demixing is exothermic. Differential scanning calorimetry may be used to detect heat effects related to phase separation. Experimental results are reported for an unreactive system (castor oil/epoxy resin) and reactive systems (modifier/epoxy resin/diamine) using either castor oil or epoxy-terminated copolymers of acrylonitrile and butadiene as modifiers.

(Keywords: rubber-modified epoxies; phase separation; d.s.c.)

Introduction

A common method to toughen epoxy resins is to dissolve rubbers or other modifiers that become phase-separated in the course of polymerization. The resulting two-phase structure exhibits an increase in the fracture resistance at the expense of lower values of the elastic modulus and yield stress.

Monitoring the phase separation process is important in two respects: (i) for unreactive epoxy-rubber formulations, i.e. devoid of hardeners, cloud-point determinations are employed for the preliminary estimation of the rubber miscibility[1–3] (which depends on the chemical structure, molecular weight distribution and type of chain ends); (ii) for reactive formulations the cloud-point conversion and the corresponding cloud-point viscosity are significant factors determining the morphology generated[4–7]. Light transmission is a common technique employed to detect the phase separation process[1–6]. Radiation scattering, i.e. light scattering[8] and small angle X-ray scattering (SAXS)[2], is also used. The possibility of using differential scanning calorimetry (d.s.c.) to monitor the phase separation process during polymerization has not been reported. This is the aim of this communication.

Thermal effects associated with phase separation

The Gibbs free energy associated with the mixing of component A of molar volume V_A with component B of molar volume V_B, expressed per unit volume of mixture, is given by[9]:

$$\Delta G = RT[(\phi_A/V_A)\ln\phi_A + (\phi_B/V_B)\ln\phi_B] + \Lambda\phi_A\phi_B \quad (1)$$

where R is the gas constant, T is temperature, ϕ_A and ϕ_B are the volume fractions of components A and B, respectively, and Λ is the interaction parameter.

The first term in equation (1) is the combinatorial part (entropic contribution) while the second term represents the residual free energy of mixing (part or all of it may be considered as an enthalpic contribution). The interaction parameter Λ, expressed in units of energy per unit volume, is usually a positive value. This means that mixing occurs due to the prevailing influence of the combinatorial part of the equation over the interaction term. Dissimilar molecules (positive Λ) are thus obliged to mix due to an entropic driving force; their intrinsic repulsion is manifested by an endothermic effect in the mixing process and an opposite exothermic process when demixing (phase separation). These thermal effects may be recorded by d.s.c.

Experimental

The epoxy resin (Araldite MY 790, Ciba Geigy), based on diglycidyl ether of bisphenol A (DGEBA), had a weight per epoxy equivalent of 174.3 g eq^{-1}, as determined by acid titration. Its density (ρ at 25°C) was 1.2 g cm^{-3}. It was dried by heating under vacuum at 80°C prior to use.

The curing agent employed in reactive formulations was a cycloaliphatic diamine based on dimethylamine dicyclohexylmethane. It was used in stoichiometric proportions with the epoxy resin (equivalent weight of diamine = 59.5 g eq^{-1}).

One of the modifiers was castor oil (CO), a natural triglyceride containing 88% ricinoleic acid as determined by hydrolysis followed by gas chromatography of the fatty acids. It has a molecular weight of 928 g mol^{-1} and a ρ value of 0.96 g cm^{-3}. It was dried by heating under vacuum at 80°C before use.

The other modifier was a commercial carboxyl-terminated butadiene–acrylonitrile copolymer (CTBN 8, BF Goodrich). It was end-capped with DGEBA following a standard procedure[5,10], to give an epoxy-terminated copolymer (ETBN).

The following formulations were studied:

A unreactive mixture of DGEBA and CO containing a volumetric fraction of modifier, $\phi_{CO} = 0.349$;

B reactive mixture of DGEBA/diamine and 15 wt% CO;

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C reactive mixture of DGEBA/diamine and 15 wt% ETBN (expressed as the mass fraction of the original CTBN in the formulation).

The differential scanning calorimeter used was a Du Pont 990 thermal analyzer with a 910 DSC cell. Runs were carried out under a nitrogen atmosphere. Isothermal scans were used to obtain the conversion *versus* time at a particular temperature. Cloud points, at constant temperature, were obtained by light transmission[1]. This technique was sensitive to the presence of dispersed phase particles with sizes > ~0.1 μm.

Unreactive formulations

The miscibility of DGEBA/CO formulations has been previously studied by conventional light transmission techniques[3]. By fitting equation (1) to the experimental cloud-point curve, the following expression for Λ (in J cm^{-3}) was obtained:

$$\Lambda = 28.25 - 0.05467T \qquad (2)$$

Figure 1 shows the miscibility curve (binodal) obtained from equation (1) using Λ from equation (2). The molar volumes are $V_A = 966.7$ cm^3 mol^{-1} and $V_B = 290.5$ cm^3 mol^{-1} (A = CO, B = DGEBA). The composition of the critical point is given by[3]:

$$\phi_{AC} = V_B^{1/2}/(V_A^{1/2} + V_B^{1/2}) = 0.354 \qquad (3)$$

When a solution is cooled below the binodal curve it is demixed into an α-phase rich in DGEBA and a β-phase rich in CO. Horizontal tie lines join phases at equilibrium with the relative proportions indicated by segments f^α and f^β (Lever rule).

D.s.c. thermograms obtained by cooling and heating a DGEBA/CO formulation ($\phi_{CO} = 0.349$) are shown in *Figure 2*. The exothermic effect produced by the phase separation process is observed in the cooling scan while the opposite endothermic peak, characteristic of the mixing process, is shown in the heating scan. The cloud-point temperature arising from the cooling run is 44.8°C, i.e. practically the same value as that obtained by light transmission. The cloud-point temperature located in the binodal curve of *Figure 1*, at $\phi_{CO} = 0.349$, is 44.5°C. Hence, d.s.c. constitutes a very simple and accurate technique for determining cloud-point curves.

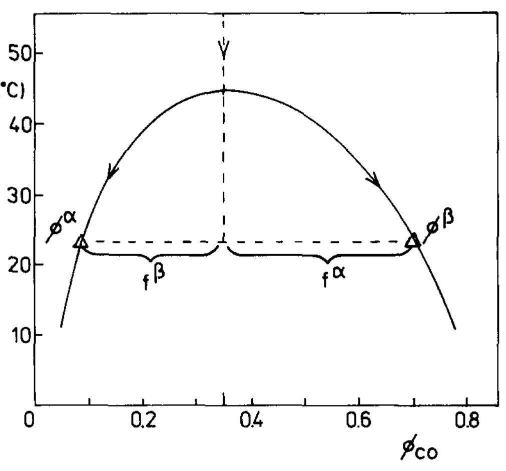

Figure 1 Miscibility curve (binodal) of the DGEBA/CO system. When a solution is cooled below the binodal curve it is demixed into an α-phase rich in DGEBA and a β-phase rich in CO. Horizontal tie lines join phases at equilibrium with the relative proportions indicated by segments f^α and f^β

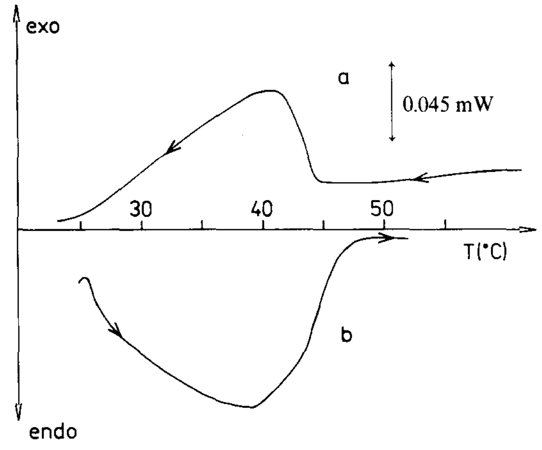

Figure 2 D.s.c. thermograms obtained by cooling (a) and heating (b) a DGEBA/CO formulation with $\phi_{CO} = 0.349$. The cooling rate was variable (see text) while the heating rate was 2°C min^{-1} (nitrogen atmosphere, mass 40 mg)

In order to quantify the heat evolved in the phase separation process it is convenient to use the cooling scan because of the uncertainty in establishing the base line in the heating scan. However, as our device had no control over the cooling rate it was necessary to determine it experimentally. By measuring temperature as a function of time in several cooling runs, the following cooling rate was derived:

$$-\frac{dT}{dt} = U(T - T_0) \qquad (4)$$

where U is proportionality constant and T_0 is room temperature (21°C). As the U value was in the range of 0.05–0.06 min^{-1}, the cooling rate in the 45–25°C range varied from 1.4 to 0.2°C min^{-1}.

The heat evolved (in J g^{-1}) during the cooling scan could be obtained from:

$$-\Delta H = \frac{1}{m}\int_{T_1}^{T_2} \frac{Y}{U(T - T_0)}\,dT \qquad (5)$$

where Y is the d.s.c. signal (departure from the base line in the cooling scan), expressed in J min^{-1}, m is the mass of sample (g) and T_2 and T_1 are, respectively, the cloud-point temperature (44.8°C for $\phi_{CO} = 0.349$) and the final temperature where the integration was performed (23.5°C). The resulting value of $-\Delta H$ was 1.5 ± 0.1 J g^{-1} (average of three runs).

An estimation of the expected heat evolution may be obtained from equations (1) and (2), by taking an average value of Λ in the 25–45°C temperature range (Λ = 11.5 J cm^{-3}). The enthalpic contribution for preparing a solution of CO in DGEBA with $\phi_{CO} = 0.349$, may be calculated as:

$$(-\Delta H)_0 = \Lambda\phi_{CO}(1 - \phi_{CO})v = 2.4 \qquad (6)$$

where v (= 0.90 cm^3 g^{-1}) is the specific volume of the mixture. On the other hand, at $T = 23.5$°C, the solution will be demixed into a volume fraction $f^\alpha = 0.573$ of phase α ($\phi^\alpha = 0.0874$), and a volume fraction $f^\beta = 0.427$ of phase β ($\phi^\beta = 0.7006$) (*Figure 1*). The enthalpic contribution for preparing both solutions is:

$$(-\Delta H)_1 = \Lambda[f^\alpha\phi^\alpha(1 - \phi^\alpha) + f^\beta\phi^\beta(1 - \phi^\beta)]v = 1.4 \qquad (7)$$