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Phase Separation in a Poly(ether sulfone) Modified Epoxy-Amine System Studied by Temperature Modulated Differential Scanning Calorimetry and Dielectric Relaxation Spectroscopy

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Summary: The phase separation induced by the curing reaction of an epoxy based on diglycidylether of bisphenol A (DGEBA) with methylene dianiline (MDA) modified with poly(ether sulfone) (PES) at a concentration of 20 wt% was studied by temperature modulated differential scanning calorimetry (TMDSC) and dielectric relaxation spectroscopy (DRS). The effect of phase separation on the curing kinetics and vitrification phenomena is analysed. The dependence of the log of the measuring frequency on the degree of conversion allows the correlation between the dipolar relaxation of each phase and the vitrification observed by TMDSC to be established.

Keywords: dielectric properties, kinetics, phase separation, temperature modulated DSC, vitrification

Introduction

The toughness of thermosetting networks can be improved by modifying the epoxy formulation with the inclusion of a thermoplastic.[1,2] One procedure for obtaining this modification involves dissolving the thermoplastic in the epoxy-hardener system and further curing. As the reaction proceeds, the molecular weight of the resin increases and a phase separation takes place at a given conversion. In the case of thermoplastics with a high glass transition temperature (T_g), at relatively low concentration, the phase separation generates a thermoplastic-rich phase dispersed in the epoxy-rich phase. Each phase undergoes the corresponding vitrification process when T_g reaches the curing temperature. The morphology of the multiphase system, which determines the final thermal and mechanical properties of the modified thermoset, depends on the curing conditions.

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Poly(ether sulfone) (PES) is a high-T_g thermoplastic which is used as a modifier for thermosets. The phase separation induced by the curing of an epoxy-diamine system modified by PES has been monitored by optical light transmission[3] and light scattering.[4] The vitrification processes of this system have been studied using calorimetric techniques,[5-7] dynamic mechanical analysis[8-10] and dielectric relaxation spectroscopy (DRS).[6,11]

The objective of this paper is to analyse the effect of PES on the reaction kinetics and vitrification phenomena by temperature modulated differential scanning calorimetry (TMDSC). The relaxation process occurring in each phase is also studied using DRS and it is correlated with the vitrification observed by TMDSC.

Experimental

The unmodified system was an epoxy based on DGEBA (Araldite F from Ciba Speciality Chemicals), with an epoxy equivalent weight of 193.7 $g.eq^{-1}$, which was cured with methylene dianiline (MDA) (from Aldrich) in a stoichiometric ratio. The DGEBA-MDA system was modified with 20 wt% of commercial poly(ether sulfone) (PES) (Ultralon E2010 from BASF). In order to obtain a homogeneous PES modified epoxy-amine system, the PES was dried in a vacuum chamber at 90°C for 24h before being dissolved in methylene chloride at about 10 wt%. The epoxy was dissolved in the PES solution at room temperature with continuous stirring, and the solution was then heated to 80°C in an oil bath in order to evaporate as much solvent as possible. The residual solvent was removed after 14h under vacuum at 80°C. The appropriate amount of MDA was added to the clear viscous mixture of epoxy and PES and heated to 100°C for 5 min in order to melt and disperse the solid MDA. Finally, the samples were enclosed in aluminium pans or spread on ceramic cells for calorimetric or dielectric analysis respectively.

The temperature modulated DSC measurements were performed with a METTLER TOLEDO 821e equipped with an intracooler, and STAR© software was used for alternating DSC (ADSC) evaluation. The temperature and heat flow calibrations were performed using indium and zinc standards. The modulation conditions used in the quasi-isothermal curing reaction were an amplitude of 0.5 K and a period of 1 min. The sample weight was approximately 8-10 mg. The calorimetric scans were performed with a nitrogen gas flow of 50 mL min^{-1}.

A dynamic electric analyser DEA 2970 from TA Instruments was used to measure both the dielectric permittivity (ε') and the dielectric loss factor (ε") of the isothermally cured epoxy samples at different frequencies in real time. Dielectric measurements were performed using a single-surface ceramic cell. The dielectric permittivity and the dielectric loss factor were measured at nine frequencies within the interval 10 Hz to 100 kHz. The time taken to scan at the different frequencies was 1.2 min. All dielectric measurements were performed under a nitrogen atmosphere with a gas flow of 500 mL min^{-1}.

Temperature Modulated DSC Results

The effect of the PES on the isothermal curing of the DGEBA-MDA system was analysed from the three TMDSC signals: the total heat flow <ϕ>, the modulus of the complex heat capacity $|C_p^*|$ and the phase angle δ. The fundamental aspects of ADSC signals, which appear during the cure, have been described elsewhere.[12] Figure 1a shows the total heat flow of the unmodified system and the PES modified system during the curing at 80°C. The <ϕ> curve of the modified system is shifted to longer times, which *a priori* indicates a slowdown of the global kinetics. The degree of conversion, α, for both systems at 80°C is shown in Figure 1b. Total conversion is not achieved due to the vitrification of both systems. The limiting conversion in the unmodified system is higher than in the modified system.

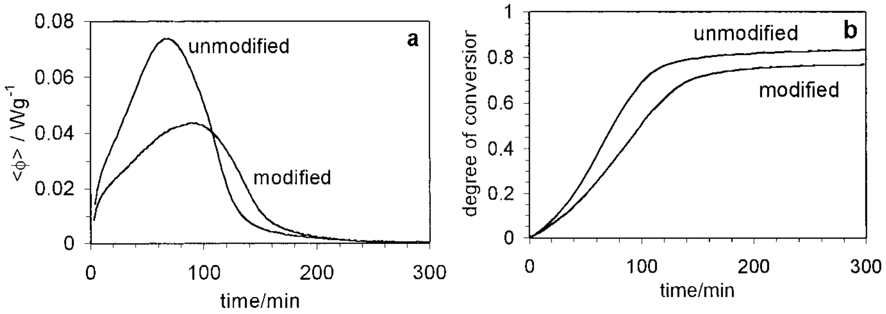

Fig. 1. Total heat flow (a) and degree of conversion (b) of the unmodified (DGEBA-MDA) and the modified (DGEBA-MDA/20%PES) systems during isothermal curing at 80°C. The modulation conditions were: amplitude 0.5K, and period 60s.

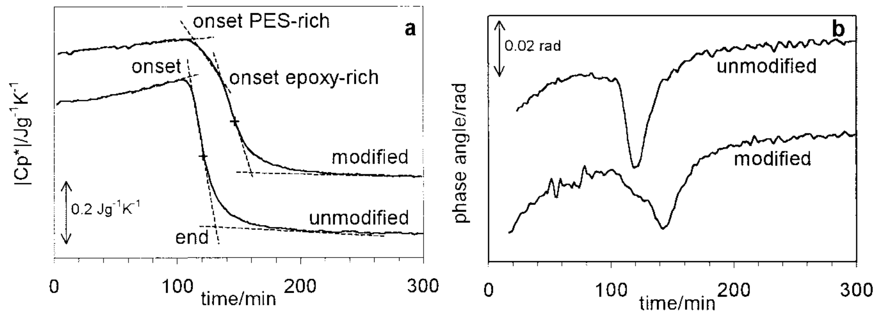

Fig. 2. Modulus of C_p* (a) and phase angle (b) for the unmodified (DGEBA-MDA) and the modified (DGEBA-MDA/20%PES) systems at a curing temperature of 80°C. Modulation conditions: 0.5 K amplitude, and 60s period. The onset time for vitrification is indicated in $|C_p*|$ for each phase. The crosses show the vitrification midpoint for the epoxy matrix.

TMDSC allows the heat evolved during the cure to be measured in conjunction with the heat capacity of the system. The evolution of the modulus of the complex heat capacity $|C_p*|$ for the unmodified DGEBA-MDA system (Fig. 2a) follows the general trend of other epoxy-amine systems.[5,12] Initially $|C_p*|$ increases due to the increase in the number of configurational states or the vibrational modes during the growth of the linear chains. A drastic decrease in $|C_p*|$ follows which may be attributed to the vitrification of the system.[5,12] During this process, the system goes from a rubber-like state corresponding to the highest $|C_p*|$ value to a glassy state at the lowest value of $|C_p*|$. As shown in Figure 2a, a time corresponding to the onset, midpoint and end of the vitrification may be defined. At the same time the phase angle for the unmodified system (Fig. 2b) shows a relaxation peak in the region where the drop in $|C_p*|$ appears.

The evolution of $|C_p*|$ for the modified system shows a two-step decrease. The first decrease may be attributed to the vitrification of a PES-rich phase, which results from the phase separation induced by the progress of the curing reaction. This step is followed by an abrupt decrease, whose slope is similar to that observed in the unmodified system. The second decrease in $|C_p*|$ corresponds to the vitrification of the epoxy matrix. The relaxation process associated with each vitrification is also shown in the phase angle by a shoulder and a peak

(Fig. 2b). The vitrification of the epoxy-rich phase is shifted to longer times with the inclusion of PES. This shift has also been observed at the other curing temperatures (60, 100 and 120°C). These results are in good agreement with those of Swier and Van Mele.[5]

As in other thermosetting systems, the curing kinetics is controlled chemically by the reactivity of the functional groups, but as the reaction progresses, the viscosity of the medium increases and the systems transforms from a liquid (or gel) into a glass. When the vitrification sets in, the kinetics becomes diffusion-controlled. The chemical kinetics for this epoxy-amine system fits the autocatalytic model proposed by Kamal[13] well:

$$\left(\frac{d\alpha}{dt}\right)_{chem} = (k_1 + k_2\alpha^m)(1-\alpha)^n \qquad (1)$$

In this equation k_1 and k_2 are rate constants which are dependent on the temperature assuming an Arrhenius form, $k(T)=A\exp(-E_a/RT)$, where A is the pre-exponential factor, R is the gas constant and E_a is the apparent activation energy. The exponents m and n indicate the empirical reaction order. The values for k_1 and k_2 from fitting the Kamal equation at different temperatures, together with the corresponding apparent activation energies, are shown in Table 1. These results confirm that the inclusion of PES slows down the chemical kinetics due to a dilution effect.[5]

Table 1. Rate constants and apparent activation energies for the curing reaction of the unmodified and modified system.

T(°C)	Unmodified system		Modified system	
	$k_1 \cdot 10^5$ (s^{-1})	$k_2 \cdot 10^4$ (s^{-1})	$k_1 \cdot 10^5$ (s^{-1})	$k_2 \cdot 10^4$ (s^{-1})
60	2.1	4.2	1.4	1.1
80	5.4	12.5	2.9	4.0
100	127.5	21.4	125.1	17.0
120	416.4	101.9	380.3	55.1
E_a (kJmol^{-1})	$E_a(k_1)$=52.9	$E_a(k_2)$=54.8	$E_a(k_1)$=61.4	$E_a(k_2)$=71.3

The diffusion-controlled regime may be analysed by the chemical reaction rate given by equation (1) corrected by a diffusion factor. In the present epoxy-amine system this diffusion factor coincides with a mobility factor MF((T,α), which may be calculated from the values of the specific heat at vitrification:[14]

$$\mathrm{MF}(\mathrm{T},\alpha)=\frac{\left|C_p^*\right|(t,T)-\left|C_{p,g}^*\right|(T)}{\left|C_{p,l}^*\right|(t,T)-\left|C_{p,g}^*\right|(T)} \qquad (2)$$

where $|C_p^*|(t,T)$ is the actual value of $|C_p^*|$, and $|C_{p,g}^*|(T)$ and $|C_{p,l}^*|(t,T)$ are the values of $|C_p^*|$ in the glassy and the liquid state respectively. This coincidence allows the calculation of a simulated reaction rate from the chemical reaction rate corrected by the mobility factor. The simulated reaction rate is shown in Figure 3a for the unmodified epoxy system. As in other epoxy-amine systems,[12,14] the simulated reaction rate agrees quite well with the experimental reaction rate. A similar procedure has been applied to the modified system using an overall mobility factor calculated by $|C_p^*|$. The overall simulated reaction rate for the modified system is shown in Figure 3b.

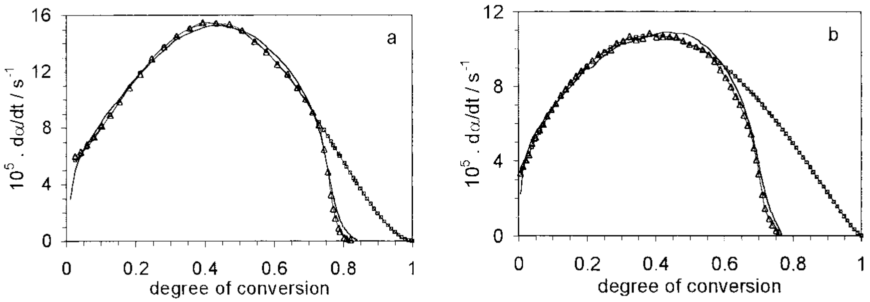

Fig. 3. Reaction rate (dα/dt) against the degree of conversion for the unmodified (a) and the modified (b) system at 80°C. The solid line shows the experimental reaction rate. The reaction rate obtained by Kamal model (□) and the simulated rate (Δ) are also plotted.

The deviation of the experimental reaction rate respect to the chemical reaction rate in the modified system corresponds to the onset of the vitrification of the PES-rich phase, the conversion values for which are shown in Figure 4 at different temperatures. As expected, the degree of conversion at this point increases with temperature. It is observed that the conversion between the onset of vitrification of the PES-rich phase and the onset of vitrification of the epoxy matrix tends to increase with temperature. One may assume that this change of conversion takes place in the epoxy matrix. It is observed that the conversion during vitrification of the epoxy matrix, which is given by the variation between the onset of vitrification of this phase and the limiting value of the conversion, tends to decrease with temperature. In the unmodified system, it is also observed that the restricted change in conversion during the diffusion-controlled step decreases with temperature. This effect is due to the increase of the crosslinking density of the network.

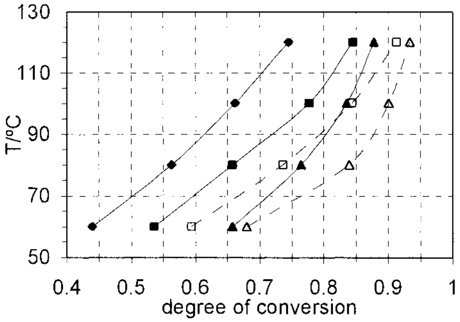

Fig. 4. Degree of conversion corresponding to the vitrification in both modified and unmodified systems: onset vitrification of the PES-rich phase (♦) and the epoxy matrix (■) in the modified system, onset vitrification in the unmodified system (□). The limiting conversion in the unmodified (Δ) and the modified (▲) system is also shown.

Dipolar Relaxation and its Correlation with Vitrification

At a fixed frequency ω, the complex permittivity is calculated by $\varepsilon^* = \varepsilon' - i\,\varepsilon''$, where the real component ε' is the permittivity, which is proportional to the capacitance, and the imaginary component ε'' is the loss factor, which is proportional to the conductance. The angular frequency ω is 2πf, where f is the measuring frequency. Both components ε' and ε'', which are shown in Figures 5a and 5b, have dipolar and ionic, or charge, contributions. At low frequencies, the permittivity ε' (Fig. 5a) shows very large values and decreases drastically due to an electrode polarisation effect, caused by the ionic impurities present in the reactants. At frequencies higher than 1 kHz the curves for ε′ show a decrease from the relaxed permittivity ε_0 to the unrelaxed permittivity ε_∞. In the modified system, the variation of ε′ shows a two-step decrease. However, an increase in this property is observed at low frequencies before the drop to the unrelaxed value. According to other authors[15] this peak may be attributed to an interfacial polarisation process, which occurs at the onset of the phase separation.

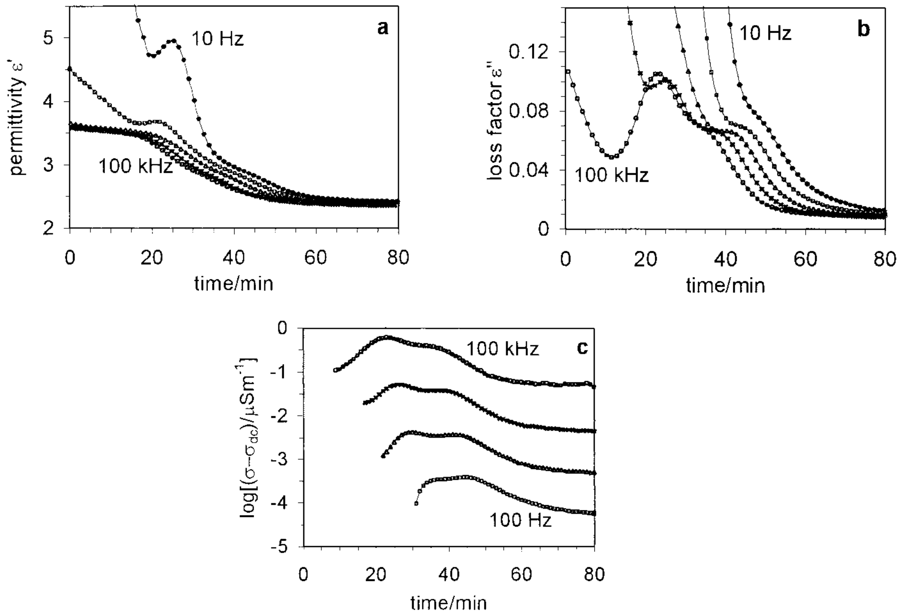

Figure 5. Permittivity ε′ (a), loss factor ε″ (b) and conductivity after the subtraction of dc-conductivity (c) of the DGEBA-MDA/20%PES system at a curing temperature of 100°C, for the indicated frequencies: 10 Hz(◇), 100 Hz(□), 1 kHz(Δ), 10 kHz(x) and 100 kHz(o).

The loss factor in the neat epoxy-amine system shows only one dipolar peak, whereas the modified system shows two peaks (Fig. 5b). The first peak is well defined at high frequencies and corresponds to the relaxation of the PES-rich phase. The latter is less clearly defined, it appears as a shoulder, and corresponds to the relaxation of the epoxy-rich phase. This is supported by the lower mobility of the PES chains, which is due to the higher T_g of PES

(226°C) compared with the T_g of the neat epoxy (163°C). Other arguments are given below taking into account the correlation of the DRS and TMDSC data.

In order to study the dipolar relaxation during the curing reaction, the loss factor has been corrected from the ionic contribution $\varepsilon''_i(\omega)$. This ionic contribution is obtained from the dc-conductivity $\sigma_{dc}(T,t_c)$, which is independent of the frequency and decreases with increasing curing time t_c : $\sigma_{dc}(T,t_c) = e_o\omega\ \varepsilon_i''$, where e_o is the permittivity of free space (8.85 pF m^{-1}). The value of $\sigma_{dc}(T,t_c)$ was calculated by the method proposed by Mangion and Johari,[16] and others,[11] using an exponential equation. The dc-conductivity contribution is subtracted from the conductivity data, σ-σ_{dc}, which values are shown in Figure 5c. This quantity allows to calculate the loss factor of the dipolar relaxation, which is not shown in this work, by the relation $\varepsilon''_d(\omega)=(\sigma-\sigma_{dc})/e_o\omega$.

The time for the peak value of $\varepsilon''_d(\omega)$ at a given frequency, which is the same as in the peak of conductivity after the subtraction of dc-conductivity (σ-σ_{dc}), characterises the dipolar relaxation at a given frequency. As in other epoxy-amine systems, the logarithm of the measuring frequency has been observed to have a linear dependence on the time of the dipolar peak $\varepsilon''_d(\omega)$, t_m:[17,18]

$$\log f_m = \log f_m(0) - \frac{k_d\, t_m}{\ln 10} \qquad (3)$$

where f_m is the frequency of the maximum dipolar relaxation, and $f_m(0)$ and k_d are temperature dependent constants, whose values are shown in Table 2 for the neat epoxy and the modified epoxy-amine systems. Two sets of values are shown for the modified system corresponding to the relaxation of the PES-rich phase (first dipolar peak) and the epoxy-rich phase (second peak). Extrapolating this equation to a frequency of 16.7 mHz (the value used in TMDSC experiments) gives a value of t_m situated within the interval where the corresponding vitrification occurs. This correlation is better understood by plotting the log of frequency against the degree of conversion, as in Fig. 6.

Table 2. Dependence of the frequency on the time of maximum loss factor: temperature dependent constants $f_m(0)$ and k_d according to equation (3).

	Unmodified system		Modified system 1st peak		Modified system 2nd peak	
T/°C	$\log(f_m(0)/\mathrm{Hz})$	k_d $10^3/s^{-1}$	$\log(f_m(0)/\mathrm{Hz})$	k_d $10^3/s^{-1}$	$\log(f_m(0)/\mathrm{Hz})$	k_d $10^3/s^{-1}$
60	18.18	1.38	9.09	1.08	-	-
80	20.26	3.32	13.62	2.43	17.79	2.63
100	16.90	6.18	11.48	4.74	14.28	4.62

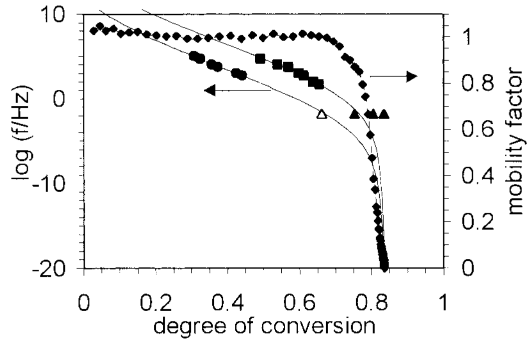

Figure 6. Plots of the logarithm of frequency against the degree of conversion for the first (•) and second (▪) dipolar relaxation peaks during the curing of the modified system at 100°C. The values at log(f/Hz)= -1.78 correspond to the TMDSC measurements: the triangle (Δ) corresponds to the onset of PES-rich phase vitrification and the three filled triangles indicate (from left to right) the onset, midpoint and limiting conversion values for the vitrification of the epoxy matrix. The solid lines correspond to the continuous variation of log(f) on α. The mobility factor under the same curing conditions is also shown (◆).

In the range of dielectric frequencies, $\log(f_m)$ decreases steadily with the degree of conversion, but in the region of the diffusion-controlled regime indicated by the decrease in the mobility factor, the change of log(f) with the conversion becomes steeper. In the modified system log(f) for the first dipolar peak correlates very well with the onset of vitrification of the PES-rich phase, which, using TMDSC, is observed at a frequency of 16.7 mHz. Similarly, log(f) for the second dipolar peak correlates with the vitrification of the epoxy-rich phase, which takes place at a slightly higher conversion. In the case of the unmodified system (not shown in this work) the results agree with those obtained in other neat epoxies.[17,18]

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