Reaction-induced phase separation in polyethersulfone-modified epoxy-amine systems studied by temperature modulated differential scanning calorimetry

Steven Swier, Bruno Van Mele[*]

Department of Physical Chemistry and Polymer Science, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

Abstract

In epoxy-amine systems with a thermoplastic additive, the initially homogeneous reaction mixture can change into a multiphase morphology as a result of the increase in molecular weight or network formation of the curing matrix. Temperature modulated DSC (TMDSC) allows the real-time monitoring of this reaction-induced phase separation. A linear polymerizing epoxy-amine (DGEBA–aniline) and a network-forming epoxy-amine (DGEBA–methylene dianiline), both with an amorphous engineering thermoplastic additive (polyethersulfone, PES), are used to illustrate the effects of phase separation on the signals of the TMDSC experiment. The non-reversing heat flow gives information about the reaction kinetics. The heat capacity signal also contains information about the reaction mechanism in combination with effects induced by the changing morphology and rheology such as phase separation and vitrification. In quasi-isothermal (partial cure) TMDSC experiments, the compositional changes resulting from the proceeding phase separation are shown by distinct stepwise heat capacity decreases. The heat flow phase signal is a sensitive indication of relaxation phenomena accompanying the effects of phase separation and vitrification. Non-isothermal (post-cure) TMDSC experiments provide additional real-time information on further reaction and phase separation, and on the effect of temperature on phase separation, giving support to an LCST phase diagram. They also allow measurement of the thermal properties of the in situ formed multi-phase materials. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

To expand the applicability of polymer networks, continuous efforts are made to improve their properties. An interesting route consists of introducing an additive to the two-component reactive mixture prior to cure. Rubbery additives are widely used to generate a rubber-toughened thermoset. The introduction of a rubbery phase, however, results in a lower elastic modulus. Linear amorphous engineering thermoplastics can also be expected to reduce the brittleness of a thermoset, without affecting the other properties significantly [1].

Starting from a homogeneous mixture, the system transforms into a phase-separated structure due to the increasing molecular weight or network formation of the reacting matrix [2].

The competition between the rates of cure and of phase separation determines the mechanism of this

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*Corresponding author. Tel.: +32-(0)2-629-3276; fax: +32-(0)2-629-3278; e-mail: bvmele@vub.ac.be

reaction-induced phase separation, i.e. nucleation and growth or spinodal demixing [1,3]. Controlling this mechanism is crucial for the final network morphology and resulting properties. The influence of parameters like composition and cure temperature on the final morphology has been investigated with scattering techniques [3–6]. However, information about the continuously changing morphology in the course of reaction-induced phase separation is difficult to obtain with these ex-situ methods. Girard-Reydet et al. [5] deduced changes in morphology by means of in situ or real-time diffraction techniques using different observation windows. In situ dielectrical measurements also provide information about morphology using the interfacial polarization due to phase separation [7,8]. These real-time techniques, however, are limited to the rate of phase separation and the accompanying mechanism, without information about the competing rate of network formation.

Temperature modulated DSC (TMDSC) has proven to be a valuable thermal analysis technique in studying reacting polymer systems. TMDSC provides information about the reaction kinetics and the continuously changing chemorheology, allowing for example the real-time monitoring of vitrification [9]. A model system consisting of a linearly growing epoxy-amine macromolecule in the presence of the engineering thermoplastic polyethersulfone (PES) was already used to highlight the potential of TMDSC for the real-time monitoring of reaction-induced phase separation [10]. The glass-transition temperatures of both phases could be detected with TMDSC in a subsequent heating, even after isothermal phase separation without full-cure. Alig et al. [11] also showed the benefits of TMDSC to measure both glass-transition temperatures after partial cure of a PES-modified epoxy-amine network system. However, the phase separation process of the latter system was not noticed in situ with TMDSC during the preceding isothermal cure.

In this paper, the methodology for real-time monitoring of reaction-induced phase separation is further developed and extended to a network-forming epoxy-amine system modified with PES. Emphasis will be on the information obtained from the (quasi)isothermal heat capacity and heat flow phase signals with respect to phase separation during cure.

2. Experimental

2.1. Materials

Two epoxy-amine systems were studied: a bifunctional epoxy, diglycidyl ether of bisphenol A (DGEBA, Epon825 from Shell), with an epoxy equivalent weight of 180 g.eq^{-1}, in combination with a stoichiometric amount of a bifunctional amine (aniline from Fluka), or a tetrafunctional amine hardener (methylene dianiline, MDA from Janssen Chimica), with an amine equivalent weight of 46.5 and 49.5 g.eq^{-1}, respectively. Stoichiometric mixtures of these pure systems were modified with 20 wt% of low molecular weight, Mw=20 000 g mol^{-1}, polyethersulfone (PES from Aldrich). Both epoxy-amine systems were studied in unmodified (pure systems) and modified (with 20 wt% PES) compositions.

To obtain a homogeneous mixture of the thermoplastic modified epoxy-amine, PES was first dissolved in the epoxy using CH_2Cl_2, which was evaporated at about 120°C under extensive stirring followed by vacuum evaporation at 100°C. Aniline or MDA was mixed afterwards for about 5 min at 80°C or 100°C, respectively. This procedure is reducing preliminary reaction to a minimum and was checked for reproducibility (see Section 3).

2.2. Techniques

Cure experiments were performed on a TA Instruments 2920 DSC with MDSC^{TM} option and a refrigerated cooling system (RCS). Helium was used as a purge gas (25 ml min^{-1}). Indium and cyclohexane were used for temperature calibration. The former was used for enthalpy calibration. Heat capacity calibration was performed with a PMMA standard (supplied by Acros [12]), using the heat capacity difference between two temperatures, one above and one below the glass transition temperature of PMMA, to make sure that heat capacity changes were adequately measured.

Cure was performed in hermetic aluminum pans (TA Instruments), with sample weights between 10 and 20 mg. Quasi-isothermal measurements were conducted between 80°C and 130°C, with a modulation amplitude of 1°C and a 60 s period. Non-isothermal post-cures and final heatings were conducted at

2.5°C min^{-1} up to 240°C, with the same modulation conditions.

3. Results and discussion

Isothermal (partial cure) and non-isothermal (post-cure) TMDSC experiments are compared for the two epoxy-amines, both without PES (homogeneous unmodified mixtures) and in the presence of 20 wt% PES (homogeneous modified mixtures). The major changes during the step-growth polymerization of the epoxy-aniline system are an increase in molecular weight, viscosity, and glass-transition,

while in the epoxy-MDA system gelation and network formation is interfering too.

The real-time monitoring with TMDSC and the effects of reaction-induced phase separation, both in isothermal and non-isothermal conditions, are illustrated in Figs. 1–8.

Some calculated partial (ΔH_{iso}), residual (ΔH_{res}), and total (ΔH_{tot}) reaction enthalpies are summarized in Table 1, in combination with glass-transition temperatures of epoxy-rich (lower T_g or T_{gEPAM}) and PES-rich (higher T_g or T_{gPES}) phases. T_g values are given as intermediate thermal properties after (partial) isothermal cure, and also as final thermal properties after non-isothermal post-cure (measured in a final heating

Table 1

TMDSC results for isothermal cure, post-cure (heating at 2.5°C min^{-1}) and final properties (heating at 2.5°C min^{-1}) for the unmodified and modified epoxy-amine systems

Experimental system	Isothermal cure				Post-cure		Final properties[a]	
	T_{iso} (t_{iso})	$-\Delta H_{iso}$	T_{gEPAM}	T_{gPES}	$-\Delta H_{res}$	$-\Delta H_{tot}$	T_{gEPAM}	T_{gPES}
PES								223
DGEBA–aniline	100 (0)	0	−41		110	110	94[b]	
	100 (100)	86	34		27	113		
	100 (200)	109	81		4	113		
	100 (400)	116	93		0	116		
	80 (1000)	109	89		6	115		
DGEBA–aniline/20%PES	100 (0)	0	−29[c]	−29[c]	118	118	94	202[d] (218)[e]
	100 (100)	60	26[c]	26[c]	48	108		
	100 (200)	101	71	97	14	115		
	100 (400)	113	94	112	2	115		
	130 (700)	116	93	139	0	116		
	80 (1200)	99	91	99	8	107		
	70 (1600)	89	84	90	14	103		
DGEBA–MDA	100 (0)	0	−17		105	105	175[b]	
	100 (150)	90	125		13	103		
	80 (300)	85	105		19	104		
DGEBA–MDA/20%PES	100 (0)	0	−6[c]	−6[c]	100	100	182[d]	194[d]
	100 (150)	85	124	160	17	102		
	120 (100)	97	141	160	10	107		
	90 (200)	82	118	160	22	104		
	80 (300)	75	105	160	31	106		

T_{iso} (t_{iso}): isothermal cure temperature (in °C) and cure time (in min); ΔH_{iso}: isothermal reaction enthalpy; ΔH_{res}: residual reaction enthalpy; ΔH_{tot}: total reaction enthalpy (all in kJ mol epoxy^{-1}); T_{gEPAM} and T_{gPES}: glass transitions of the epoxy-rich and PES-rich phases (in °C).
[a] Values apply for all cure conditions of the system studied.
[b] Full cure glass transition temperature of the unmodified epoxy system ($=T_{g\infty}$).
[c] Modified system showing one glass transition.
[d] Value calculated at the peak in the derivative of the heat capacity signal (see also Fig. 8).
[e] Value obtained after a post-treatment of 100 min at 230°C.

at $2.5°C\,min^{-1}$). After the non-isothermal post-cure at $2.5°C\,min^{-1}$ up to $240°C$, each system studied is considered to be fully cured with characteristic final properties, independent of the preceding cure schedule. Only for the unmodified epoxy systems, the final glass-transition value is denoted as $T_{g\infty}$ in the following paragraphs. Note that DGEBA–aniline and DGEB–MDA were also studied in [10], but with different properties of DGEBA and MDA (from dif-

ferent suppliers), so that cure kinetics and final thermal properties (e.g. $T_{g\infty}$) cannot be compared.

3.1. Phase separation during linear step-growth polymerization

Fig. 1 shows the non-reversing heat flow, in combination with the changes in heat capacity and heat flow phase, as a function of reaction time for the quasi-
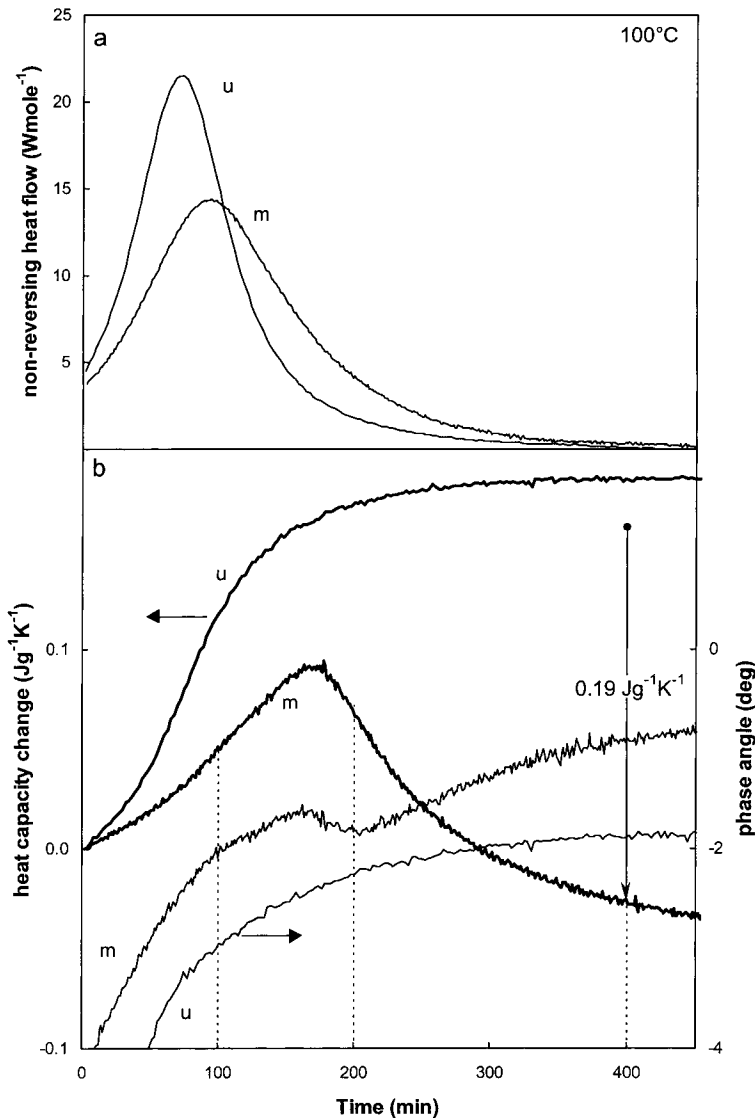

Fig. 1. Cure at 100°C of DGEBA–aniline (unmodified: u) and DGEBA–aniline/20%PES (modified: m): (a) non-reversing heat flow per mole epoxy; (b) change in heat capacity and heat flow phase; the heat capacity change due to phase separation is indicated.

isothermal cure at 100°C of a stoichiometric DGEBA–aniline mixture. The bifunctionality of both resin and hardener gives rise to the formation of linear uncross-slinked chains. To avoid interference with vitrification, cure has been performed above the full-cure glass transition ($T_{g\infty}$=94°C) [13]. The typical autocatalytic nature of this linear step-growth polymerization is evident from the markedly increasing heat flow during the first 80 min of isothermal cure. A value for ΔH_{tot} of −116 kJ mol epoxy^{-1} after 400 min cure is calculated (see Table 1), which is in agreement with [14].

The heat capacity is increasing due to chemical reaction, resulting in a total change of 40 J mol epoxy^{-1} K^{-1} at the end of isothermal cure. This signal contains supplementary information about primary and secondary amine reaction steps [10]. Note that the increasing slope of the heat capacity evolution in the early stages of the reaction is also the result of the autocatalytic cure behavior.

The corrected heat flow phase evolves towards zero during reaction and shows no local extremes, confirming a chemically-controlled reaction without vitrification at 100°C [9].

The same cure schedule has been imposed to the PES-modified linear system (see also Fig. 1). A value for ΔH_{iso} of −113 kJ mol epoxy^{-1} is calculated with an almost negligible ΔH_{res} of −2 kJ mol epoxy^{-1} (measured in a post-cure at 2.5°C min^{-1}), to obtain the same ΔH_{tot} as the unmodified system (see Table 1). Note the broadening of the non-reversing heat flow signal, which is probably the result of a dilution effect by addition of PES and requires a quantitative analysis of the different steps in the epoxy-amine reaction mechanism [15]. In this paper, however, emphasis will be on the real-time monitoring of phase separation using the additional TMDSC signals. In the early stages of reaction, the heat capacity evolution is comparable to the unmodified linear system, until a stepwise decrease sets in at a conversion of about 81%, accompanied by a relaxation peak in the heat flow phase. This decrease in heat capacity can be attributed to the vitrification of a PES-rich phase, segregating as a result of the increasing molecular weight of the growing epoxy-aniline linear macromolecules. This reaction-induced phase separation is confirmed by isothermal partial cure experiments with reaction times chosen before and beyond the observed maximum in heat capacity, as indicated

in Fig. 1, followed by a heating at 2.5°C min^{-1} shown in Fig. 2 (see also [10]). As depicted in Fig. 2(b), the system exhibits only one distinct glass transition after a partial cure stopped before the maximum in heat capacity of Fig. 1. On the contrary, beyond this maximum, the occurrence of two glass transitions indicates a heterogeneous phase separating system. So, by the progressing reaction, a homogeneous system is transformed into a heterogeneous one. The dispersed PES-rich phase corresponds to the higher glass transition, due to the high T_g (223°C) of this engineering thermoplastic. In Fig. 2(b), the evolution of the heat capacity after 400 min cure at 100°C (T_{iso}) shows that the epoxy-rich phase stays mobile during isothermal curing ($T_{gEPAM}<T_{iso}$), and no vitrification of this matrix phase will occur. The dispersed PES-rich phase, on the other hand, vitrifies at some point ($T_{gPES}>T_{iso}$). Taking into account the total heat capacity change of 40 J mol epoxy^{-1} K^{-1} after 400 min of isothermal cure for the unmodified epoxy-aniline (due to chemical reaction), and the dilution effect of 20% PES in the hypothetical case of a homogeneous mixture, Fig. 1(b) shows that a heat capacity decrease ΔC_p of 0.19 J g^{-1} K^{-1} can be assigned to vitrification of a segregating phase in the modified epoxy-aniline. This is in agreement with a calculated ΔC_p of 0.17 J g^{-1} K^{-1} at T_g of the PES-rich phase in the residual scan (see Fig. 2(b)). The non-reversing heat flow signals of these post-cures at 2.5°C min^{-1} are also depicted (Fig. 2(a)), illustrating the power of TMDSC to separate (partly) overlapping phenomena such as T_g and residual cure. The small ΔH_{res} after 400 min cure at 100°C (−2 kJ mol epoxy^{-1}) can be attributed to remaining reactive epoxy-amine groups, trapped during phase separation in the vitrifying PES-rich phase (see also Table 1). Note also in Fig. 2(a) the higher cure rate up to 120°C of the post-cure after 100 min pre-cure at 100°C (corresponding with 56% conversion) in comparison with the non-isothermal cure at the same heating rate of a fresh reaction mixture (no pre-cure, 0% conversion), illustrating again the autocatalytic nature of the reaction.

3.1.1. Interference of vitrification of the matrix

The epoxy-aniline system allows to follow accurately isothermal cure above and below $T_{g\infty}$ (94°C). Choosing an isothermal cure temperature below $T_{g\infty}$ will provoke vitrification of the epoxy-aniline matrix
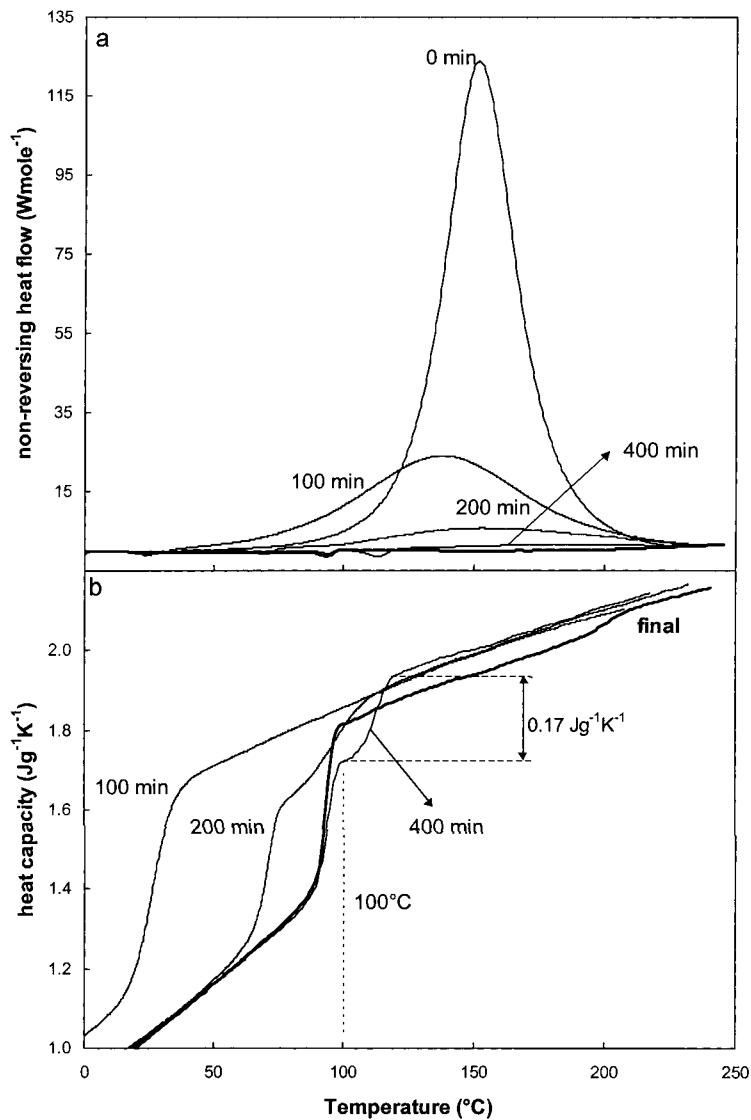
Fig. 2. Post-cure at 2.5°C min^{-1} of DGEBA–aniline/20%PES after 0, 100, 200, and 400 min partial cure at 100°C (see also Fig. 1), and final heating: (a) non-reversing heat flow per mole epoxy; (b) heat capacity (0 min not shown).

[13]. Fig. 3 shows the quasi-isothermal cure at 80°C for both modified and unmodified epoxy-aniline systems. In the latter, vitrification is seen after 91% conversion as a stepwise decrease in heat capacity, accompanied by a relaxation peak in the heat flow phase. The modified epoxy-aniline exhibits two subsequent C_p decreases, which can be associated with vitrification of a segregating dispersed PES-rich phase and vitrification of the epoxy-rich matrix, respectively.

Two clearly separated extremes can also be observed in the heat flow phase, which will prove to be valuable in the analysis of phase separation during network formation (see Section 3.2). The PES-rich phase is segregating and vitrifying first, while the epoxy matrix is still mobile. Vitrification of the epoxy-rich phase is occurring afterwards due to the progressing reaction. Starting from the decrease in heat capacity for a totally vitrified PES-modified system (ΔC_p=0.45 J g^{-1} K^{-1},
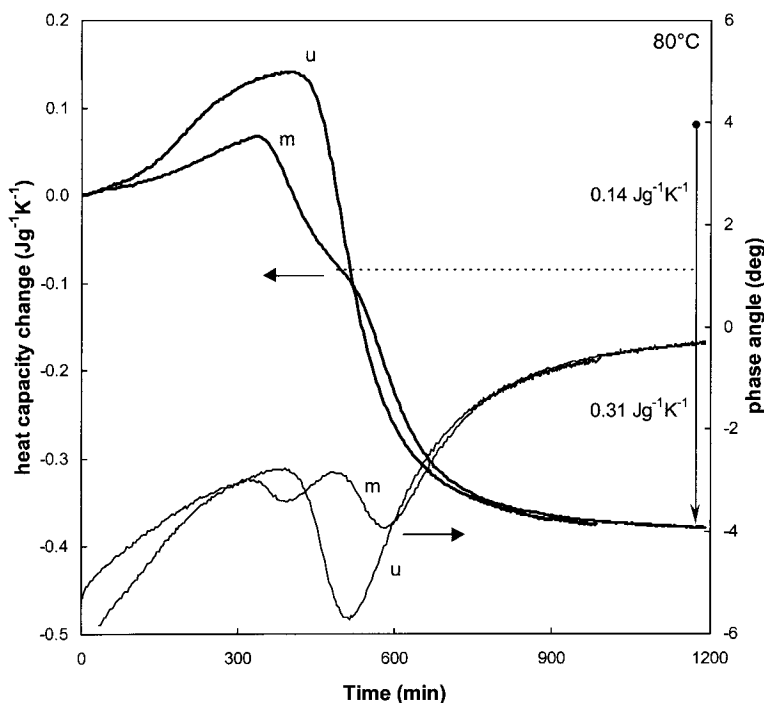
Fig. 3. Cure at 80°C of DGEBA–aniline (unmodified: u) and DGEBA–aniline/20%PES (modified: m): change in heat capacity and heat flow phase; the heat capacity change due to phase separation and vitrification is indicated.

as calculated from the measured heat capacity changes at T_g for a totally cured unmodified system, $\Delta C_p = 0.51 \text{ J g}^{-1} \text{ K}^{-1}$, and for pure PES, $\Delta C_p = 0.21 \text{ J g}^{-1} \text{ K}^{-1}$), ΔC_p values of 0.14 and $0.31 \text{ J g}^{-1} \text{ K}^{-1}$ for vitrification of the segregated PES-rich phase and vitrification of the epoxy-rich matrix, respectively, are calculated (indicated in Fig. 3). These ΔC_p values are in total agreement with those measured in a subsequent heating, 0.15 and $0.30 \text{ J g}^{-1} \text{ K}^{-1}$, respectively (see Fig. 5).

The quantitative nature of the TMDSC results is of importance for a reliable modeling of the cure rate law. Fig. 4 illustrates that the reproducibility of the TMDSC signals for three independently prepared mixtures is excellent, proving the reliability of the mixing, sampling, and measuring protocol for these thermoplastic modified reacting polymer systems. The small deviations noticed are within experimental error, taking into account that slight stoichiometric unbalances in the mixing ratio of epoxy and amine create important changes in the conversion rate.

3.1.2. Influence of isothermal cure temperature and final thermal properties

The heat capacity evolutions at 2.5°C min^{-1} after isothermal cure at different temperatures for PES-modified epoxy-aniline are shown in Fig. 5. Isothermal cure times were chosen long enough so that the non-reversing heat flow tended to zero, and reaction was completed or frozen by vitrification. In all conditions studied, two glass transitions are observed, corresponding to the epoxy-rich (T_{gEPAM}) and PES-rich (T_{gPES}) phases.

For the scans following isothermal cure at 100°C and 130°C, the value of T_{gEPAM} is almost equal to the full-cure glass transition of the unmodified system ($T_{g\infty} = 94°C$). Moreover, no marked difference in T_{gEPAM} is seen for the final heating at 2.5°C min^{-1}, after the first heating or post-cure (note that the final heating shown is valid for all preceding reaction conditions). The same observation holds for the final heating in Fig. 2 (see also Table 1). This is indicative for an almost totally demixed epoxy-rich phase, or at least for a phase with a glass transition nearly un-
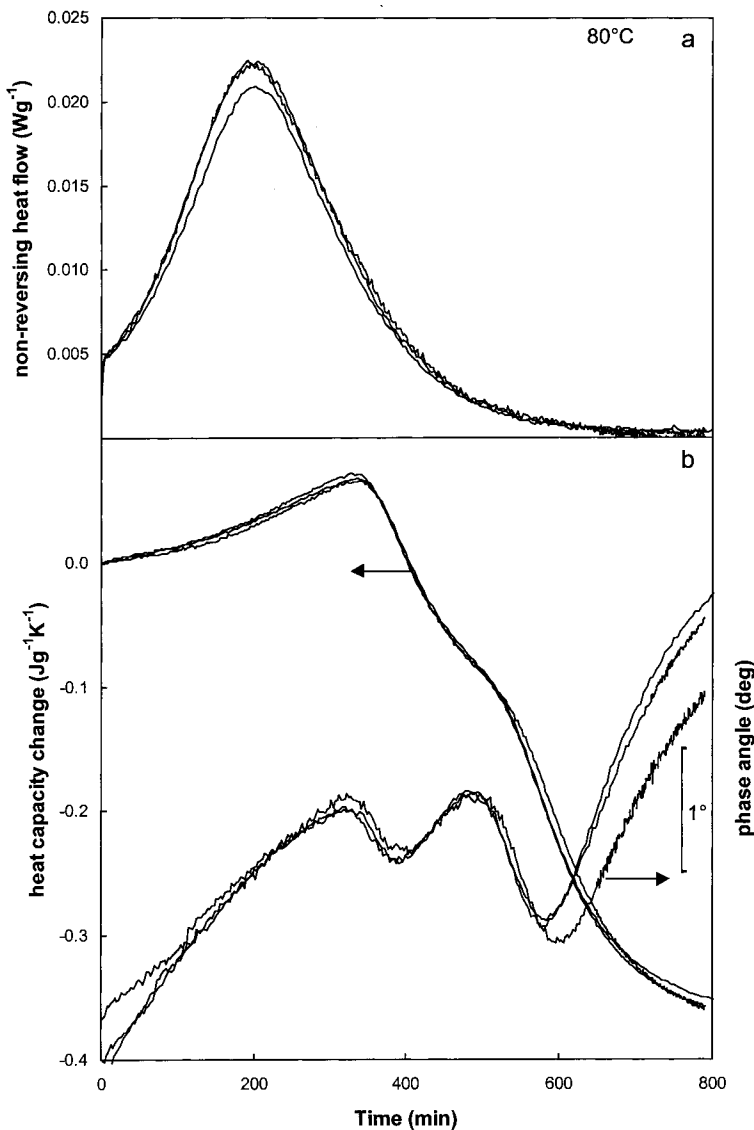
Fig. 4. Overlay of three independent cure experiments at 80°C for DGEBA–aniline/20%PES (see also Fig. 3): (a) non-reversing heat flow; (b) change in heat capacity and heat flow phase.

affected by small amounts of remaining PES. It should be noted here that, after cure at 100°C, T_{gEPAM} is slightly increased or broadened, probably due to remaining PES. On the contrary, for the lower cure temperatures (70°C and 80°C), a lower value of T_{gEPAM} is observed, in accordance with isothermal vitrification of the matrix and a significant residual reaction (see Table 1). Fig. 5

also depicts the heat capacity change at T_{g} of the epoxy-rich phase (ΔC_{pEPAM}) as a function of the isothermal cure temperature, illustrating the increasing fraction of this phase with increasing cure temperature. Note that ΔC_{pEPAM} after isothermal cures at 70°C and 80°C are not shown, because these results reflect only partially cured systems.
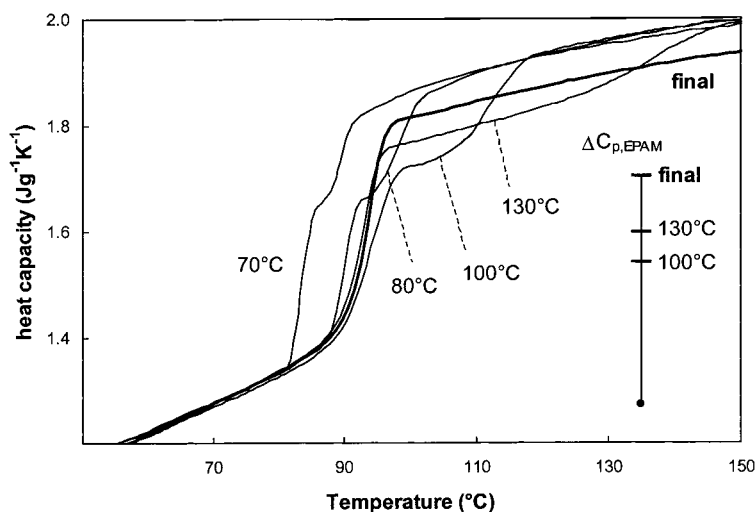
Fig. 5. Heat capacity evolution of DGEBA-aniline/20%PES for non-isothermal post-cure after isothermal cure at 70°C, 80°C, 100°C, and 130°C, and for the final heating; the heat capacity change at the glass transition of the epoxy-amine-rich phase is also indicated (ΔC_{pEPAM}).

The glass transitions of the PES-rich phase (T_{gPES}) are much broader. For the lower isothermal cure temperatures, T_{gPES} is not clearly separated from the epoxy-rich phase, indicating a significant amount of interphase with intermediate compositions. Taking into account the heat capacity changes at T_g of the pure full-cured DGEBA–aniline (0.51 J g^{-1} K^{-1}) and of the pure PES (0.21 J g^{-1} K^{-1}), the decrease in heat capacity change at T_{gPES} (ΔC_{pPES}) in combination with the increase in T_{gPES} for higher isothermal cure temperatures can be understood as a further PES-enrichment of this phase or interphase. This finding is in accordance with the properties measured in the final heating, Figs. 2 and 5 (see also Table 1), and with the increase in ΔC_{pEPAM} discussed in the previous paragraph.

These results point out that the PES-modified epoxy-aniline exhibits a lower critical solution temperature (LCST) behavior [10], as already proven with other methods for PES-modified DGEBA systems [4,6,16]. Fig. 6 illustrates this finding, showing the growing gap between T_{gEPAM} and T_{gPES} as a function of isothermal cure temperature. Full-cure of the matrix is attained for all conditions (T_{iso}>final T_{gEPAM}), so the increase in T_{gPES} with temperature corresponds to further PES-enrichment by expulsion of remaining epoxy-amine chains towards the matrix. This growing compositional difference between the epoxy-rich and
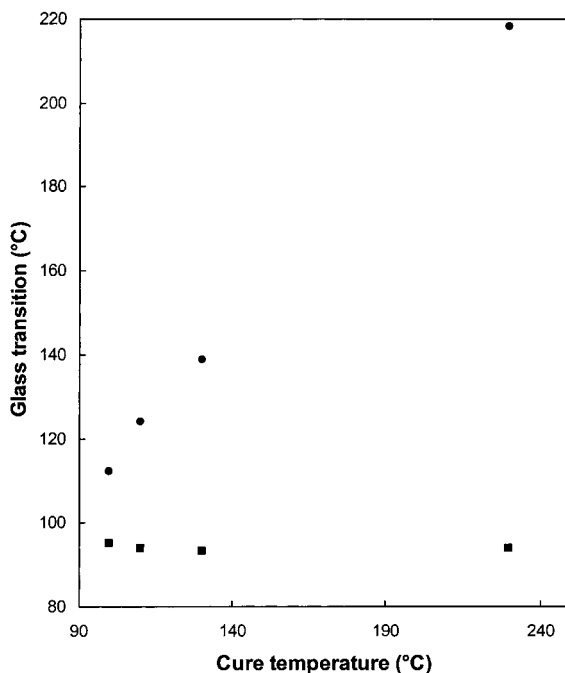

Fig. 6. Glass-transition temperature of the epoxy-amine-rich, T_{gEPAM} (■), and PES-rich, T_{gPES} (●), phases of the DGEBA–aniline/20%PES system vs. isothermal cure temperature, with T_{iso}>final T_{gEPAM}.
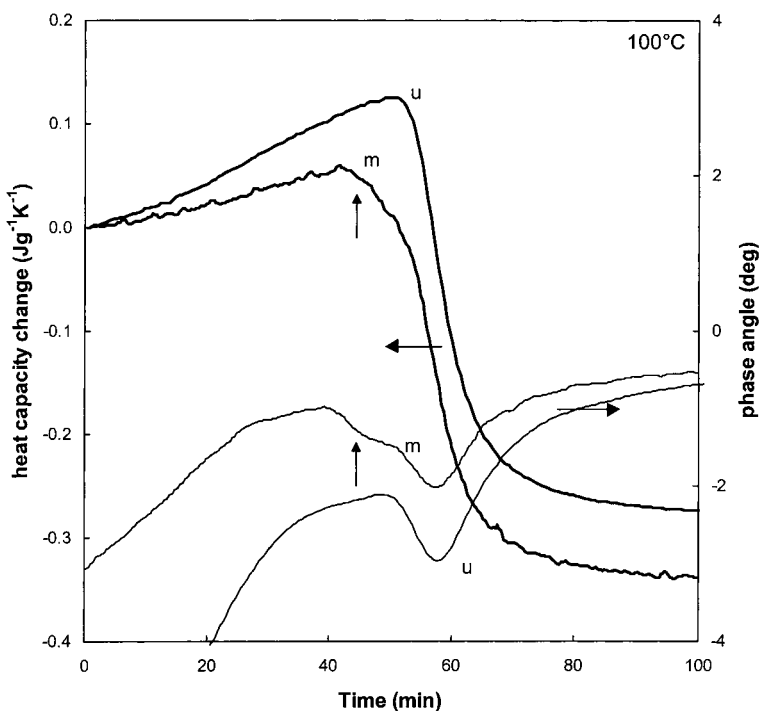
Fig. 7. Cure at 100°C of DGEBA–MDA (unmodified: u) and DGEBA–MDA/20%PES (modified: m) change in heat capacity and heat flow phase.

PES-rich phases with increasing temperature is in agreement with LCST behavior. Note that the highest imposed temperature in Fig. 6 should not be considered as a direct isothermal cure, but in this specific case as an isothermal post-treatment after a pre-cure at a lower temperature.

3.2. Phase separation in combination with vitrification of the matrix during step-growth network formation

The previous discussion can be extended to thermoset cure with network formation. As an example, the quasi-isothermal cure at 100°C of a stoichiometric network-forming epoxy-MDA mixture is depicted in Fig. 7. The tetrafunctionality of the MDA-hardener gives rise to a network structure. In comparison with the linear polymerizing epoxy-aniline of Fig. 1, the reactivity at 100°C of the epoxy-MDA system is approximately two times higher (e.g. measured after 20% reaction conversion). Due to the combination of a high reactivity and high $T_{g\infty}$ (175°C), isothermal cure

is usually performed at a temperature below $T_{g\infty}$ and vitrification will interfere. After an initial increase in heat capacity due to chemical reaction of the unmodified epoxy-MDA curing at 100°C (see also the unmodified epoxy-aniline), vitrification is seen as a fast stepwise decrease in heat capacity with a relaxation peak in the heat flow phase.

For the PES-modified epoxy-MDA, the heat capacity shows two effects, more sensitively depicted in the heat flow phase, indicating again the vitrification of a PES-rich phase as a result of reaction-induced phase separation (see arrows in Fig. 7), followed by vitrification of the matrix. Note that this twofold effect was not measured in situ by Alig et al. [11] for an analogous DGEBA–MDA system (modified with 10 wt% PES), while subsequent non-isothermal experiments clearly indicate that phase separation of a PES-rich phase (with vitrification) should start at least before 70 min at 100°C. As already mentioned for the linear polymerization (see Section 3.1.1), the heat flow phase is a very sensitive tool and valuable in the analysis of phase separation during network for-
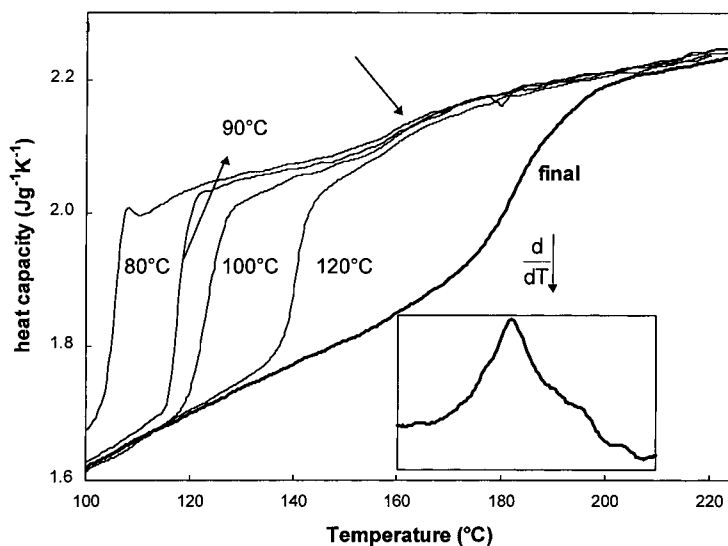
Fig. 8. Heat capacity evolution of DGEBA–MDA/20%PES for non-isothermal post-cure after isothermal cure at 80°C, 90°C, 100°C, and 120°C, and for the final heating; the inset depicts the derivative of the heat capacity for the glass transition region in the final heating.

mation. The high reactivity of this modified network system in combination with its chemorheology, resulting in a higher ratio between the rate of reaction and of phase separation, are probably important for the less pronounced separation of the two effects. The values of ΔH_{iso} for the isothermal steps equal -90 and -85 kJ mol epoxy^{-1} for the unmodified and modified network systems, respectively. Taking into account the corresponding post-cures, with ΔH_{res} of -13 and -17 kJ mol epoxy^{-1}, respectively, results in almost the same values for ΔH_{tot} (-103 vs. -102 kJ mol epoxy^{-1}). The decreased ΔH_{iso} in the modified network system is more pronounced at 80°C (see Table 1). Phase separation of the PES-rich phase and vitrification of the matrix at a lower reaction conversion could both cause this effect.

3.2.1. Influence of isothermal cure temperature and final thermal properties

Apart from the real-time monitoring of phase separation during isothermal cure, the power of TMDSC to separate overlapping thermal phenomena can be used to study the thermal properties (glass transitions) developed in this preceding step via the heat capacity signal, in combination with the residual reaction exothermicity via the non-reversing heat flow signal (see also Section 3.1.2).

The heat capacity evolutions during post-cure experiments after isothermal cure steps at different temperatures for the PES-modified epoxy-MDA system are shown in Fig. 8. Isothermal cure times were chosen long enough so that the reaction rate fell to zero caused by vitrification. As in the linear system, two glass transitions are always observed, corresponding to the epoxy-rich matrix (T_{gEPAM}) and PES-rich dispersed (T_{gPES}) phases. A pronounced evolution in epoxy-rich glass transition illustrates the significant influence of vitrification for cures performed well below $T_{g\infty}$ (175°C). In comparison with the linear polymerizing system, the higher T_g regions, corresponding to the PES-rich phases, are less clearly separated from the narrower T_{gEPAM} regions, corresponding to the epoxy network. This poorer separation was already observed in the isothermal heat capacity evolution of Fig. 7. Moreover, the end temperatures of the T_{gPES} regions almost coincide for the different isothermal cure schedules (see arrow in Fig. 8). This probably means that in this modified network system, phase separation continues during heating before the onset of T_{gPES}, due to devitrification of the epoxy-rich phase followed by residual reaction. After devitrification, phase separation is going on by the combination of increase in conversion (residual reaction) and temperature rise (LCST behavior). A final heating after

full cure shows an increased glass transition for the epoxy-rich phase (T_{gEPAM}>175°C) and a decreased one for the PES-rich phase (T_{gPES}<223°C) in comparison with the pure phases (see Fig. 8 and Table 1). Note that the T_g values for both phases are determined with the derivative of the heat capacity signal (see inset of Fig. 8) [17]. In contrast with the PES-modified linear system, where phase separation resulted in an almost pure epoxy phase, the phases in the PES-modified network system seem more interpenetrated and partially mixed in the experimental conditions studied.

The difference between both epoxy-amines is the result of a complex balance between specific chemical interactions (attractions and repulsions), the reaction chemistry, the simultaneous evolution of thermoset morphology (chemorheology) and phase separation, the ratio of rate of reaction conversion vs. rate of phase separation, etc. Moreover, the imposed experimental conditions can alter the ultimate material properties of these PES-modified epoxy-amines. As an example, T_{gPES} measured after a post-treatment of 100 min at 230°C is higher than the value mentioned as final property for the PES-modified epoxy-aniline (see Fig. 6 and Table 1). Although the final properties mentioned in Table 1 were considered to be characteristic for each full-cured system studied, and independent of the preceding cure schedule, this example shows that the properties, especially for T_{gPES}, can still be altered slightly by applying an isothermal post-treatment at a temperature beyond T_g of pure PES. In comparison with a heating at 2.5°C min^{-1} up to 240°C, more time in mobile conditions during such an isothermal post-treatment is available to reach the thermodynamic equilibrium composition.

4. Conclusions

Temperature modulated DSC allows the real-time monitoring of phase separation induced by cure in epoxy-amine reactive mixtures modified with an amorphous high-T_g engineering thermoplastic, such as polyethersulfone. In quasi-isothermal TMDSC conditions, it has been shown for PES-modified epoxy-aniline (linear polymerization) and epoxy-MDA (network formation) that reaction-induced phase separation is observed as a vitrification of a segregating PES-rich phase. A stepwise decrease of the heat capacity is seen, accompanied by a relaxation peak in the heat flow phase. If cure is performed sufficiently below the full cure glass transition of the unmodified epoxy-amine, both the vitrification of the dispersed PES-rich phase and vitrification of the epoxy-rich matrix can be observed. The heat flow phase signal proves to be valuable to monitor these effects, especially in a thermosetting system. Non-isothermal (post-cure) TMDSC experiments contain information on the in situ formed phases and on the effect of temperature on phase separation, giving support to a LCST phase diagram.

It can be concluded that TMDSC, in combination with other established techniques for studying multi-phase materials, is an excellent new analytical tool for the real-time monitoring of morphology development in complicated reacting systems. Especially the simultaneous information on reaction kinetics via the non-reversing heat flow seems promising. The excellent control of temperature during cure enables reproducible and meaningful results on kinetics of phase separation and cure. The TMDSC method will further be explored and extended to topics such as:

1. The effect of additives (thermoplastic modifiers, fibers in composites) on the kinetics of imposed cure schedules, studied with the simultaneous information of the non-reversing heat flow; a mechanistic approach is needed in this case, taking into account the effect on the reaction rate of the concentration of all components in the reacting mixture.
2. The balance between the kinetics of cure, reaction-induced phase separation and crystallization of reacting polymer systems in the presence of crystallizable thermoplastic modifiers.

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