Macromol. Symp. **2003**, *198*, 363-375

In Situ Monitoring of Reaction-Induced Phase Separation with Modulated Temperature DSC

*Steven Swier, Bruno Van Mele**

Vrije Universiteit Brussel (VUB), Department of Physical Chemistry and Polymer Science, Pleinlaan 2, B-1050 Brussels, Belgium

Summary: A linearly polymerizing and network forming epoxy-amine system, DGEBA-aniline and DGEBA-MDA, respectively, will be modified with 20 wt% and 50 wt% of a high-T_g thermoplastic poly(ether sulphone) (T_g=223°C), respectively, both showing LCST-type demixing behavior. Reaction-induced phase separation (RIPS) in these modified systems is studied using Modulated Temperature DSC (MTDSC) as an in situ tool. Phase separation in the linear system can be probed by vitrification of the PES-rich phase, occurring at a higher conversion than the actual cloud point from light scattering measurements. The negative slope of the cloud point curve in a temperature-conversion-transformation diagram unambiguously shows the LCST-type demixing behavior of this system, while the relation between the composition/glass transition of the PES-rich phase and the cure temperature is responsible for the positive slope of its vitrification line. Phase separation in the network forming system appears as reactivity increases at the cloud point due to the concentration of reactive groups. Different mixture compositions alter the ratio between the rate of phase separation and the rate of reaction, greatly affecting the morphology. Information about this in situ developed structure can be obtained from the heat capacity evolutions in non-isothermal post-cures.

Keywords: curing of polymers, epoxy-amine, modulated temperature differential scanning calorimetry, poly(ether sulphones), reaction-induced phase separation

Introduction

Reaction-induced phase separation (RIPS) is the result of a decrease in the entropic contribution to the free energy of mixing during polymerization.[1] The increase in conversion leads to a 'chemical quench' from the miscible to the immiscible region of the phase diagram by either a decrease of the lower critical solution temperature (LCST: case of poly(ether sulphone), PES) or an increase of the upper critical solution temperature (UCST: case of poly(ether imide), PEI).[2-7] Depending on the composition of the quasi-binary blend, the metastable or unstable region will be entered during this process, in principle resulting in the nucleation and growth or spinodal

DOI: 10.1002/masy.200350831

decomposition mechanism, respectively. However, especially in the case of these high-T_g modifiers, thermodynamics is merely the driving force for phase separation, while the kinetics of interdiffusion between the coexisting phases will become determining at some point.[8,9] Crucial in this respect is the ratio between the rate of phase separation and that of chemical reaction. For a certain modifier chemistry and composition, the cure temperature (T_{cure}) will be the most important parameter influencing both rates at the same time.[10] The interdependence of these rates reveals the complexity in controlling the morphology in these systems. An increase in T_{cure} in a system showing LCST type demixing behavior, for example, will, together with the resulting lower conversion at phase separation (x_{ps}), increase the interdiffusion rates at x_{ps}. However, the corresponding higher cure rate also results in a faster molecular weight increase of the epoxy-amine beyond this point, reducing the diffusion rate of the components in the reactive mixture. Additional points of interest are the gel point of the epoxy-amine and possible vitrification of either of the coexisting phases. The former corresponds to the onset of network formation of the epoxy-amine rich phase, arresting phase separation.[11] The latter occurs in case T_{cure} is below the full cure glass transition of either the epoxy-amine rich phase, T_{gfull} or the modifier-rich phase, T_{gMOD}. Vitrification of either or both these phases can fix the morphology at a certain conversion, thus freezing in a thermodynamically unstable polymer system. To clarify these aspects, Gillham proposed cure diagrams to optimize processing and material properties of epoxy resins.[12] By including the onset of phase separation, the succession of chemical and physical events during isothermal RIPS can be predicted.[13,14] These time-temperature-transformation (TTT) and time-conversion-transformation (TxT) diagrams have to be used with caution, since, in principle, the two phases originating at the cloud point have their own cure diagrams. Thus, cure diagrams can be used to pinpoint the crucial events during RIPS, but adequate control over the morphology requires a measuring technique capable of studying the evolution in chemorheology in situ. Modulated Temperature DSC (MTDSC) has the potential to measure both the reaction advancement and morphological evolution in one experiment with excellent temperature control.[15,16] This was illustrated for PES-modified epoxy-amine systems, for which RIPS can be detected *indirectly* as a stepwise decrease of the heat capacity due to vitrification of the segregating PES-rich phase. The applicability of MTDSC for in situ monitoring of cure advancement (non-reversing heat flow signal) and chemorheological effects (heat capacity signal) will be extended in this work, in combination with optical microscopy as a complementary technique.

Experimental

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 appropriate amounts 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 $g.eq^{-1}$ and 49.5 $g.eq^{-1}$, respectively. Mixtures of these pure systems were modified, respectiviely, with 20 wt% and 50 wt% of low molecular weight, M_w=20,000 $g.mol^{-1}$, poly(ether sulphone) (PES from Aldrich).

Cure experiments were performed on a TA Instruments 2920 DSC with MDSC™ option and a Refrigerated Cooling System (RCS). Helium was used as a purge gas (25 $ml.min^{-1}$). Cure was performed in hermetic aluminum pans (TA Instruments), with sample weights between 5 and 10 mg. Modulation conditions were: amplitude of 1°C and a 60s period. Cloud points were detected by measuring the light transmitted through thin samples (held between glass slides) in a Mettler Toledo FP82HT hot stage equipped with a photodetector. A Spectratech optical microscope was used with a magnification of 4.

Results and Discussion

RIPS as Measured by Vitrification of the PES-Rich Phase

RIPS in the epoxy-amine systems DGEBA+aniline and DGEBA+MDA, modified with the high-T_g engineering thermoplastic PES, can be probed as vitrification of the PES-rich phase.[15,16] The former system modified with 20wt%PES is shown at three cure temperatures in Figure 1. The non-reversing heat flow and the initial increase in the heat capacity signal contain complementary information on the epoxy-amine reaction.[15] The decrease in the heat capacity signal accompanied by a relaxation peak in the heat flow phase marks the time at which the T_g of the PES-rich phase (T_g pure PES =223°C) rises above the cure temperature and the mobility of this phase is frozen in. In case the cure temperature is below the full cure glass transition of the epoxy-amine (T_{gfull}=94°C), vitrification of the segregating phase rich in this component can also take place. This clearly occurs in Figure 1 for the reaction at 80°C, while only partial vitrification is seen at 90°C. Upon curing an unmodified epoxy-amine in a temperature range corresponding to the glass transition region of the fully cured system this effect was also seen.[15]

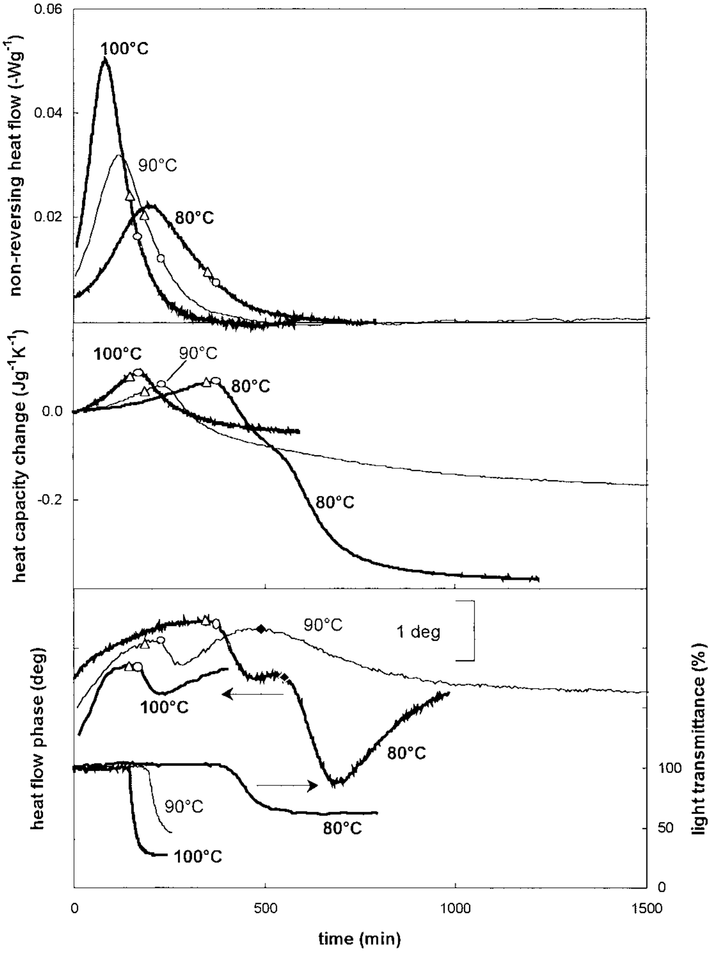

Fig. 1. Non-reversing heat flow, heat capacity change and heat flow phase signal from MTDSC and % of light transmittance from optical microscopy (OM) for the reactive blend DGEBA+aniline(r=1)/20wt%PES cured at 100°C, 90°C and 80°C; the cloud point from OM (Δ), onset of heat flow phase relaxation corresponding to vitrification of PES-rich phase (O) and epoxy-amine-rich phase (♦) are also shown (see text).

The fact that RIPS is not measured directly with MTDSC in this system can be inferred from light transmittance experiments, also performed at 80°C, 90°C and 100°C in Figure 1: the onset of phase separation (cloud point) obtained in this way (Δ) occurs prior to the onset of vitrification of the PES-rich phase calculated from the heat flow phase (○). The latter signal is also used to pinpoint the vitrification of the epoxy-amine rich phase (♦).

Time-Conversion-Transformation (TxT) Diagram for DGEBA+Aniline/20wt%PES

Partial integration of the non-reversing heat flow signal gives the epoxy conversion corresponding to the three major events discussed in Figure 1. A wide range of cure temperatures (60°C-155°C) was studied in this way to construct the TxT diagram of the DGEBA+aniline system modified with 20wt% PES (Figure 2). Cure temperatures higher than 140°C were measured without modulation to decrease the equilibration time for these fast cures. Therefore only the cloud point conversion could be calculated. The negative slope of this curve (Δ) holds proof of the LCST-type demixing behavior of this system: for a higher cure temperature the onset of phase separation will be encountered at lower conversions.[1,10,17]

The vitrification line of the epoxy-amine-rich phase has also been included in Figure 2 (♦) and reflects the expected T_g-x behavior.[12] Further phase separation accompanied by morphology changes will be inhibited beyond this point. This line is also shown for the unmodified epoxy-amine system (×) and matches that of the modified one, meaning that the epoxy-amine-rich phase contains little or no PES. Otherwise, this high-T_g component would increase the glass transition of this phase and decrease the conversion at which vitrification sets in.

In contrast to the cloud point curve, a positive slope is also found for the vitrification line of the PES-rich phase (○). This can be understood by realizing that the T_g of this phase is determined by its *composition* and by the T_g of its constituents. At higher cure temperatures, vitrification occurs for a phase richer in PES. This means that the LCST will have decreased more to achieve purer coexisting phases in comparison to lower cure temperatures. In case a pure PES-phase would be formed at phase separation, vitrification of this phase would occur immediately, resulting in a coinciding cloud point curve and vitrification line.

While this information could also be obtained from the combination of dynamic rheometry or dynamic mechanical analysis, providing the onset of vitrification, and DSC, providing the conversion,[18] the advantage of using one technique that can measure both is evident. By using these complementary techniques, the TxT diagram of an epoxy-amine system modified with PEI has been obtained, where an UCST-type demixing behavior is observed.[13] In this case both the cloud point curve and the vitrification curve were found to exhibit a positive slope, characteristic for this specific demixing behavior.

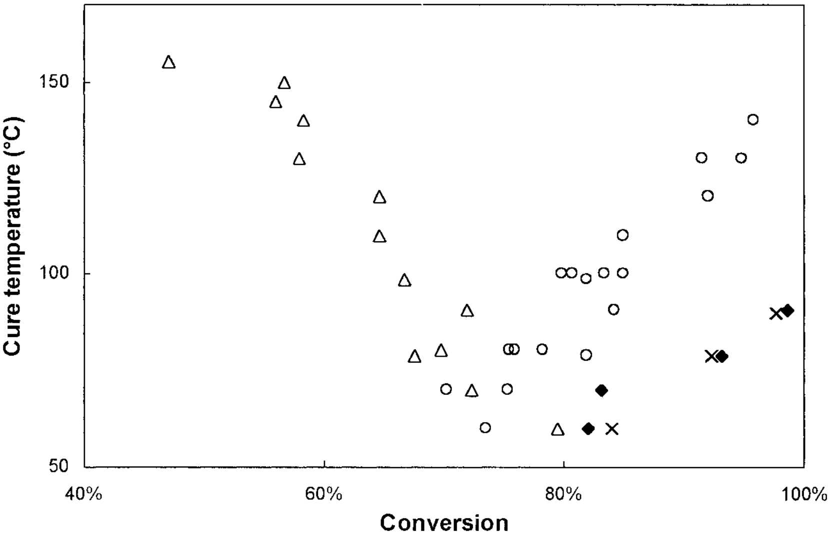

Fig. 2. TxT diagram for a stoichiometric DGEBA+aniline/20wt%PES mixture with: cloud points from optical microscopy (Δ), onset of heat flow phase relaxation corresponding to vitrification of PES-rich phase (O) and epoxy-amine-rich phase (♦); the cloud point at 60°C was obtained by using UV/Vis spectrometry in transmittance at 450nm; the onset in the heat flow phase relaxation corresponding to vitrification of the pure DGEBA+aniline(r=1) is given for reference (×).

The combination of an almost pure epoxy-amine rich-phase and a PES-rich phase changing in composition, reveals the asymmetry of the phase diagram: one branch will be close to the pure epoxy-amine, while the other branch will gradually evolve to purer PES as conversion rises. This has also been simulated within the framework of the Flory-Huggins theory and is related to the difference in molecular weight between PES and the epoxy resin.[7] Phase diagrams constructed for mixtures of DGEBA and PES with different molecular weights also confirm this idea.[2,20] Moreover, non-isothermal post-cure experiments after isothermal cure above T_{gfull} have already shown that the epoxy-amine-rich phase does not attain a glass transition higher than 95°C [16]. Curing at higher temperatures just results in a higher fraction of this phase. While the proposed TxT diagram is essential to control the curing of blends with appropriate pre-curing and post-curing schedules, more information is present about the time-dependency of phase separation and morphology development in the MTDSC experiments itself. This can be seen, for example, in the slow heat capacity and heat flow phase evolutions with time in Figure 1.

Network Forming DGEBA+MDA/50wt%PES: Effect of Reactive Mixture Composition

Reactivity Increase as a Probe for Phase Separation

When epoxy-amine network systems are cured with higher thermoplastic contents, sudden reactivity increases were found at phase separation.[21,22] This can be seen in the DGEBA+MDA (T_{gfull}=175°C for r=1) system, modified with 50wt% PES in Figure 3. In case a stoichiometric mixture of the epoxy-amine is introduced ① , RIPS results in a shoulder in the non-reversing heat flow signal after 20 and 7 min for T_{cure} equaling 130°C and 150°C, respectively. Note that high cure temperatures had to be used here to induce phase separation at low enough conversions. Otherwise vitrification of the relatively high-T_g homogeneous reactive blend occurs prior to the cloud point, and no RIPS can be seen (not shown). The disadvantage of using these high cure temperatures is, however, that the first collected data points are unreliable (dashed line in Figure 3). Instead of using different cure temperatures, the rate of phase separation and reaction can be changed more independently by using different mixture compositions for the reactive epoxy-amine component. This only holds in case this change in epoxy-amine ratio does not affect the position and shape of the phase diagram too much, resulting in a similar driving force at the onset of phase separation, while the reaction rate will increase for higher amounts of the amine. Note, however, that adding an excess of the amine reactive component could increase the miscibility with PES and therefore delay the onset of RIPS. Three mixture compositions of DGEBA+MDA are shown in Figure 3, all cured at 150°C. A decrease in reactivity is seen in the order: excess amine (r=1.4, ②), stoichiometric mixture (r=1, ①) and excess epoxy (r=0.7, ③). The shoulder in the non-reversing heat flow, indicating a reactivity increase accompanying RIPS, is absent in the first mixture.

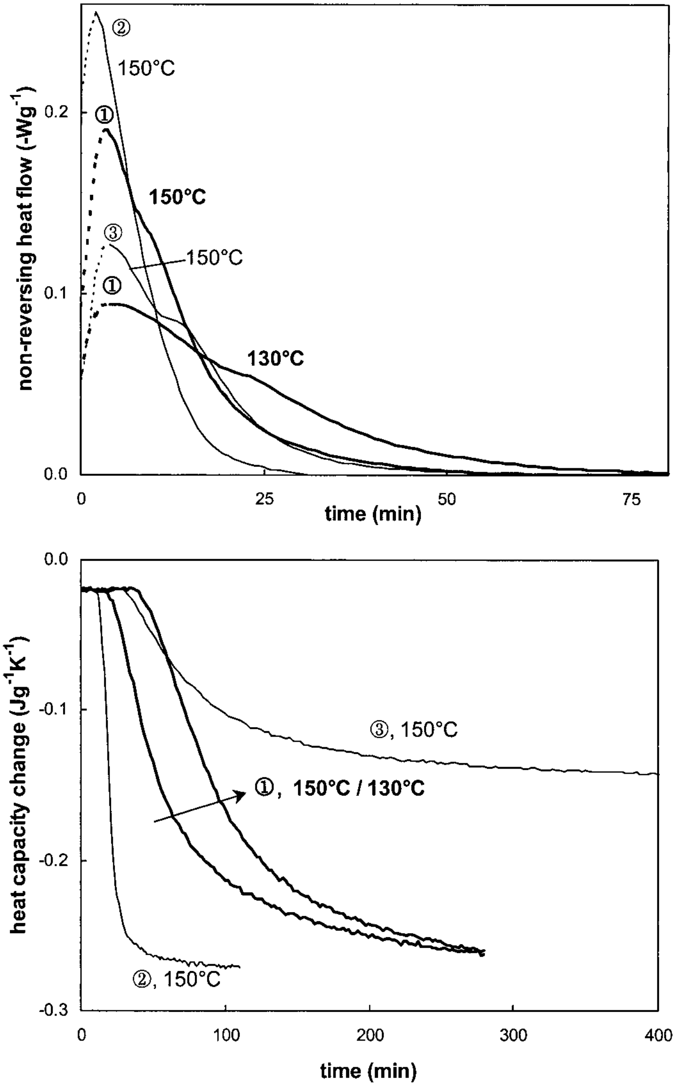

Fig. 3. Non-reversing heat flow and change in heat capacity (note the longer time scale) for the reactive blend DGEBA+MDA/50wt%PES: stoichiometric mixtures of the epoxy-amine are cured at 150°C and 130°C (r=1: ①); an excess amine (r=1.4: ②) and excess epoxy (r=0.7: ③) mixture is cured at 150°C; dashed line corresponds to the time the sample temperature needs to reach the cure temperature within 0.5°C.

Chemorheological Information Obtained in quasi-Isothermal Conditions

The change in heat capacity, also shown in Figure 3, does not exhibit the double step-wise decrease as obtained in the linearly polymerizing system in any of the studied compositions. The fact that the glass transitions of both phases are close together could be responsible for this insensitivity in the stoichiometric system, which was already commented for the same epoxy-amine modified with 20wt% PES.[16] The glass transition of PES (223°C) can be compared to the full cure glass transition of both epoxy-amine systems (T_{gfull}): 175°C for the network-forming system in comparison to 95°C for the linearly polymerizing one. On the other hand, the lower glass transitions of both off-stoichiometric systems means that no vitrification of a *pure* epoxy-amine phase can occur: T_{gfull} for the excess epoxy and amine mixture is 91°C and 140°C, respectively (compare with T_{cure}=150°C). The total decrease in heat capacity can shed some light on these issues. This value is related to the amount of material that has vitrified during the isothermal cure step at, for example, 150°C. For the stoichiometric system with 50wt%PES, this corresponds to vitrifying almost all the material in the mixture. In case of the excess epoxy system, a close correspondence is found with vitrification of the PES phase only. When the excess amine is used, however, the decrease in heat capacity is more than what would be expected for the PES phase alone. This therefore indicates vitrification of a homogeneous, partially reacted mixture of epoxy-amine and PES having a higher glass transition in comparison to the unmodified system.

Derivative of the Heat Capacity Signal in Relation to the in situ Formed Morphology

To clarify the isothermally obtained information, Figure 4 depicts the derivative of the heat capacity signal as a function of temperature for different preceding cure schedules. This method was already proposed to study interphase behavior in interpenetrating polymer networks.[23,24] After the isothermal cure of the stoichiometric system at 150°C this signal has a maximum at 172°C with a shoulder about 10°C lower (a, ①), indicating two phases with a similar glass transition and thus composition. To initiate phase separation at a lower conversion, thus increasing diffusion rates, cure can be performed non-isothermally at a high heating rate (c, ①). It is clear that this method results in a better segregation of the coexisting phases, pointing out the diffusion rate as the rate-determining step. Another issue which is frequently addressed in literature is that the network fixes the morphology, therefore freezing in a thermodynamically unstable system.[1,2] This can be easily shown here by adding a post-cure step at 230°C to the system which was isothermally cured at 150°C and measuring the resulting thermal properties (b, ①). While a better separation of both T_g's is achieved after this post-cure step, the system does not attain the segregation of the non-isothermal cure. Thus looking at the derivative of the heat capacity signal can be useful in the design of cure schedules to achieve a desired end material in view of interphase and morphology. As indicated, curing at lower temperatures increases the interphase, which corresponds to a decrease in particle size[25] For the excess amine system, the non-isothermal post-cure experiment in Figure 4 after the isothermal cure at 150°C only shows one glass transition at 172°C (a, ②), corresponding to the absence of phase separation as envisioned before. The higher reactivity seen in Figure 3 can be held responsible for a reduction in the time available for the development of phase separation. Another possible explanation would be that diffusion rates are lower in comparison to the stoichiometric system, which does show phase separation. This can however be negated by realizing that the highest glass transition is found for the stoichiometric DGEBA+MDA system. As indicated before, a better miscibility of the excess amine mixture could also postpone RIPS in this system. By applying the non-isothermal cure, phase separation can be initiated at a higher temperature (c, ②) and thus lower conversion, resulting in higher diffusion rates. For the excess epoxy system, a much lower glass transition in combination with the lower reactivity will respectively result in higher diffusion rates and more time for morphology evolution at 150°C. The resulting marked segregation is translated in two distinct glass transitions already seen after the isothermal cure at 150°C (a,③: at 110°C and 160°C). Note that while a T_{gEPAM} higher than T_{gfull} is found, due to residual PES present, no vitrification of this phase can occur at 150°C, as concluded from Figure 3. Other cure schedules (non-isothermal at 10°Cmin^{-1} and post-cure at 230°C after cure at 150°C) are also shown here, again pointing out the importance of designing cure schedules with the required morphology in mind. The fact that both schedules result in similar end properties for the excess epoxy means that further interdiffusion to attain the thermodynamically stable end state is not restricted to the same extent as in the other mixtures. The lower crosslink density of this system can be responsible for this effect.[26]

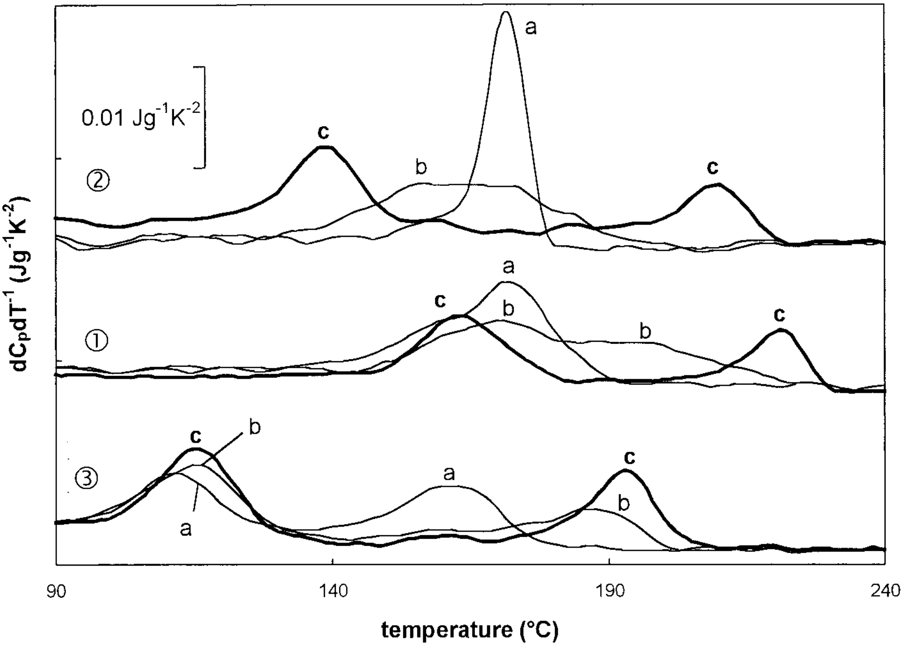

Fig. 4. Derivative of heat capacity to temperature (dCpdT^{-1}) for non-isothermal post-cure measurements at 2.5°Cmin^{-1} following: isothermal cure at 150°C (see Figure 3) (a); isothermal cure at 150°C followed by post-cure at 230°C for 30 min (b) and non-isothermal cure at 10°Cmin^{-1} to 230°C (c); studied systems: stoichiometric (r=1: ①), excess amine (r=1.4: ②) and excess epoxy (r=0.7: ③) DGEBA+MDA/50wt%PES; T_{gfull} equals 175°C, 137°C and 95°C for r=1, r=1.4 and r=0.7, respectively.

Conclusions

The TxT diagram of RIPS in the linearly polymerizing DGEBA+aniline modified with 20wt% PES can be constructed by using MTDSC in conjunction with optical microscopy. This diagram can be used to design appropriate cure schedules. Vitrification times of both the high-T_g PES-rich phase and the low-T_g epoxy-rich phase can be obtained in quasi-isothermal conditions from step-wise decreases in the heat capacity signal, while the corresponding conversions are calculated from the simultaneous non-reversing heat flow information. The cloud point exhibits a negative slope, confirming the LCST-type demixing behavior, while a positive slope is found for the vitrification lines of the PES-rich and epoxy-rich phases, corresponding to their T_g-x behavior. Vitrification lines for the low-T_g phase and the unmodified epoxy-amine coincide, indicative for an asymmetric phase diagram with one branch close to the pure epoxy-amine component.

Both the time-dependency of phase separation and the morphology advancement influence the evolution in the heat capacity signal. This was further illustrated in the network forming system DGEBA+MDA/50wt% PES where the amount of material that freezes in during RIPS can be estimated. When the amine is used in excess (T_{gfull}=140°C), more material is found to freeze in at 150°C than the fraction expected in case only the PES-rich phase would vitrify. The high reactivity of this system, however, does not allow enough time for phase separation to occur. A postponed RIPS can also be held responsible for this effect. Thus, vitrification of a higher T_g homogeneous reactive blend takes place. Lower reactivities are found for the stoichiometric and excess epoxy mixtures (also cured at 150°C), where the non-reversing heat flow does show a reactivity increase in isothermal conditions, indicating a concentration effect of reactive groups at RIPS. The derivative of the heat capacity signal in non-isothermal post-cure experiments confirms the statements made in this paragraph and can also be used to study the effect of cure temperature on the final morphology.

The proposed methodology in this work is further extended for low-T_g triblock copolymer modifiers, where higher interdiffusion rates result in an additional excess contribution in the heat capacity signal.[27] In this way MTDSC can be used as a direct probe for phase separation, instead of measuring an indirect effect like vitrification of the modifier-rich phase or noticing a reactivity increase at the cloud point.

[1] Williams RJJ, Rozenberg BA, Pascault J-P. Advances in Polymer Science 1997;95:128.
[2] Yamanaka K, Inoue T. Polymer 1989;30:622.
[3] Riccardi CC, Borrajo J, Williams RJJ, Girard-Reydet E, Sautereau H, Pascault J-P. Journal of Polymer Science: Part B 1996;34:349.
[4] Jansen BJP, Meijer HEH, Lemstra PJ. Polymer 1999;40:2917.
[5] Yamanaka K, Takagi Y, Inoue T. Polymer 1989;60:1839.
[6] de Graaf LA, Hempenius MA, Möller M. Polymer Preprints 1995;36:787.
[7] Clarke N, McLeish TCB, Jenkins SD. Macromolecules 1995;28:4650.
[8] Kiefer J, Hilborn JG, Hedrick JL. Polymer 1996;37:5715.
[9] Rajagopalan G, Gillespie JW, McKnight SH. Polymer 2000;41:7723.
[10] Tran-Cong Q, Shibayama M. In:"Structure and Properties of Multiphase Polymeric Materials", Ed. Araki T, Marcel Ackker, 1998.
[11] Kim BS, Chiba T, Inoue T. Polymer 1993;34:2809.
[12] Gillham JK, Enns JB. Trends in Polymer Science 1994;2:406.
[13] Girard-Reydet E, Vicard V, Pascault J-P, Sautereau H. Journal of Applied Polymer Science 1997;65:2433.

[14] Boogh L, Pettersson B, Månson J-A. Polymer 1999;40:2249.
[15] Swier S, Van Assche G, Van Hemelrijck A, Rahier H, Verdonck E, Van Mele B. Journal of Thermal Analysis 1998;54:585.
[16] Swier S, Van Mele B. Thermochimica Acta 1999;330:175.
[17] Inoue T. Progress in Polymer Science 1995;20:119.
[18] Ishii Y, Ryan AJ. Macromolecules 2000;33:167.
[19] Bucknall CB, Gomez CM, Quintard I. Polymer 1994;35:353.
[20] Bucknall CB, Gomez CM, Quintard I. Polymer 1994;35:353.
[21] Bonnet A, Pascault J-P, Sautereau H, Taha M., Camberlin Y. Macromolecules 1999;32:8517.
[22] Ritzenthaler S, Girard-Reydet E, Pascault JP. Polymer 2000;41:6375.
[23] Hourston DJ, Song M, Pollock HM, Hammiche A. Journal of Thermal Analysis 1997;49:209.
[24] Hourston DJ, Song M, Schafer F-U, Pollock HM, Hammiche A. Polymer 1999;40:4769.
[25] Martinez I, Martin MD, Eceiza A, Oyanguren P, Mondragon I. Polymer 2000;41:1027.
[26] Oleinik EF. Advances in Polymer Science 1986;80:49.
[27] Swier S, Van Mele B. submitted in Polymer.