ALTERNATING DIFFERENTIAL SCANNING CALORIMETRY: ISOTHERMAL CURING OF THE EPOXY RESIN

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Abstract

In this study the quasi-isothermal curing of diepoxide resin with triamine was investigated by alternating differential scanning calorimetry (ADSC), which is a temperature modulated DSC technique. The complex heat capacity measurements were carried out to analyze the vitrification process at curing temperatures (T_c) below the maximum glass transition of the fully cured epoxy. The modulus of the complex heat capacity $/c_p^*/$ increases until a maximum and then an abrupt decay of $/c_p^*/$, due to the vitrification of the system was observed. The phase angle and out-of phase heat capacity show an asymmetric wide peak during the vitrification process. The abrupt decay of $/c_p^*/$ at vitrification decreases with the increase of T_c and disappears at temperature $T_{g\infty}$. The decay of $/c_p^*/$ during vitrification may be normalized between unity and zero by defining a mobility factor. This mobility factor was used to simulate the reaction rate during the stage where the reaction is controlled by diffusion. The observed reaction rate was simulated by the product of the kinetic reaction rate, determined by the auto-catalytic model, and the mobility factor.

Introduction

Along with "classical" methods of calorimerty, so-called alternating differential scanning calorimetry (ADSC), or temperature modulated differential scanning calorimetry (TMDSC) has been used since 1992, when it was introduced by Reading et al.[1,2] It differs from conventional DSC in that a low-frequency sinusoidal or non-sinusoidal perturbation is overlaid on the baseline temperature profile.[3] The reported advantages of ADCS include improved resolution and sensitivity, in addition to being able to separate overlapping phenomena.[4,5] In the past decade, since the commercialization of ADSC, there has been much work on the theoretical and practical aspects of ADSC.[4-9] Differential scanning calorimetry with a modulated temperature input signal has proven to be very beneficial for the thermal characterization of many materials, especially polymers.[10,11] The simultaneous measurement of heat capacity, heat flow, and the phase angle between heat flow and heating rate also enables a more detailed study of reacting polymer systems,[12] both in isothermal or quasi-isothermal[13-17] and non-isothermal[18,19] conditions and it allows unique insights into the structure and

behavior of materials.

ADSC is based on the temperature modulation during a constant heating rate[13] in the non-isothermal experiments, but the quasi-isothermal conditions mean that the temperature is altered in a sinusoidal fashion with an angular frequency ω (radian s^{-1}) and a sufficiently small amplitude A_T about a constant temperature T_0. In general, it follows:

$$T = T_0 + q_0 t + A_T \sin(\omega t), \tag{1}$$

$$\omega = \frac{2\pi}{t_p}$$

where T_0 is the initial temperature, q_0 is the underlying heating rate which is zero in isothermal experiments and t_p is the period. These three heating - related experimental variables (q_0, A_T, ω) may be used to improve DSC results.[20]

Time dependence of the heating rate is

$$q = q_0 + A_T \omega \cos(\omega t), \tag{2}$$

or in isothermal experiments,

$$q = A_T \omega \cos(\omega t). \tag{3}$$

As a consequence of the periodical variation of *q*, a periodic heat flow signal is obtained, which is shifted by a phase angle δ with respect to the heating rate. The Fourier transformation of the cycles of the heating rate and the heat flow gives the following quantities: q_0 = underlying heating rate, ‹*HF*› = average or total heat flow, A_T = amplitude of the temperature modulation, A_{HF} = amplitude of the heating flow modulation, δ = phase angle between the sinusoidal heat flow and the sinusoidal heating rate.[3]

Schawe[10] defined a complex heat capacity as:

$$C_p^* = C_p' - i C_p'', \tag{4}$$

where C_p' is the real (in-phase) component, and C_p'' the imaginary (out-of-phase) component. This definition of C_p^* shows the connection of the heat capacity with time-dependent molecular movements. The real part of the heat capacity describes molecular motions, the imaginary part is linked to dissipation. The modulus of C_p^* is:

$$\left|C_p^*\right| = \frac{A_{HF}}{A_q}, \tag{5}$$

where A_q is the amplitude of the heating rate modulation ($A_q = A_T\,\omega$). The real and imaginary heat capacities are defined as follows:

$$C_p^{'} = \left|C_p^*\right|\cos\delta, \tag{6}$$

$$C_p^{''} = \left|C_p^*\right|\sin\delta. \tag{7}$$

The in-phase component may be considered as the thermodynamic heat capacity, since it is directly related to the heat flow that is in phase with the heating rate. On the other hand, $C_p^{''}$ should not be approximated to a non-reversing heat capacity.

Furthermore, the approach of reversing and non-reversing heat flow defines the reversing heat flow as

$$\langle HF \rangle_{Rev} = \left|C_p^*\right| q_0 \tag{8}$$

and the non-reversing heat flow as the difference between the total heat flow, $\langle HF \rangle$, and the reversing heat flow,[3] $\langle HF \rangle_{Rev}$.

$$HF_{non-Rev} = \langle HF \rangle - \langle HF \rangle_{Rev}. \tag{9}$$

For isothermal experiments, the curve of the total heat flow is the same as the non-reversing heat flow because the reversing heat flow is zero ($q_0 = 0$).

In this study, the results of quasi-isothermal curing of diepoxide resin with triamine by alternating differential scanning calorimetry (ADSC) will be presented to highlight the unique benefits of the technique to characterize reacting polymer systems. The aim of this work was to study the benefits of this method compared to the conventional DSC. The mechanistic information contained in heat capacity, heat flow, and heat flow phase signals of ADSC will be discussed. The mobility factor determined from the heat capacity was used to simulate the reaction rate during the stage where the reaction is controlled by diffusion. The observed reaction rate was expressed by the product of the kinetic reaction rate, determined by the auto-catalytic model, and the mobility factor. The results are compared with experimental data.

Experimental

Commercial epoxy based on diglycidylether of bisphenol A (CIBA-GEIGY Araldite 250 with an epoxy equivalent of 183 - 189 g eq^{-1}) and diethylene triamine

(Aldrich) were used as a thermosetting system. The substances were mixed together in the stoichiometric ratio.

The measurements were performed on a METTLER TOLEDO 821^e with intra-cooler, using the STAR software with Alternating DSC (ADSC) module. The temperature calibration and the determination of the time constant of the instrument were performed by standards of In and Zn, and the heat flow calibration by In.

The modulation conditions used in the curing reaction were an amplitude of 0.5 K and a period of 1 min. In order to calibrate the heat flow signal, a blank run with an empty pan on the reference side and an empty pan plus a lid at the sample side was performed before the sample measurements. Standard aluminium pans were used and the sample mass was about 10 mg. The experiments of quasi-isothermal curing of the resin were performed at temperatures below and above the glass transition, from 40 °C to 130 °C.

The dynamic glass transition temperature of the fully cured epoxy resin was obtained by ADSC using the same conditions of modulation, 0.5 K and 1 min, and an underlying heating rate of 1 K min^{-1}.

Conventional DSC measurements were also performed by a METTLER TOLEDO 821^e instrument in the temperature range from 25 °C to 200 °C at heating rate 10 °C min^{-1}.

Results and discussion

During the curing reaction, the initial low molecular liquid mixture of the epoxy resin and the curing agent is transformed into a three dimensional cross-linked macromolecule. Clear indication of dramatical changes in the molecular dynamics and macroscopic behavior of the material in this process is the increase of the glass transition temperature (vitrification temperature). The glass transition shifts to higher temperatures during curing. If the glass transition temperature reaches the region of the curing temperature, the sample vitrifies and the reaction kinetics change from being chemically-controlled to diffusion-controlled. The time at which the glass transition temperature equals the reaction temperature is defined as a vitrification time. Beyond the vitrification time, the reaction rate slows down.

If the isothermal reaction temperature is below the glass transition temperature of the fully cured material, the glass transition temperature of the reactive system can pass the actual sample temperature and the molecular mobility is reduced and further reaction becomes diffusion controlled. This process was widely studied by conventional DSC[21] but the change of the heat capacity during reaction is masked by the large exothermal reaction peak. Modulated DSC provides the ability to measure heat capacity directly in a single experiment, and to measure it even at very slow underlying heating rates.[2]
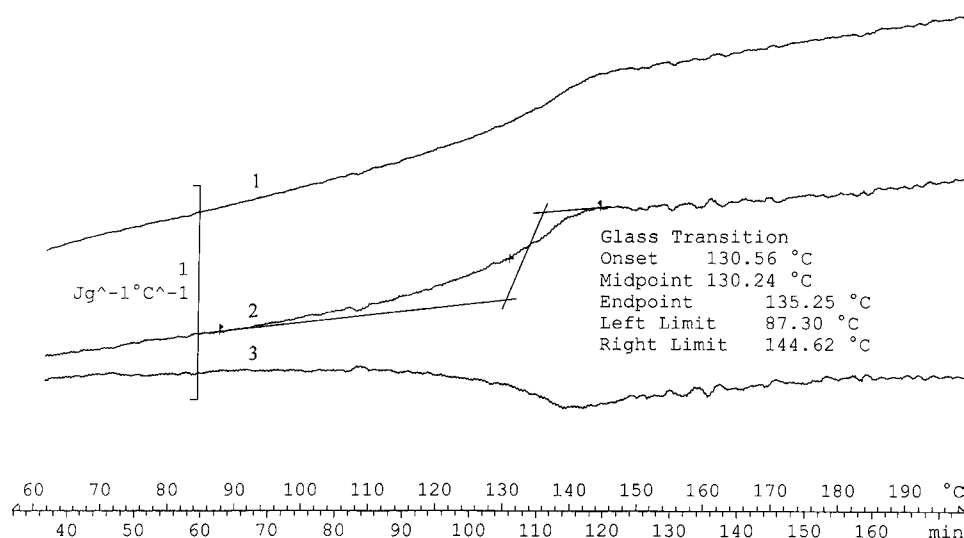

Figure 1. ADSC curves of in-phase (1), modulus of the complex (2) and out-of-phase (3) heat capacities in the glass transition region of the fully cured epoxy resin obtained at heating rate 1 K min^{-1}, amplitude 0.5 K and period 1 min.

The dynamic glass transition was determined at the midpoint of the variation in the modulus of the complex heat capacity for the fully cured epoxy obtained at an underlying heating rate of 1 K min^{-1} and a modulation of 0.5 K at the period of 1 min. As it is shown in Figure 1 this variation gives a value of 130.2 °C. The value of 130.2 °C was taken for the maximum glass transition temperature of the fully cured epoxy, $T_{g\infty}$, which is comparable to previously published results,[4,5,19] where T_g was found to be about 100 °C, however different amines were used as curing agents.

The ADSC signal of the total heat flow shows an exothermic peak (Figure 2) whose area is practically equal to that obtained by conventional DSC at the same curing conditions. The total heat of curing obtained non-isothermally by conventional DSC was 435.6 J g^{-1} which is comparable to the total heat of curing of epoxy resin using different

amines.[4,5] The curing at $T_c < T_{g\infty}$ gives lower heats of curing due to the vitrification effects.
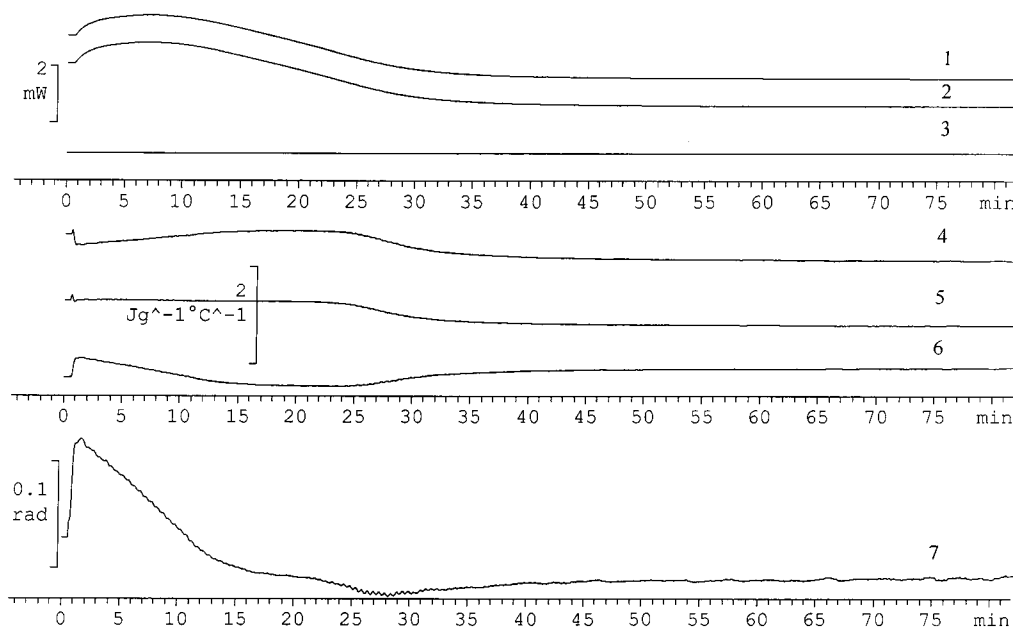

Figure 2. Total (1), non-reversible (2), reversible (3) heat flow, in-phase (4), modulus of the complex (5), out-of-phase (6) heat capacities and phase angle (7) for the quasi-isothermal curing of the epoxy-triamine system at 60 °C with 0.5 K and 1 min modulation.

The values of the total heat flow, heat capacities and phase angle have been analyzed during the quasi-isothermal curing of an epoxy resin cured by triamine at different T_c.

In studied system, the modulus of the complex heat capacity follows a two step variation as it is shown in Figure 2 for the epoxy cured at 60 °C. Initially, the modulus of the complex heat capacity $/c_p^*/$ increases to a maximum and then dramatically decreases. This variation shows a broader peak at $T_c = 50\ °C$ which becomes sharper and shifts to lower times at higher T_c (Figure 3). The initial increase in $/c_p^*/$ may be attributed to the formation of the linear and branched structure by reaction of the primary and secondary amine with epoxy groups. The in-phase part of the complex heat capacity increases slightly at short reaction times ($t_{react.} < 25$ min). In this time interval, the heat capacity measured is related to the liquid state. The almost linear increase in $C_p^{'}$ with time during the initial interval of curing seems to reflect an increase in configurational and/or vibrational contributions in the liquid state originating from network growth.[15]
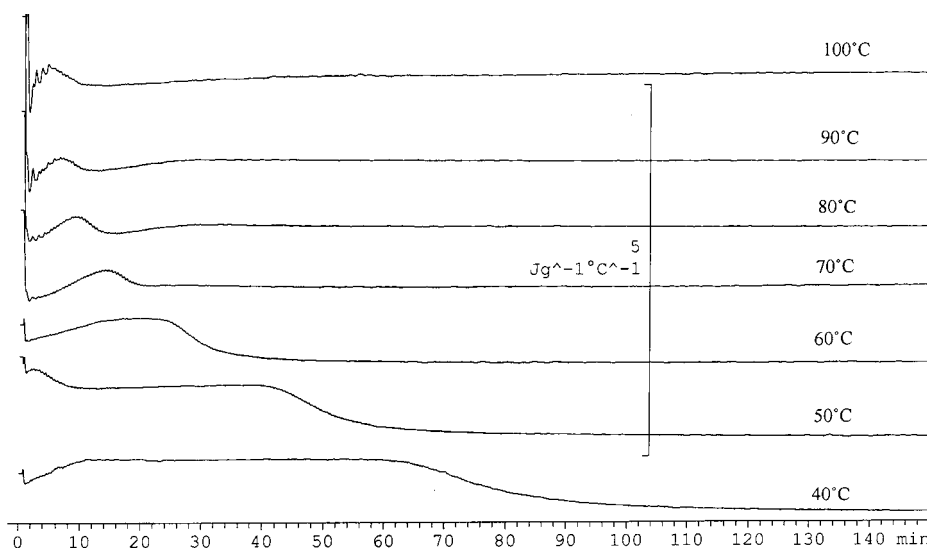
Figure 3. Modulus of the complex specific heat capacity for the quasi-isothermal curing of the epoxy-triamine system at 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, and 100 °C with 0.5 K and 1 min modulation.

It should be noted that in all experimental conditions presented in Figure 3, primary amine-epoxy in combination with secondary amine-epoxy addition reactions are predominant in the reaction mechanism. We could not distinguish between primary and secondary amine-epoxy reactions from the modulus of the complex heat capacity as Montserrat and Cima[13] showed for curing of the epoxy resin with another amine. The ability of ADSC to distinguish between primary and secondary amine-epoxy reactions can be explained in terms of a group additivity estimation method of thermodynamic properties of organic compounds at 298.15 K in the liquid and solid phase.[22,23] According to this method, primary amine-epoxy reactions always give rise to positive variations in heat capacity, whereas the predicted changes in heat capacity for secondary amine-epoxy reactions are almost zero or even negative.

After the maximum is reached the conversion approaches values close to the final depending on the curing conditions (0.68 for $T_c = 40\ ^oC$, or 0.83 for $T_c = 80\ ^oC$). At this conversion the heat capacity drops from a value of the liquid state to the glassy heat capacity. This step is characterized by an abrupt decay of $/c_p^*/$, due to the vitrification of the system. Therefore, an empirical vitrification time $t_{v(mp)}$ may be defined as the midpoint of the Δc_p^* decay. This decay in $/c_p^*/$ is also shown at 90 °C, although less abruptly than at $T_c \geq 100\ ^oC$, due to the proximity to the glass transition region (Figure 3).

The decay in /c_p^*/ during the vitrification is a consequence of a restriction in the mobility of the reactive centres, the system reaches the glassy state and at these conditions the reaction becomes controlled by diffusion. Consequently, the kinetics slows down and conversion tends to a constant value.

After this abrupt decay, /c_p^*/ changes very slowly and becomes nearly constant. This tendency was observed at all curing temperatures for curing times longer than 900 min. When the vitrification of the resin is completed, the conversion remains practically constant and /c_p^*/ should remain constant during the physical ageing process at T_c.

The phase shift signal is very sensitive for changes in the reaction kinetics. The phase angle δ, and the out-of-phase heat capacity $C_p^{''}$ show an asymmetric wide peak in this region (Figure 4). The phase shift shows a negative peak which corresponds to the maximum reaction rate. When the reacting system changes from a viscous liquid to a glassy polymer there is a relaxation process and the phase angle between the temperature modulation and the heat flow changes. At $T_c \geq 100\ ^oC$, both the phase angle and $C_p^{''}$ show an initial decrease and subsequent constancy is observed. If the isothermal cure temperature is chosen close to the glass transition of the fully reacted polymer or network, $T_{g\infty,}$ the system stays in the relaxation region at the end of cure.
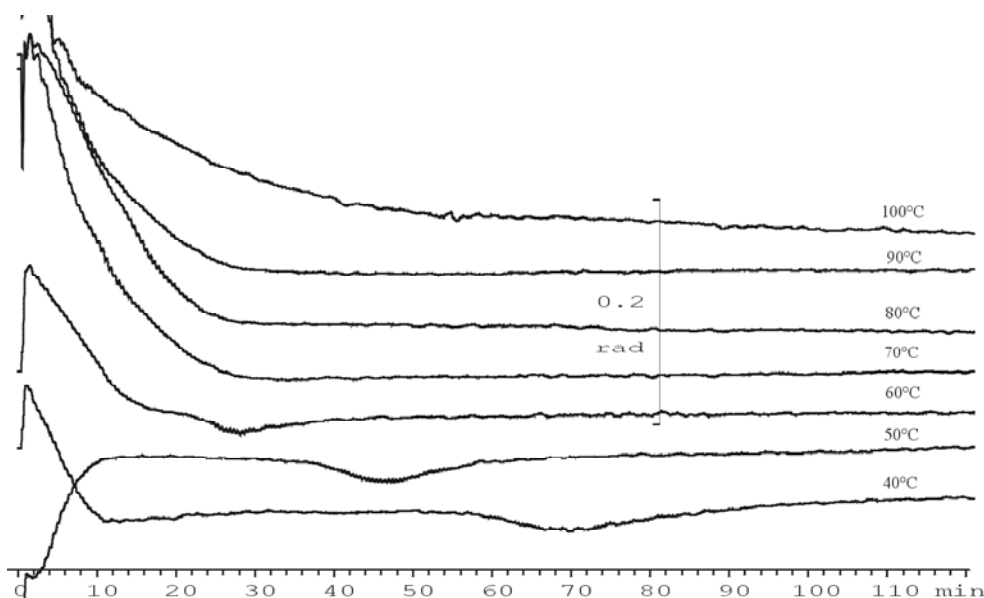

Figure 4. Phase angle in radians for the quasi-isothermal curing of the epoxy-triamine system at 40 ℃, 50 ℃, 60 ℃, 70 ℃, 80 ℃, 90 ℃, and 100 ℃ with 0.5 K and 1 min modulation.

Van Mele et al.[4,5] used the heat capacity change during the reaction measured by ADSC to determine a mobility factor that describes the amount of vitrification during the reaction and which may be used to model the change from a chemically - into a diffusion - controlled reaction. Following this interpretation, the heat capacity change during the reaction measured by ADSC represents the vitrification process or, in other word, the discrepancy between the actual reacting mixture and a physically equilibrated liquid.

The decay in $/c_p{}^*/$ during vitrification may be normalized by a mobility factor, MF:

$$MF = \frac{\left|C_p^*\right|(t,T) - \left|C_{p,g}^*\right|(T)}{\left|C_{p,l}^*\right|(t_0,T) - \left|C_{p,g}^*\right|(T)}, \tag{10}$$

where MF = 1 is assigned up to the onset of the vitrification decay when $\left|C_p^*\right|(t,T) = \left|C_{p,l}^*\right|(t_0,T)$, and MF = 0 is assigned to the end of vitrification at $\left|C_{p,g}^*\right|(T)$.

Van Mele[4,5] proposed an empirical model based on a normalized diffusion factor in order to describe the effects of the decrease of the mobility on the reaction rate:

$$\left[\frac{d\alpha}{dt}(\alpha,T)\right]_{exp} = \left[\frac{d\alpha}{dt}(\alpha,T)\right]_{kin} DF(\alpha,T), \tag{11}$$

where

α is conversion, $\left(\dfrac{d\alpha}{dt}\right)_{exp}$ is the experimentally observed reaction rate, and $\left(\dfrac{d\alpha}{dt}\right)_{kin}$ is the chemical rate calculated by a model for the chemical kinetics in the absence of diffusion control.

Authors[4,5] show that for the epoxy systems this diffusion factor coincides with the mobility factor calculated from the complex heat capacity measurements. Then, in order to simulate the reaction rate of the curing process, the following equation may be used:

$$\left[\frac{d\alpha}{dt}(\alpha,T)\right]_{exp} = \left[\frac{d\alpha}{dt}(\alpha,T)\right]_{kin} MF(\alpha,T). \tag{12}$$

The chemical reaction rate may be calculated by the autocatalytic model (Sesták - Berggren model):[19]

$$\left[\frac{d\alpha}{dt}(\alpha,T)\right]_{kin} = k\alpha^m(1-\alpha)^n. \tag{13}$$

where *k* is a rate constant of Arrhenium type.

This problem may be solved, however, if the activation energy is known. An alternative method of calculation of the activation energy is the isoconversional method, which follows from the logarithmic form of the kinetic equation:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[A\,f(\alpha)] - \frac{E_a}{RT} \qquad (14)$$

The slope of ln(dα/dt) versus 1/T for the same value of α gives the value of the activation energy. This procedure may be repeated for various values of α, from which an average value of the activation energy of 51.2 kJ mol^{-1} was calculated.

The kinetic parameters were calculated by the method proposed by Málek.[18] Table 1 shows the kinetic parameters *m*, *n* in *lnA* obtained by multilinear regression of ADSC heat flow data using Eq. 13.

Table 1. Kinetic parameters obtained by ADSC heat flow data.

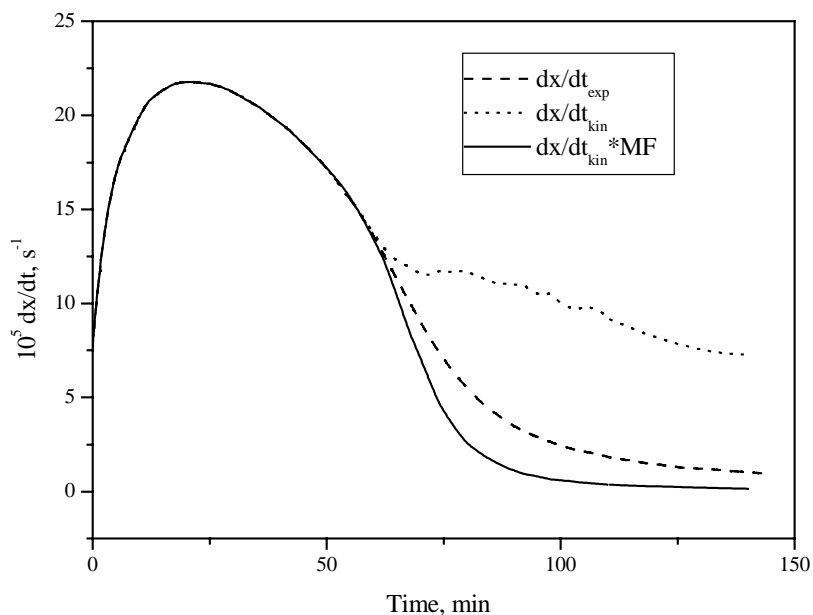|	
$\underline{m}$, /	0.21 ± 0.05
$\underline{n}$, /	0.74 ± 0.06
lnA	11.8 ± 1.3
E_a , kJ mol^{-1}	51.2 ± 3.6

Figure 5. Rate of conversion against curing time for the curing at 40 °C. The dash line shows the experimental reaction rate, the dot line corresponds to the kinetic rate without mobility restrictions and the solid line shows the simulated rate obtained by the product of the kinetic rate and the mobility factor.

In Figure 5, the rate of conversion against curing time for the curing of epoxy - triamine system at 40 ℃ is shown. The dash line shows the experimental reaction rate calculated from the ADSC heat flow data, the dot line corresponds to the kinetic reaction rate without mobility restrictions calculated from Eq. 13 and the solid line shows the simulated reaction rate obtained by the product of the kinetic rate and the mobility factor applying Eq. 12. In general, there is a good agreement between the experimental and the simulated reaction rate of curing epoxy-triamine system in chemical controlled reaction at 40 ℃ as well as at other curing temperatures T_c = 50 ℃ - 100 ℃. After the vitrification time a small uncertainty in the description of the diffusion control influence on the reaction kinetics was observed. The reason for this is the frequency dependent heat capacity, which was not taken into account in our calculations of simulated reaction rate.

Conclusions

Alternating DSC is a technique that promises to significantly enhance the diversity of information which can be obtained from DSC. The ability to separate reversing and non-reversing transitions, as well as the ability to directly measure heat capacity, offers thermal analysts another tool for solving difficult materials characterization problems. This technique allows the study of the kinetics of the curing reaction when it is controlled mainly by the chemical reactivity of the functional groups and also when it is controlled by the diffusion of the reactive centers, as it is the case for low curing temperatures. Furthermore, it is shown that the ADSC measurements of the heat capacity during reactions yield additional information on the reactions kinetics and the mechanism of cross-linking.

In studied epoxy triamine system, the complex heat capacity shows a variation in two steps. Initially, $/c_p^*/$ increases until a peak is reached, followed by an abrupt decay. The decay of $/c_p^*/$ during vitrification may be normalized by defining a mobility factor. This mobility factor was used to simulate the reaction rate during the stage where the reaction is controlled by diffusion.

Acknowledgements

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Povzetek

V prispevku je predstavljen študij kvazi-izotermnega utrjevanja diepoksidne smole s triaminom z izmenično diferenčno dinamično kalorimetrijo (ADSC), ki je temperaturno modulirana DSC tehnika. Z meritvami kompleksne toplotne kapacitete smo spremljali proces zamreževanja epoksi smole pri temperaturah utrjevanja pod maksimalno temperaturo steklastega prehoda popolnoma utrjene epoksi smole. Na začetku vrednost kompleksne toplotne kapacitete /c_p^*/ narašča do maksimuma in nato zaradi zamreževanja sistema drastično pade. Spremljali smo čas zamreževanja pri različnih temperaturah utrjevanja. Fazni kot in izvenfazna c_p kažeta nesimetričen širok signal med zamreževanjem. Sprememba v /c_p^*/ pri zamreževanju pada z naraščajočo temperaturo utrjevanja in ima vrednost nič pri $T = T_{g\infty}$. Spremembo /c_p^*/ med zamreževanjem lahko normaliziramo med 1 in 0 z vpeljavo mobilnega faktorja (MF). Mobilni faktor smo vpeljali pri simulaciji hitrosti reakcije v območju, kjer je reakcija kontrolirana z difuzijo. Opazovano hitrost reakcije simuliramo kot produkt kinetične hitrosti reakcije, določene z avtokatalitičnim modelom, in mobilnega faktorja.