

DSC STUDY OF CURE KINETICS OF DGEBA-BASED EPOXY RESIN WITH POLY(OXYPROPYLENE) DIAMINE

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A kinetic study of cure kinetics of epoxy resin based on a diglycidyl ether of Bisphenol A (DGEBA), with poly(oxypropylene) diamine (Jeffamine D230) as a curing agent, was performed by means of differential scanning calorimetry (DSC). Isothermal and dynamic DSC characterizations of stoichiometric and sub-stoichiometric mixtures were performed. The kinetics of cure was described successfully by empirical models in wide temperature range. System with sub-stoichiometric content of amine showed evidence of two separate reactions, second of which was presumed to be etherification reaction. Catalytic influence of hydroxyl groups formed by epoxy-amine addition was determined.

Keywords: cure kinetics, DSC, epoxy resin, poly(oxypropylene) diamine

Introduction

Epoxy resins are polymer materials with wide area of application, either unmodified or as matrices for composite materials. To achieve desired end-properties of this thermosetting material, it is essential to control the degree of cure. However, the cure follows a complex reaction mechanism, further influenced by the effects of gelation and vitrification, and therefore most authors use empirical models to describe the kinetics of epoxy cure.

Differential scanning calorimetry (DSC) has been widely recognised as useful method to determine cure kinetics of thermoset resins [1–6]. With presumption that the heat flow as measured by DSC, dH/dt , is proportional to the rate of reaction, $d\alpha/dt$, it is possible to determine extent of fractional conversion, α , directly from the experimental curve by partial integration:

$$\alpha = \frac{1}{\Delta H_T} \int_0^t \frac{dH}{dt} dt \quad (1)$$

where ΔH_T stands for the total heat of reaction as determined by dynamic DSC scans.

In this work, we investigated cure kinetics of diglycidyl ether of bisphenol A (DGEBA) with poly(oxypropylene) diamine (Jeffamine D230), both in stoichiometric and sub-stoichiometric ratio. To our knowledge, cure kinetics of this system has not as yet been investigated. Several workers investigated DGEBA-poly(oxypropylene) amine systems [7–14], but only Montserrat *et al.* [15] studied the cure kinetics of DGEBA, with a poly(oxypropylene) triamine, Jeffamine T-430, as a curing agent.

Experimental

Materials

An epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Epikote 828 EL, Shell Chemicals), with the epoxy equivalent mass of 190 g mol^{-1} , was used. Poly(oxypropylene) diamine (Jeffamine D230, Huntsman Corporation) with N–H equivalent mass of 57.5 g mol^{-1} was added as a curing agent for epoxy groups. The materials were used as received. To prepare the thermoset system, Jeffamine D230 was added to DGEBA in stoichiometric (30 phr) and sub-stoichiometric (20 phr) amount. The two systems are referred to as DGEBA-30a and DGEBA-20a, respectively. Components were blended at room temperature in a closed vessel for 90 min.

Methods

The cure of investigated systems was studied by means of DSC on a Netzsch DSC 200 differential scanning calorimeter, using an empty aluminium pan as a reference. For isothermal experiments, sample was placed in the pre-heated DSC cell, and scan was started when the temperature equilibrium was regained. In non-isothermal experiments, sample was heated from room temperature to 520 K, with linear heating rates of 5 and 10 K min^{-1} . The total heat of reaction, ΔH_T , was estimated from non-isothermal experiments by drawing a linear baseline and integrating the area under the peak. The heat of isothermal reaction, ΔH_i , was estimated by extrapolating the final baseline.

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Dynamic DSC experiments were also performed to determine the glass transition temperature, T_g , of an uncured and completely cured material. To determine the latter, the sample was heated from room temperature to 520 K at 10 K min^{-1} , then cooled in the DSC cell to 273 K at 10 K min^{-1} and immediately reheated to 520 K at 10 K min^{-1} . T_g was taken as the midpoint of the endothermic step transition.

Results and discussion

Dynamic DSC characterization

DSC curves of investigated systems obtained at heating rates of 5 and 10 K min^{-1} are shown in Fig. 1. While the exothermic peaks for the system DGEBA-30a are symmetrical, the peaks for system DGEBA-20a are markedly asymmetrical and have lower intensity. This asymmetry could be due to different reactions taking place. It is generally agreed [1, 16] that in reaction between epoxides and amines the epoxy-amine addition, which occurs in two stages, is the most important. This reaction is catalysed by acids, and the hydroxyl groups generated by the amine-epoxide addition act as active catalysts. Thus the curing reaction usually shows an accelerating rate in its early stages, typical of auto-catalysis. When epoxy groups are present in excess, etherification reaction between secondary hydroxyl groups and epoxy groups becomes significant as well.

The total heat of all reactions, ΔH_T , was found to be 270 and 430 J g^{-1} for DGEBA-20a and DGEBA-30a, respectively. Upon conversion of ΔH_T into J mol^{-1} of epoxy, obtained values were 61.6 and $106.3 \text{ kJ mol}^{-1}$, respectively. Value of $106.3 \text{ kJ mol}^{-1}$ for stoichiometric mixture is in accordance with the literature value for epoxy-amine reaction [1], and indicates a complete conversion of epoxy groups, while

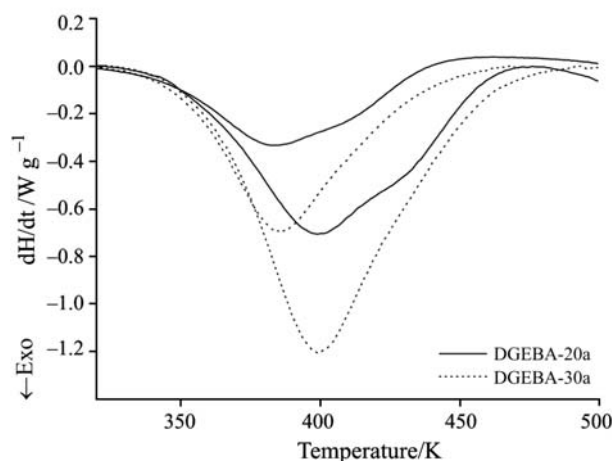


Fig. 1 Dynamic DSC curves for investigated systems at heating rates of 5 (shallower minima) and 10 K min^{-1}

61.6 kJ mol^{-1} is approximately two-thirds of this value. From this it is presumed that, due to sub-stoichiometric ratio of amine to epoxy, only a part of epoxy groups in DGEBA-20a were able to react.

The glass transition temperatures of fully cured stoichiometric system (DGEBA-30a) is higher than $T_{g\infty}$ of non-stoichiometric DGEBA-20a system (356 and 314 K, respectively), as was expected from the literature data [17].

Isothermal DSC characterization

Isothermal DSC characterization was performed at three (DGEBA-30a) or four (DGEBA-20a) temperatures in 5 K increments. The calculated values of the total heat developed, ΔH_i , are given in Table 1. It is worth noting that for both systems all isothermal cure temperatures were higher than $T_{g\infty}$ (356 and 314 K) so isothermal vitrification was avoided [18].

Table 1 Heat of reaction in isothermal conditions and final fractional conversion for investigated systems

System	T_i/K	$\Delta H_i/\text{J g}^{-1}$	α_{max}
DGEBA-30a	370	425	1.000
	375	421	1.000
	380	426	1.000
DGEBA-20a	369	189	0.700
	374	216	0.800
	379	223	0.826
	384	224	0.830

For DGEBA-30a ΔH_i are comparable to the heat developed during dynamic DSC characterization, and the complete cure can be supposed. DGEBA-20a shows much smaller ΔH_i in comparison with ΔH_T . Final fractional conversion, α_{max} , of isothermal cure for DGEBA-20a was thus calculated, with ΔH_T as determined by dynamic DSC tests as the basis for ultimate fractional conversion $\alpha_{\text{max}}=1$. These values are also listed in Table 1. In the investigated interval of curing temperatures for DGEBA-20a system, a linear variation of the final fractional conversion vs. the temperature of isothermal cure was obtained.

Kinetic modelling of the cure for DGEBA-30a system

The rate of reaction, $d\alpha/dt$, as a function of time was obtained from the rate of heat flow measured in isothermal DSC experiments, dH/dt , by:

$$d\alpha/dt = (dH/dt)/\Delta H_T \quad (2)$$

The experimental data were tested first to the auto-catalytic reaction model developed by Kamal [19], which is widely applied to model the cure of epoxy resins [2–4]:

$$d\alpha/dt=(k_1+k_2\alpha^m)(1-\alpha)^n \quad (3)$$

Parameters of the model (3), k_1 , k_2 , m and n , were determined from each isothermal curve by Levenberg–Marquardt non-linear regression analysis (program Microcal Origin 6.0), with assumption that $m+n=2$ [2, 3]. Parameters m and n were found to be insensitive to temperature, and the average values were used in modelling. The temperature dependence of the apparent rate constants, k_1 and k_2 , was found to follow an Arrhenius relationship:

$$k=k_0\exp(-E_a/RT) \quad (4)$$

The parameters of the kinetic model (3) are summarised in Table 2.

To test the calculated parameters, differential Eq. (3) was solved numerically (program Wolfram Mathematica 4.1) for non-isothermal conditions. Figure 2 shows satisfying overlap of modelling results with experimental data. Thus, the kinetic model with parameters determined by isothermal measurements in relatively narrow temperature interval could be used to describe the dependence of reaction rate on temperature in non-isothermal conditions and for much wider temperature interval.

Kinetic modelling of the cure for DGEBA-20a system

For system DGEBA-20a, a modification of Kamal model suggested by Kenny *et al.* [20], which can account for the variation of fractional conversion α_{\max} , was applied:

$$d\alpha/dt=(k_1+k_2\alpha^m)(\alpha_{\max}-\alpha)^n \quad (5)$$

Parameters of the model (5), k_1 , k_2 , m , n and α_{\max} were determined as already described, with assumption that $m+n=2$. Good correlation of $(d\alpha/dt)$ vs. α data was observed up to approximately 40% conversion at all in-

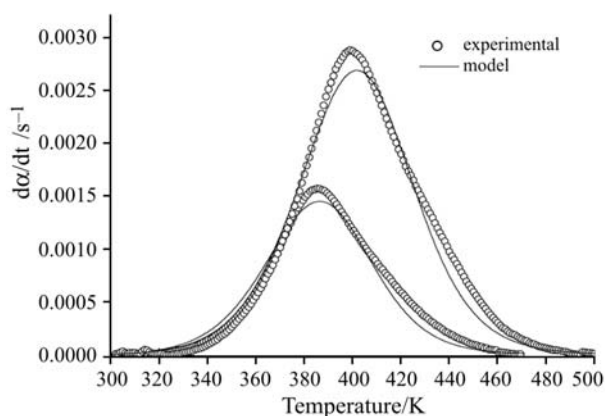


Fig. 2 Comparison of experimental data for DGEBA-30a system with the kinetic model data at heating rates of 5 (lower maximum) and 10 K min⁻¹

Table 2 Parameters of the kinetic model (3) for DGEBA-30a system

Pre-exponential factor	Activation energy	m	n
$k_{01}/s^{-1} \exp(14.8)$	$E_{a1}/kJ \text{ mol}^{-1} 67.2$	0.58	1.42
$k_{02}/s^{-1} \exp(0.9)$	$E_{a2}/kJ \text{ mol}^{-1} 22.5$		

vestigated temperatures (Fig. 3). In order to obtain a better fit for the whole conversion range, two reactions were assumed: amine addition and etherification. The reaction rate profiles were correspondingly divided in two contributions, $d\alpha_1/dt$ and $d\alpha_2/dt$, by subtracting the ‘theoretical’ $d\alpha_1/dt$ curve (obtained as described for $\alpha \leq 0.4$) from the experimental $d\alpha/dt$ vs. t curve to obtain $d\alpha_2/dt$ contribution (Fig. 4). By partial integration of the area under this curve the fractional conversion α_2 as a function of time was obtained. The data were tested on the phenomenological autocatalytic model:

$$(d\alpha_2 / dt) = k\alpha_2^m (\alpha_{\max 2} - \alpha_2)^n \quad (6)$$

Parameters of the model (6), k , m , n and $\alpha_{\max 2}$ were determined as already described, also with assumption that $m+n=2$. $\alpha_{\max 2}$ is the maximum fractional conversion at a given temperature that corresponds to the second assumed reaction. As seen in Fig. 3, the theoretical values for $\alpha_{\max 1}$ at all investigated temperatures were very similar, ranging from 0.63 to 0.69. To reduce the number of parameters, an average value of 0.67 was assumed. Therefore, $\alpha_{\max 2}$ cannot be higher than 0.33. Parameters m and n were found to be insensitive to temperature for both models (5) and (6). The temperature dependence of the apparent rate constants, k_1 and k_2 (model (5)), and k (model (6)), follows an Arrhenius relationship. Parameters of the kinetic models for DGEBA-20a are summarized in Table 3.

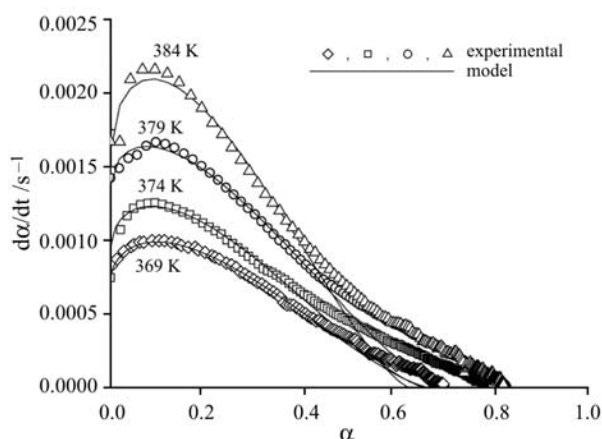
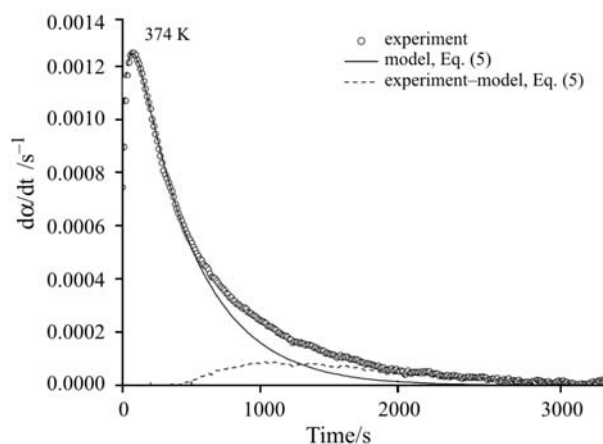
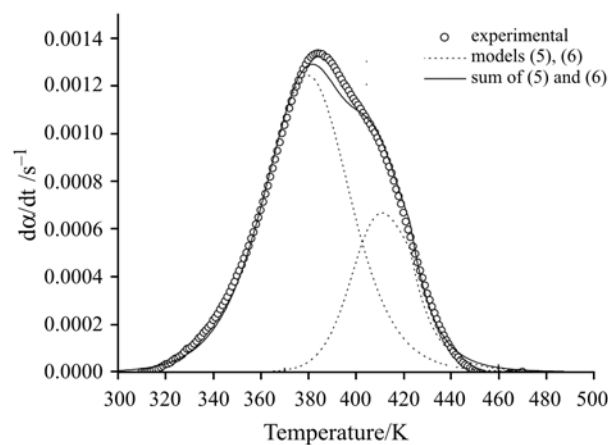


Fig. 3 Fitting of the $d\alpha/dt$ vs. α curves for DGEBA-20a to the kinetic model (5) at reported temperatures of isothermal curve

Table 3 Parameters of the kinetic models (5) and (6) for DGEBA-20a system

Model	Pre-exponential factor	Activation energy	m	n	α_{\max}
(5)	$k_{01}/s^{-1} \exp(15.4)$ $k_{02}/s^{-1} \exp(11.1)$	$E_{a1}/kJ \text{ mol}^{-1}$ 67.7 $E_{a2}/kJ \text{ mol}^{-1}$ 51.4	0.58	1.42	0.67
(6)	$k_0/s^{-1} \exp(9.6)$	$E_a/kJ \text{ mol}^{-1}$ 43.2	0.56	1.44	$-0.99+0.003T$

**Fig. 4** Separation of the experimental reaction rate profile for DGEBA-20a in contributions of two assumed reactions**Fig. 5** Comparison of experimental data for DGEBA-20a system with the kinetic model data at heating rate of 5 K min⁻¹

To test the calculated parameters, differential Eqs (5) and (6) were solved numerically as already described, and good correspondence with experimental data is shown in Fig. 5.

Comparison of kinetic parameters for both systems shows great similarities between parameters of model (3) for DGEBA-30a and model (5) for DGEBA-20a. Parameters m and n are identical, and E_{a1} and k_{01} very similar and comparable to those from [1], which is to be expected since both kinetic models describe the same reaction. However, DGEBA-30a has much lower E_{a2} , which is characteristic for epoxy-ring opening catalyzed by hydroxyl groups generated by

the reaction [21, 22]. Since DGEBA-30a system contains more amine groups than the DGEBA-20a system, concentration of formed hydroxyl groups is greater, and their catalytic influence significantly lowers the activation energy.

Conclusions

Curing kinetics of DGEBA/Jeffamine D230 systems was studied by means of DSC. Cure kinetics of system DGEBA-30a, with stoichiometric content of amine, can be successfully described with Kamal model. Catalytic influence of hydroxyl groups formed by epoxy-amine addition on the reaction of cure was determined. System DGEBA-20a with sub-stoichiometric content of amine showed evidence of two separate reactions, second of which was presumed to be etherification reaction. Total heat of reaction for DGEBA-20a system was markedly lower than for DGEBA-30a system, indicating incomplete reaction of epoxy groups. The results are in good agreement with the literature data.

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