

DSC Study on Simultaneous Interpenetrating Polymer Network Formation of Epoxy Resin and Unsaturated Polyester

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ABSTRACT: A kinetic study on simultaneous interpenetrating polymer network formation of epoxy resin based on diglycidyl ether of Bisphenol A (DGEBA) and unsaturated polyester (UP) was performed by means of differential scanning calorimetry (DSC). Isothermal DSC characterizations of neat resins and their mixture (in a weight ratio of 50/50) were performed at different temperatures. Dynamic DSC characterization of the systems were performed at three different heating rates. A lower total heat of reaction developed during simultaneous polymerization in dynamic DSC tests was found, compared to the total heats developed during pure resins network formation. This phenomenon can be interpreted as an effect of network interlock that could not be compensated for completely by an increase in curing temperature. The kinetics of the reactions was described by empirical models. The DGEBA, in a 50/50 UP/DGEBA blend, indicated a higher rate constant than the pure DGEBA. The obtained results suggests that the hydroxyl end group of UP in the blend provided a favorably catalytic environment for the DGEBA cure. The results are in good agreement with the literature data. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2689–2698, 2002

Key words: DSC; IPNs; thermosets; kinetics

INTRODUCTION

In recent years, an intense research has been devoted to the development of interpenetrating polymer networks (IPNs). Interpenetrating polymer networks are a new class of polymer blends that can be defined as a mixture of two or more crosslinked polymers held together predominantly by permanent entanglement of net-

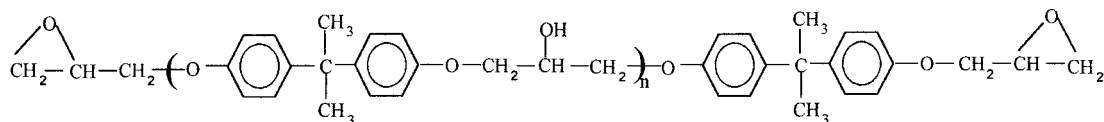
works rather than by covalent bond grafting.^{1,2} Based on synthetic routes, IPNs have been classified into sequential IPNs and simultaneous IPNs. The first are made by swelling polymer network I with a monomer or prepolymer mixture II, followed by polymerization of the latter. To prepare the second, all monomers or prepolymers and their corresponding crosslinkers are mixed together, before polymerization of either component. Such systems require noninterfering routes for the two polymerizations. In the preparation of simultaneous interpenetrating networks it is important to control the rates of both polymerizations. Polymerization kinetics

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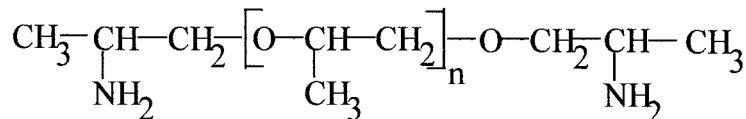
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Table I Chemical Structure of the Materials Used

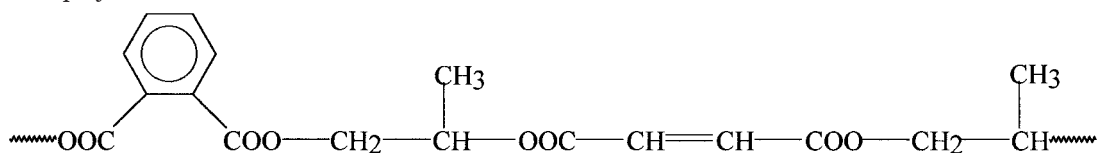
Epoxy : DGEBA



Curing agent : Poly(oxypropylene)diamine



Unsaturated polyester:



of an IPN, which is a multicomponent system, are far more complicated than those of a single polymer.

Blending of two thermosets such as epoxy resin and unsaturated polyester via interpenetrating polymer networks is reported in the literature.³⁻⁶ The epoxy and unsaturated polyester resins have gained major acceptance for the fabrication of high-performance composites. The former exhibits excellent mechanical properties and good adhesion to metals and carbon fiber, while the cost of the latter is lower. Their IPN materials could provide balanced performance and cost.

The curing of epoxy proceeds via a stepwise mechanism,⁷ while UP curing proceeds via a radical chain mechanism.⁸ Each network formation is expected to proceed independently.⁶

Lin and coworkers reported on the chemorheology,³ on the kinetics⁴ studied by Fourier transform infrared (FTIR), and on the mechanical properties⁵ of UP/epoxy IPNs.

In this article, we would like to report on DSC kinetic studies on simultaneous interpenetrating polymer network formation of epoxy resin and unsaturated polyester, and to compare the results with the kinetic data reported in the literature.⁴

EXPERIMENTAL

Materials

An epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Epikote 828 EL), with an epoxy equivalent weight of 190, was obtained from Shell Co. Poly(oxypropylene)diamine (Jeffamine D230, Huntsman Corporation) with N—H equivalent weight of 57.5 g/mol was used as a curing agent for DGEBA. General purpose UP (Chromoplast A-150) based on propylene glycol, isophthalic anhydride, and maleic anhydride in styrene was obtained from Chromos, Croatia. The acid value was 17.2 mg KOH/g, as reported by the supplier. Methyl ethyl ketone peroxide (MEKP) obtained from the same supplier was used as the free radical initiator for the polymerization of polyester resin. The materials were used as received. Chemical structures of the ingredients used are displayed in Table I.

Sample Preparation

To prepare the UP thermoset system MEKP (1 phr based on UP resin) was added to the UP resin. To prepare the DGEBA thermoset system an appropriate amount of Jeffamine D230 (20phr) was added to the epoxy resin. (The nonstoichiometric

epoxy/amine mixture was prepared to have an epoxy system with the total heat of reaction, H_T , comparable to the H_T value of the UP curing reaction). The UP/DGEBA blend in weight ratio of 50/50 was prepared by weighing the equal quantities of the UP and DGEBA systems prepared as described above. Ingredients of the all investigated systems were continuously mixed at room temperature for 20 min by means of a mechanical stirrer.

Characterization

The cure of the two pure resins and their 50/50 blend was studied under both dynamic and isothermal conditions on a Netzsch DSC 200 differential scanning calorimeter operating in the temperature range between -100 and 500°C in a nitrogen atmosphere. The dynamic DSC analysis was performed at three different heating rates: 3, 5, and $10^\circ\text{C}/\text{min}$. The sample was heated from room temperature to around 250°C . The total heat of reaction, H_T , is estimated by drawing a straight line connecting the base line before and after the peak and integrating the area under the peak.

Isothermal DSC analysis was performed at least at four temperatures. The DSC cell was preheated to the experimental temperature and the sample was then quickly placed in the DSC cell. After each isothermal run the sample was cooled rapidly in the DSC cell to 30°C and then reheated at $10^\circ\text{C}/\text{min}$ to 250°C to determine the residual heat of reaction, H_R . The digitized data were acquired by a computer and transferred to a PC for further treatment.

Measurements of the Glass Transition Temperature

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 250°C at $10^\circ\text{C}/\text{min}$ and then cooled rapidly in the DSC cell to room temperature and immediately reheated to 250°C at $10^\circ\text{C}/\text{min}$. T_g was taken as the midpoint of the endothermic step transition.

RESULTS AND DISCUSSION

Dynamic DSC Characterization

Figure 1(a) shows the dynamic DSC thermograms of the investigated systems obtained at a heating

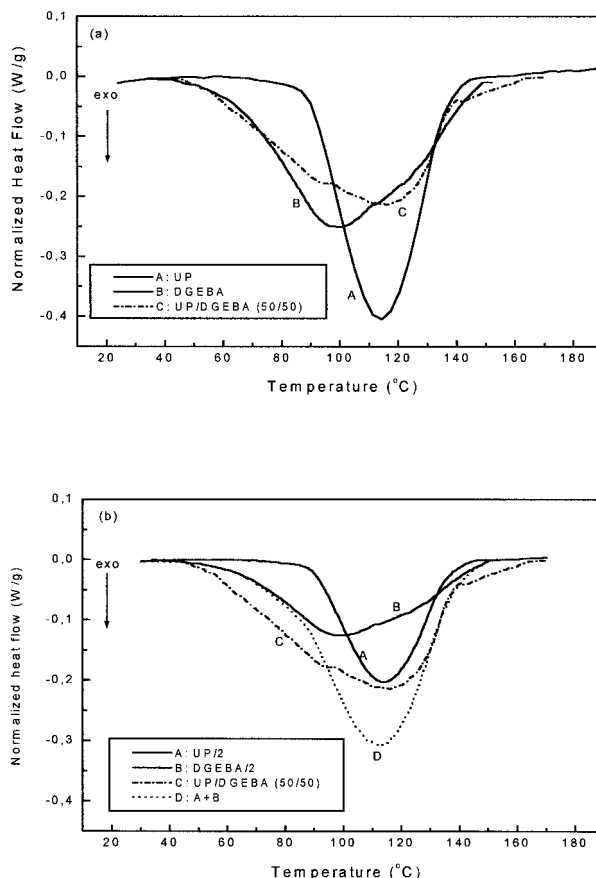
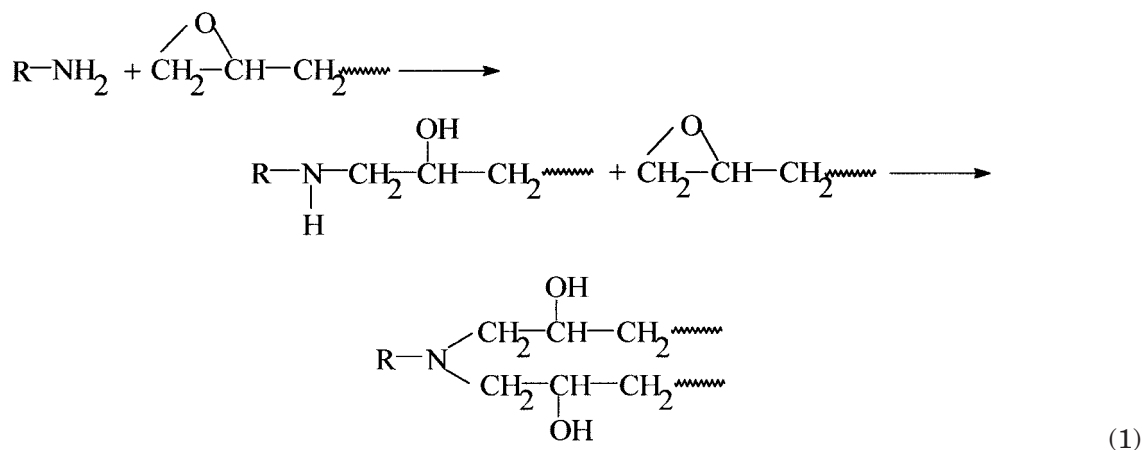


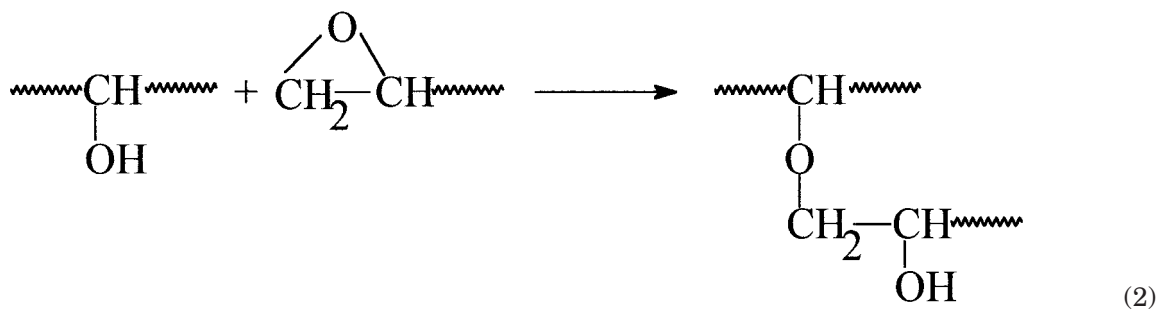
Figure 1 (a) Dynamic DSC curves for investigated systems at a heating rate of $3^\circ\text{C}/\text{min}$. (b) Curves A and B were calculated by dividing the normalized heat flow for pure UP and DGEBA resins by 2 (because of 50/50 UP/DGEBA weight ratio in the blend). Curve D was calculated from additivity principle (A + B).

rate of $3^\circ\text{C}/\text{min}$. Because UP was cured by free radicals through chain polymerization the fast chain reaction is reflected in a sharp exothermic peak (curve A). On the other hand, DGEBA was cured by poly(oxypropylene)diamine through step-wise polymerization, and the step reaction was reflected in a relatively broad asymmetrical exothermic peak (curve B). This asymmetry could be due to two different reactions taking place. This is not surprising, because the investigated epoxy system is a nonstoichiometric mixture of epoxy and amine. Several reviews on the mechanism and kinetics of epoxy-amine reactions are available.^{7,9-11} It is generally agreed that in the reaction between epoxides and amines, the addition occurring in two stages is the most important:



These reactions are catalyzed by acids such as Lewis acids, phenols, and alcohols. The hydroxyl groups generated by the amine epoxide addition are active catalysts, so that the curing reaction usually shows an accelerating rate in its early

stages, typical of autocatalysis. With excess epoxy (as in the investigated system), etherification reactions become operational as well. Namely, the secondary hydroxyl groups formed gradually add to epoxide groups:



When DGEBA and UP (containing curing agents and initiator) were mixed in the 50/50 weight ratio the exothermic peak was even broader (curve C in Fig. 1). In comparison to pure resins, both shifts, to higher and to lower temperatures, are seen. The shifts are more obvious when the normalized heat flow for pure resins shown in Figure 1(a) were divided by two (because of 50/50 UP/DGEBA weight ratio in the blend) as seen in Figure 1(b). The beginning of the UP/DGEBA cure at temperatures lower than those expected from the pure resins data is in good agreement with the unusual viscosity increase and a much shorter gelation time for a 50/50 UP/DGGBA blend cure reported in the literature.³ It can be explained by a catalytic effect of the hydroxyl end group of UP on epoxy cure. This effect is well known from the literature.^{4,12} The shift of the

other side of the exothermic peak to higher temperatures can be interpreted as an effect of network interlock.¹³ Namely, the mutual entanglements of the two networks provide an extra sterically hindered environment to the curing reactions and restrained the mobilities of both components. An increase of temperature can compensate this two factors (see the “shoulder” or the third small peak on curve C). Curve D in Figure 1(b) is the “theoretical” heat flow of the UP/DGEBA blend calculated from the additivity principle, i.e., as the sum of the normalized heat flows of pure resins (divided by 2).

The total heat of all reactions, H_T , was determined by computer integration of the exotherm peak using a linear baseline. An average value of 280, 270, and 250 J/g was obtained for UP, DGEBA, and UP/DGEBA (50/50), respectively.

The average total heat of reaction, 250 J/g, for 50/50 of UP/DGEBA blend is lower than H_T of each respective component, indicating an incomplete cure of the IPN system. It can be concluded that an increase of temperature could not compensate the interlock effect completely.

Isothermal DSC Characterization

Isothermal DSC characterization of pure UP resin was performed at four temperatures ranging from 106 to 121°C in 5° increments. The calculated values of the total heat developed during isothermal tests, H_i , were comparable to the heat developed during dynamic DSC tests. Moreover, rescanning of the isothermally cured samples indicated no residual reactivity. It is worth noting that all isothermal cure temperatures were higher than the glass transition temperature of completely cured material ($T_{g\infty} = 98^\circ\text{C}$) so the isothermal vitrification^{14,15} was avoided.

For DGEBA resin, as shown in Table II, the calculated values of the H_i , were lower than the heat developed during dynamic tests (270 J/g) and H_i is an increasing function of the test temperature. Rescanning of the isothermally cured samples indicated a residual reactivity. The incomplete curing reaction obtained in isothermal conditions can be explained in terms of diffusion control effects in the vicinity of isothermal vitrification.^{14,15} Namely, the structural changes produced by the polymerization reactions are associated with an increase of the glass transition temperature, T_g , of the reactive system. When the increasing T_g approaches the isothermal cure temperature, the molecular mobility is strongly reduced, the reaction becomes diffusion controlled, and eventually stops. Subsequent exposure to temperatures greater than the previous isothermal cure temperature results in the in-

Table II Heat of Reaction Developed in Isothermal DSC Tests and Final Fractional Conversion, α_{\max} , for DGEBA Pure Resin

Temperature (°C)	H_i (J/g)	α_{\max}
91	182	0.674
101	216	0.800
106	223	0.826
111	224	0.830
116	234	0.867
121	251	0.930

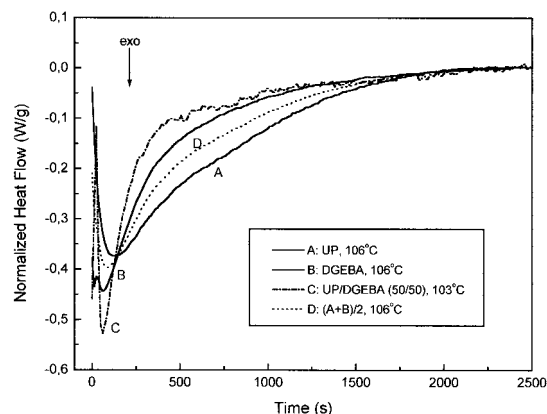


Figure 2 Isothermal DSC curves for investigated systems at reported temperatures. Curve D was calculated from additivity principle.

crease of the molecular mobility of the polymer and further reaction.

It was not possible to investigate the cure of 50/50 UP/DGEBA blend in the same temperature range as pure components. The reaction seemed to be too fast to get reliable data for the beginning of the reaction.

Namely, in isothermal DSC, there is a brief period (1–2 min) of temperature stabilization after the sample is introduced into the instrument. Because of that, the data obtained at the beginning of the test are not very reliable. All isothermal curves should be corrected, extrapolating the value of the heat flow at time = 0. At temperatures higher than 105°C the cure of 50/50 UP/DGEBA was so fast that such extrapolation was not possible.

In Figure 2, the normalized heat flow of 50/50 UP/DGEBA blend obtained at 103°C was compared to data obtained for pure resins at 106°C. Curve D in Figure 2 is the “theoretical” heat flow of the UP/DGEBA blend at 106°C obtained as the sum of the normalized heat flows of pure resins (divided by 2). As it is well known, the exotherm peak minimum corresponds to the maximal rate of the heat flow, $(dH/dt)_{\text{peak}}$ (and, as will be seen later, to the maximal reaction rate). From Figure 2 it is obvious that the absolute value of $(dH/dt)_{\text{peak}}$ for UP/DGEBA even at lower temperatures (103°C) is higher than $|(dH/dt)_{\text{peak}}|$ of each respective component. These findings are compatible with the results obtained in nonisothermal conditions and with the literature data,⁴ and can be explained by the catalytic effect of the OH end group of UP on epoxy cure.

The total heat of the isothermal cure of UP/DGEBA blend (210 J/g) at 103°C was lower than the “theoretical” value. As will be seen later it can be explained by an incomplete cure, because of two factors: vitrification of the epoxy resin, and the network interlock effect.

The Rate of Reaction and Conversion

It is well known that the basic parameter governing the state of the material is the chemical conversion. Knowledge of the kinetic rate of curing and how the rate changes with cure temperature is important and useful for predicting the chemical conversion achieved after a cure schedule. Because of that, a detailed kinetic analysis was performed.

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

$$\frac{d\alpha}{dt} = \frac{1}{H_T} \frac{dH}{dt} \quad (3)$$

The average value of the total heat developed during the dynamic DSC tests, H_T , was taken as the basis for the ultimate fractional conversion, $\alpha = 1$. By partial integration of the areas under the $d\alpha/dt$ vs. time curves, the fractional conversion as a function of time was obtained.

$$\alpha = \frac{1}{H_T} \int_0^t \frac{dH}{dt} dt \quad (4)$$

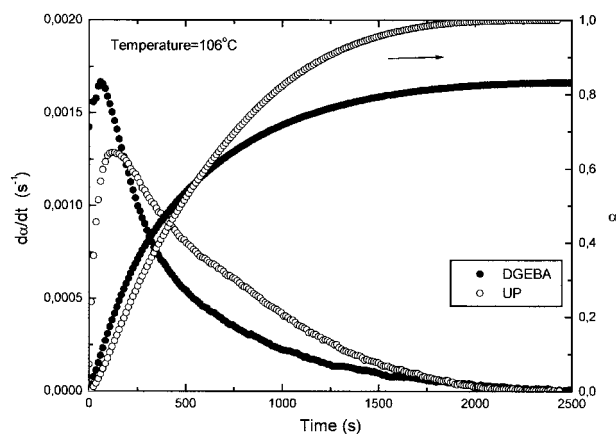


Figure 3 Isothermal reaction rate and fractional conversion as functions of time for pure resins at 106°C.

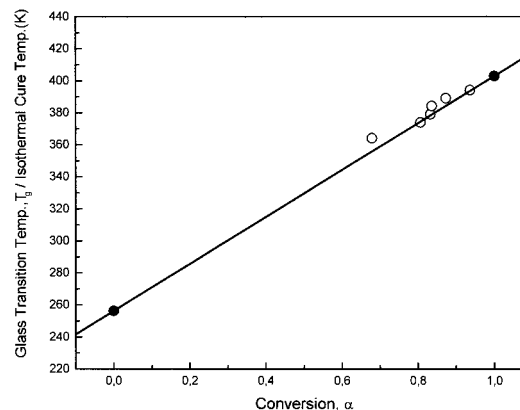


Figure 4 Comparison of isothermal cure temperature vs. final fractional conversion data (○) with the glass transition temperatures of uncured ($\alpha = 0$) and completely cured ($\alpha = 1$) DGEBA system (●).

Typical curves, showing the rate of reaction and conversion as functions of time for pure UP and DGEBA resins at curing temperature of 106°C are given in Figure 3. In Table II the final fractional conversion, α_{\max} , reached during the isothermal cure of DGEBA, is given as well. It is seen that at all investigated temperatures α_{\max} of DGEBA is lower than 1. As mentioned before, the incomplete cure of DGEBA in isothermal conditions (at temperatures lower than the glass transition temperature of the completely cured DGEBA system, $T_{g^\infty} = 129^\circ\text{C}$) can be attributed to the influence of diffusion control on the reaction kinetics in the glass transition region. Namely, it can be supposed that during isothermal cure T_g of the reactive DGEBA system reached the isothermal cure temperature ($T_g = T_{\text{cure}}$). Because of the reduced molecular mobility at vitrification the reaction probably stopped before completion. It is worth mentioning that the isothermal cure temperature vs. the final fractional conversion data for DGEBA fit well the straight line connecting the glass transition temperatures of an uncured ($T_{g0} = -17^\circ\text{C}$) and completely cured DGEBA material ($T_{g^\infty} = 129^\circ\text{C}$), as shown in Figure 4.

Analysis of the Data by Means of Kinetic Models

The essential step in the study of cure kinetics by DSC is fitting of the reaction rate profiles, obtained from isothermal and dynamic experiments, to a kinetic model. Due to the complex nature of thermosetting reactions, phenomeno-

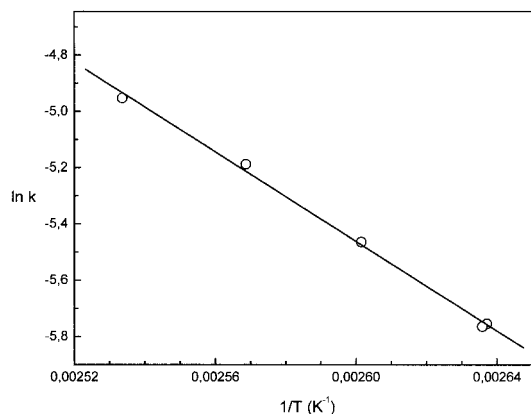


Figure 5 Arrhenius plot of isothermal reaction rate constant for UP pure resin.

logical models are the most popular for these systems.

Pure UP Resin

The experimental UP data were tested to the following kinetic model:

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \quad (5)$$

Parameters of the model k , m , and n were determined from each isothermal thermogram by a nonlinear regression analysis (Program Microcal Origin 4.1). It was assumed that $m + n = 2$.¹⁶⁻¹⁹ m and n were found to be relatively insensitive to temperature, and the average values were used in the modeling. The temperature dependence of the apparent rate constant k follows an Arrhenius relationship (Fig. 5):

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

The computed parameters of the kinetic model are summarized in Table III.

Table III Parameters of the Kinetic Model, eqs. (5) and (6) for UP Pure Resin

Preexponential Factor, k_0 (s^{-1})	$e^{25.5}$
Activation energy, E_a (kJ/mol)	98.8
m	0.33
n	1.67

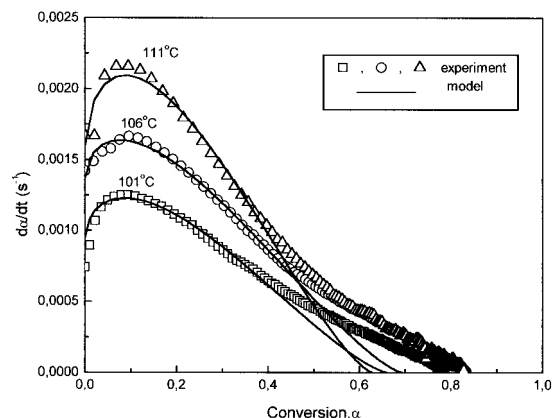


Figure 6 Fitting of the $d\alpha/dt$ vs. α curves for DGEBA pure resin to the kinetic model, eq. (7). The curing temperatures are indicated in the figure.

Pure DGEBA Resin

The experimental DGEBA data were tested first to the autocatalytic reaction model,

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_{\max} - \alpha)^n \quad (7)$$

where α_{\max} is the maximum fractional conversion at a given temperature needed to describe the vitrification phenomenon observed in isothermal cure.²⁰ The dependence of α_{\max} on the cure temperature was fitted to a linear relationship. Parameters of the model k_1 , k_2 , m , and n were determined by the procedure already described for UP. It was also assumed that $m + n = 2$.^{21,22}

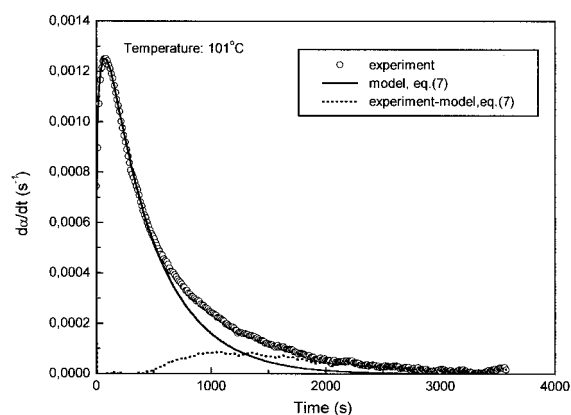


Figure 7 Separation of the experimental reaction rate profile for DGEBA pure resin in contributions of two assumed reactions (see the text).

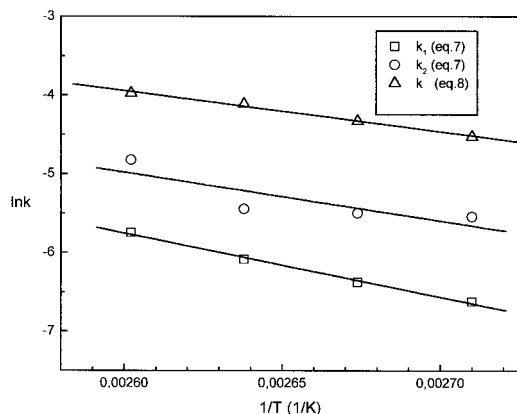


Figure 8 Arrhenius plots of isothermal reaction rate constants for DGEBA pure resin.

Good correlation of $(d\alpha/dt)$ vs. α data was obtained up to approximately 40% conversion at all investigated temperatures (see Fig. 6). To obtain better fitting for the whole range of conversion the reaction rate profiles were divided in the contributions da_1/dt and da_2/dt from two assumed reactions. The procedure was as follows: the “theoretical” da_1/dt vs. *time* curve (obtained with the da/dt vs. α data for $\alpha \leq 0.4$) was subtracted from the experimental da/dt vs. *time* curve. The second peak (da_2/dt vs. *time*) was obtained (see Fig. 7), where the area is equal to the contribution of the second assumed reaction to the total fractional conversion at a given temperature. By partial integration of the areas under the da_2/dt vs. *time* curves the fractional conversion α_2 as a function

of time was obtained. The da_2/dt vs. α_2 profiles were tested on the phenomenological model

$$\frac{d\alpha_2}{dt} = k\alpha_2^m(\alpha_{\max 2} - \alpha_2)^n, \quad \text{for } t \geq t_{\text{in}} \quad (8)$$

It was found that the induction period, t_{in} , for the second reaction can be described by an Arrhenius-type equation. Parameters of the model k , m , and n were determined by the nonlinear regression analysis as already described. It was also assumed that the sum of the reaction orders $m + n$ is constant and equal to 2. $\alpha_{\max 2}$ is the maximum fractional conversion at a given temperature that corresponds to the second assumed reaction. As seen from Figure 6, the obtained 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, $\alpha_{\max 2} \leq 0.33$. In Figure 8, Arrhenius plots of isothermal reaction rate constants k_1 and k_2 and k are given. Parameters of the kinetic models for DGEBA are summarized in Table IV. The activation energies calculated from Arrhenius plots (Fig. 8) are comparable to those from the literature.⁴

UP/DGEBA Network

In Figure 9 the experimental reaction rate profile of the UP/DGEBA system was compared to the reaction rate profiles of pure components (divided by 2) obtained by modeling. Differential eqs. (5),

Table IV Parameters of the Kinetic Models, eqs. (6), (7) and (8) for DGEBA Pure Resin

	Reaction 1 Kinetic Model [Eq. (7)]	Reaction 2 Kinetic Model [Eq. (8)]
Preexponential factor, [eq. (6)]		
k_0 (s^{-1})		$e^{9.6}$
k_{01} (s^{-1})	$e^{15.4}$	
k_{02} (s^{-1})	$e^{11.1}$	
Activation energy, [eq. (6)]		
E_a (kJ/mol)		43.2
E_{a1} (kJ/mol)	67.7	
E_{a2} (kJ/mol)	51.4	
m	0.58	0.56
n	1.42	1.44
α_{\max}	0.67	$-5.61 + 0.01543T$
Induction time, t_{in} (s)		$\exp(5.1 + 381.4/T)$

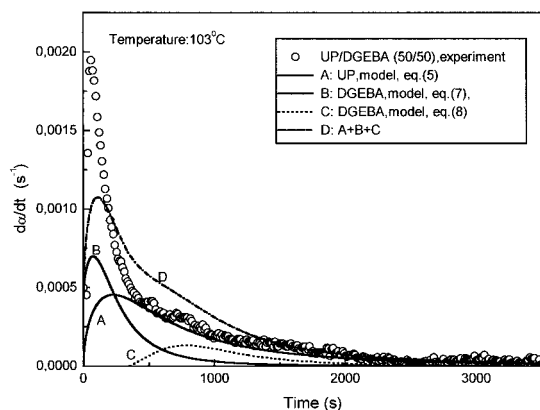


Figure 9 Comparison of experimental data for UP/DGEBA (50/50) blend with the kinetic model data for pure UP (curve A) and DGEBA resin (curves B and C): isothermal reaction rate as a function of time at reported temperature. Curve D was calculated from additivity principle (A + B + C).

(7), and (8) were solved numerically by the Runge-Kutta method. It is obvious that the experimental maximal reaction rate of the UP/DGEBA blend is higher than the maximal reaction rate calculated as the sum of the contributions of both components to the total reaction rate (curve D in Fig. 9).

Supposing that there was no chemical reaction between UP and DGEBA, the contribution of DGEBA to the total reaction rate was calculated as the difference between the experimental and the UP theoretical data (Fig. 10). By this procedure a sharp peak (curve B in Fig. 10) that over-

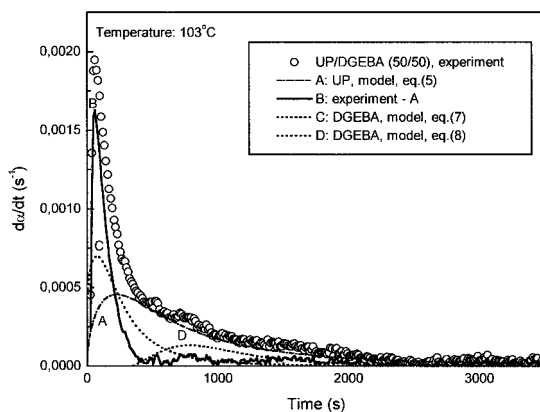


Figure 10 Estimation of the DGEBA reaction rate profile in the UP/DGEBA (50/50) blend as the difference between the experimental and the UP kinetic model data (curve B). For comparison, the kinetic model data for pure DGEBA resin are given as well.

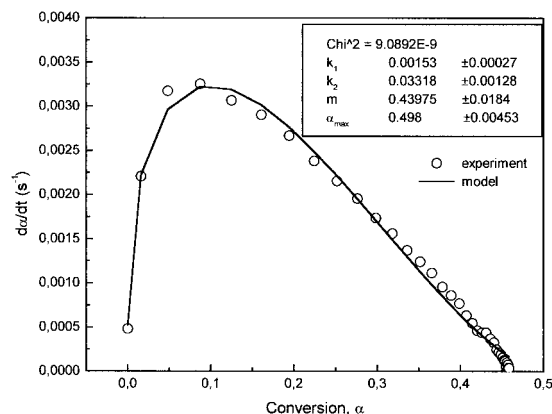


Figure 11 Fitting of the da/dt vs. α curve for DGEBA in UP/DGEBA (50/50) blend to the kinetic model, eq. (7). Curing temperature: 103°C.

laps with the beginning of a broader peak of small intensity was obtained. The sharp peak was tested on the model (7), as seen in Figure 11. In Table V, the parameters of the model k_1 , k_2 , m , n , and α_{\max} for pure DGEBA and for DGEBA in the 50/50 DGEBA/UP blend are compared for the temperature of 103°C. The values for k_1 are of the same range of the magnitude, but the reaction rate constant k_2 for DGEBA in the UP/DGEBA blend is much higher than k_2 for pure DGEBA. The latter finding is compatible with the kinetic data obtained by FTIR.⁴ Therefore, the isothermal cure results agree with the dynamic cure data, again suggesting that the hydroxyl end group of UP in the blend provided a favorable catalytic environment for the DGEBA cure. In Figure 12, the conversion profile of the 50/50 DGEBA/UP blend obtained experimentally at 103°C is compared with the kinetic models data [eqs. (5)–(8)]. Because the influence of the vitrification on the final conversion of epoxy resin is included in the model, the difference between the

Table V Parameters of the Kinetic Model, eq. (7), for DGEBA Pure Resin and for DGEBA in the DGEBA/UP Network at 103°C

	Pure DGEBA	DGEBA/UP
k_1 (s^{-1})	0.00196	0.00153
k_2 (s^{-1})	0.00476	0.03318
m	0.58	0.44
n	1.42	1.56
α_{\max}	0.67	0.50

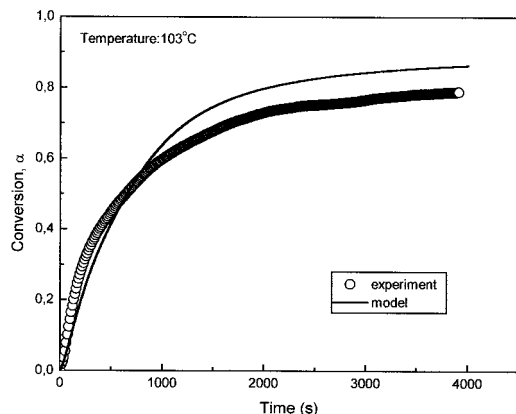


Figure 12 Comparison of experimental data for the UP/DGEBA (50/50) blend with the kinetic model data, eqs. (5)–(8): isothermal fractional conversion as a function of time at reported temperature. Theoretical curve (—) corresponds to the curve D in Figure 9.

theoretical final conversion (0.86) and the experimental one (0.80) could be an indicator of the network interlock effect.

CONCLUSIONS

Curing kinetics of simultaneous UP/DGEBA interpenetrating polymer network formation was studied by means of DSC. A lower total heat of reaction developed during simultaneous polymerization in both dynamic and isothermal DSC tests was found, compared to the total heats developed during the cure of pure resins. For curing in dynamic conditions this phenomenon can be interpreted as an effect of network interlock that could not be compensated completely by an increase of curing temperature. During isothermal cure the uncomplete cure is caused by both the network interlock and the vitrification of DGEBA resin. The kinetics of UP and DGEBA reactions was described by empirical models. The DGEBA in a 50/50 UP/DGEBA blend indicated a higher reaction rate constant than the pure DGEBA. The cure of UP/DGEBA system in dynamic conditions

started earlier (at lower temperatures) compared to cure of pure DGEBA resin. The obtained results suggests that the hydroxyl end group of UP in the blend provided a favorable catalytic environment for the DGEBA cure. The results are in good agreement with the literature data.

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