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Effects of the Branching Architecture on the Reactivity of Epoxy−Amine Groups

Raffaele Mezzenga, Louis Boogh, and Jan-Anders E. Månson*

Laboratoire de Technologie des Composites et Polymères (LTC), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Bo Pettersson

Perstorp Speciality Chemicals, S-28480 Perstorp, Sweden

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ABSTRACT: The aim of this paper is to investigate and quantify the effect of the rigidity and mobility of the reactive groups and of the functional group spatial density and to give an insight into the role these factors play in the polymerization of epoxy resins. The effect of the epoxy molecular architecture on the reactivity with amine curing agents has been studied using different epoxy-containing compounds with various configurations. DGEBA cured with isophorone diamine has been used as a reference system. Dendritic hyperbranched polymers (HBP) with epoxy groups grafted on the shell and two aliphatic epoxidized model compounds have been used to investigate the effects of chemical composition, solubility, mobility, and spatial density of reactive groups. Mobility of the reactive groups, which is inversely related to the molar stiffness, has been found to affect the mechanism of reaction, changing an autocatalytic reaction for DGEBA−amine systems into a noncatalytic reaction for HBP−amine systems. The reactive group molecular density was found to be responsible for an increase in the activation energy.

Introduction

The mechanism of the epoxy−amine curing reaction is generally well established,[1−3] and the chemistry of different epoxy resins and hardeners, among which bifunctional, trifunctional, and tetrafunctional epoxies cured with various aliphatic or aromatic amines, has been investigated.[3,4] Several reaction mechanisms may occur depending on the temperature and the stage of reaction. The most commonly observed mechanism of reaction is autocatalytic, where the epoxy ring opens under reaction with the amine forming a hydroxyl group which is able to catalyze further amine−epoxy reactions. A competitive noncatalytic reaction occurs in most cases, with relative kinetics affected by temperature, higher temperatures apparently favoring noncatalytic reactions.[5]

Above 160−180 °C, hydroxyl−epoxide reaction or epoxy homopolymerization may contribute to the amine−epoxy reaction during polymerization. Finally, the presence of impurities may catalyze any particular reaction. Therefore, the most suitable general set of equations for describing epoxy−amine polymerization may be expressed by

$$\mathrm{E} + \mathrm{A}_1\,(+\mathrm{OH}) \rightarrow \mathrm{A}_2 + \mathrm{OH}\,(+\mathrm{OH}) \quad [K_\mathrm{a}] \tag{1a}$$

$$\mathrm{E} + \mathrm{A}_1\,(+\mathrm{X}) \rightarrow \mathrm{A}_2 + \mathrm{OH}\,(+\mathrm{X}) \quad [K'_\mathrm{a}] \tag{1b}$$

$$\mathrm{E} + \mathrm{A}_2\,(+\mathrm{OH}) \rightarrow \mathrm{A}_3 + \mathrm{OH}\,(+\mathrm{OH}) \quad [K_\mathrm{b}] \tag{1c}$$

$$\mathrm{E} + \mathrm{A}_2\,(+\mathrm{X}) \rightarrow \mathrm{A}_3 + \mathrm{OH}\,(+\mathrm{X}) \quad [K'_\mathrm{b}] \tag{1d}$$

$$\mathrm{E} + m\mathrm{OH} + n\mathrm{A}_3 \rightarrow \mathrm{ether} + m\mathrm{OH} + n\mathrm{A}_3 \quad [K_\mathrm{c}] \tag{1e}$$

where the symbols E, A_1, A_2, A_3, OH, and X stand respectively for epoxy groups, primary, secondary, and tertiary amines, hydroxyl groups, and other catalytic groups, such as impurities. K_i refers to the rate constant of reaction *i*. The first two equations express the reaction of primary amines with the epoxy groups by two different catalysts specified in the parentheses. The second two equations express the reaction between secondary amines and epoxies, and the last equation expresses etherification reactions, including both homopolymerization and OH−epoxy reaction. The ratio between K_a and K_b has generally been found to be close to 2.[6] The relative weight of any of the above equations over the others depends not only on the intrinsic system chemistry and molecular architecture of the reactants but also on the processing conditions, such as pressure or temperature.

To quantitatively evaluate the polymerization kinetics by analytical models, the overall conversion rate as a function of time at different temperatures can be obtained experimentally by calorimetric analysis making the following assumption:[7]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{Q_\mathrm{T}}\frac{\mathrm{d}Q}{\mathrm{d}t} \tag{2}$$

where α is the conversion, Q is the reaction released heat flow at time *t*, and Q_T is the total heat released when full conversion is achieved. On the basis of the experimentally determined conversion rates using eq 2 and which depend on the reaction mechanisms, different analytical kinetics models can be used. It should however be observed that these analytic models based on eq 2 only consider the average enthalpy of reaction for the reaction of epoxy group with primary and secondary amines, for which different values have been proposed in the literature.[8]

The approach most often used for modeling epoxy−amine curing kinetics is based on the Kamal equation:[9,10]

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* To whom correspondence should be addressed. Tel +41 21 693 4281; Fax +41 21 693 5880; E-mail jan-anders.manson@epfl.ch.

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$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \qquad (3)$$

where α is the conversion as obtained by eq 2, and m and n are two exponents determined experimentally. In eq 3, K_1 indicates the reaction rate which is independent of the reaction advancement and is therefore said to be the noncatalytic rate constant as opposed to K_2, which is the autocatalytic rate constant. Therefore, although the Kamal equation is a semiempirical tool, K_1 can be related to the sum of K'_a and K'_b and K_2 to the sum of K_a and K_b. Both K_1 and K_2 are assumed to have an Arrhenius dependence on temperature and are expressed by

$$K_i = A_i e^{-E_i/RT} \qquad (4)$$

where E_i are the activation energies of the two reactions. Such a kinetics model allows the extraction of the activation energies of the noncatalytic and autocatalytic processes by linear regression, the latter being parameters used to classify the polymerization process.

Using new epoxidized molecules, such as epoxidized dendritic hyperbranched polymers and aliphatic monofunctional epoxies, allows one to investigate aspects in amine–epoxy reaction kinetics that were not possible to study with traditional systems.

Experimental Section

A diglycidyl ether of bisphenol A (DGEBA), Shell Epon 828, was used as the reference epoxy resin. The reactivity of aliphatic epoxy groups was studied using two model compounds, epoxidized methyl undecenoate, produced by Perstorp AB, and 1-dodecene oxide from Fluka, which are identified in this work by model compound 1 and model compound 2, respectively. As shown in Figure 1, the only chemical difference in these compounds is the nature of the opposite chain end to the epoxy group. The effect of mobility of epoxy groups was studied using the epoxidized methyl undecenoate chains grafted on the shell of 3-generation dendritic hyperbranched polymers supplied by Perstorp AB. Three HBPs were synthesized differing in the number of grafted epoxy groups and thus in the epoxy equivalent weight (EEW). HBP40, HBP60, and HBP95 identify the HBPs studied with an epoxy equivalent weight of 1050, 560, and 410 g/equiv, respectively, as measured by titration. Isophorone diamine (IPD) supplied by Fluka was used as cross-linking agent for all epoxy compounds. Stoichiometric ratios of active amine hydrogen versus epoxy groups were used in all cases.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC7 by dynamic temperature scan experiments at 10 °C/min and under isothermal conditions at 80, 100, 120, 140, and 160 °C using samples of 10–20 mg. Because of the high volatility of the model compounds, additional analytical investigations were performed by NIR experiments on a Perkin-Elmer Lambda 900 using 1 mm thick samples, sealed in a glass container and precured in an oven. The NIR measurements were performed at room temperature immediately after the oven cure. Since very slow reaction rates were observed for both model compounds at high temperatures, no polymerization was assumed to occur during the measurements at room temperature.

Results

Model Compounds. Model compounds 1 and 2 were used to determine the effect of the chemical nature of the chain onto which the epoxy groups were grafted. Furthermore, this allowed the investigation of the polymerization process of epoxidized HBPs.

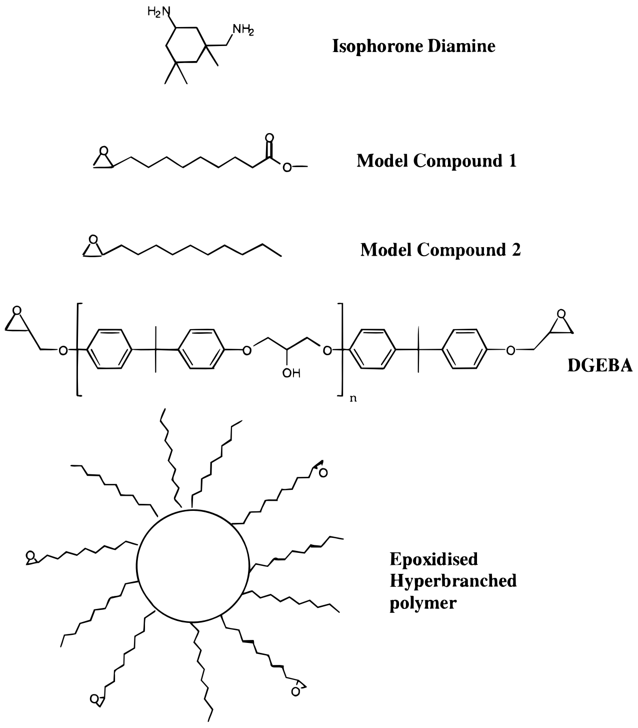

Figure 1. Molecular structure of epoxy compounds and hardener used.

To obtain conversion–time curve from NIR analysis, the epoxy group peak area has been related to conversion by using the following expression:[2]

$$\alpha = c_e(t)/c_e(0) = \{A_e(t)/A_0(t)\}/\{A_e(0)/A_0(0)\} \qquad (5)$$

where α is the conversion, $c_e(t)$ is the concentration of epoxy groups at time t, $A_e(t)$ is the epoxy group peak area, and $A_0(t)$ is the reference peak area at time t used for normalization. The reference peak used for normalization is the 4420 cm^{-1} $-CH_2-$ overtone band.[11] The epoxy bands of both model compounds were recorded at 4510 cm^{-1}, while the primary amine band of the isophorone diamine was recorded at 4920 cm^{-1}, which is in good agreement with literature.[1,2,12]

The peak areas were determined using a Voight deconvolution of the NIR spectrum. Figure 2a illustrates the evolution with time of the epoxy, hydroxyl, and primary amine peaks of the NIR spectrum of model compound 1. The amine–epoxy reaction is confirmed by the increase of the broad hydroxyl peak at the 4750 cm^{-1}. Figure 2b shows the conversion versus time curves obtained by eq 5 for both model compounds cured at 140 °C. While for model compound 1 the reaction advancement was easily followed by NIR, model compound 2 did not show any reaction.

To acquire the information about the enthalpy of reaction, DSC dynamic temperature measurements at 10 °C/min were performed on the two model compounds with isophrone diamine. A neutral atmosphere of N_2 at a pressure of 10 bar was applied to the system to avoid evaporation of the model compounds. A value of 91 ± 7 kJ/mol was obtained for both systems.

DGEBA Resin Curing Kinetics. The DGEBA resin polymerization was described by a general Kamal kinetics model equation following DSC analysis. At temperatures below T_g,[8] when a full conversion cannot be achieved due to vitrification, a modified version of

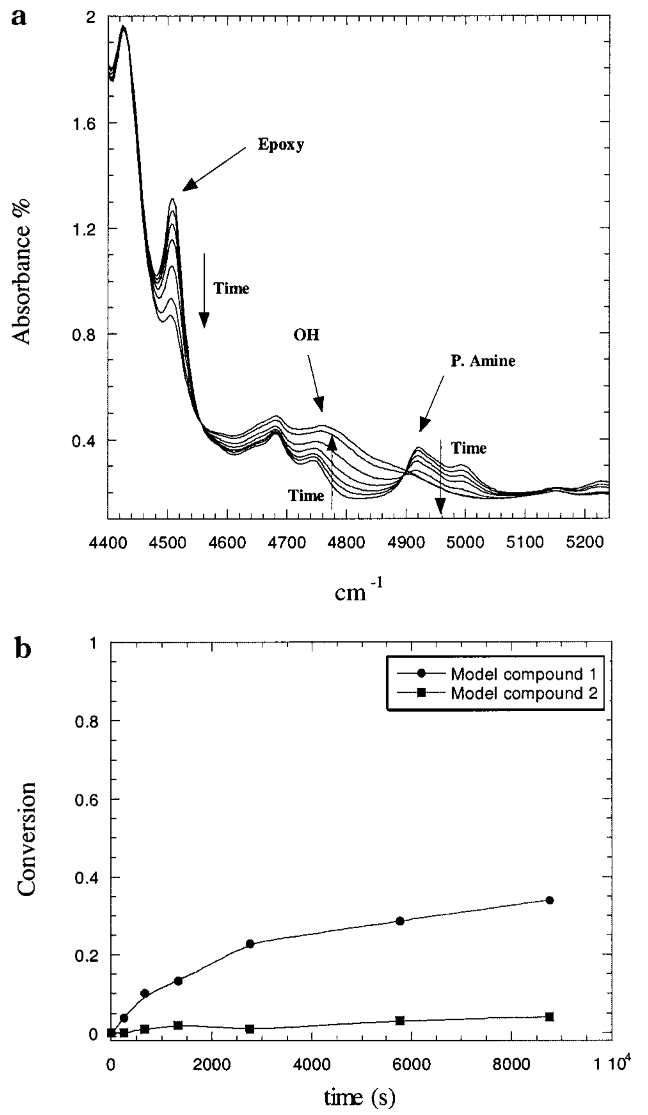

Figure 2. (a) Evolution of the epoxy, hydroxyl, and primary amine NIR peaks with time at 140 °C for model compound 1 mixed in stoichiometric ratio with IPD. (b) Conversion versus time as obtained by NIR experiments for the two model compounds studied.

the Kamal equation described by Kenny et al. was used:[13−15]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (K_1 + K_2\alpha^m)(\alpha_{\max} - \alpha)^n \qquad (6)$$

where $\alpha_{\max}$ is the maximum conversion achievable at the curing temperature used. To establish a fully analytical expression for the polymerization kinetics rate, $\alpha_{\max}$ in eq 6 was evaluated by combining DiBenedetto and Gillham theories. DiBenedetto stated that a unique expression exists in thermosets relating the glass transition temperature to the conversion of polymerization.[16] His equation was expressed in the following form by Adabbo and Williams:[17]

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{(E_x/E_m - F_x/F_m)\alpha}{1 - (1 - F_x/F_m)\alpha} \qquad (7)$$

where E_x/E_m is the ratio of lattice energies for cross-linked and un-cross-linked polymers and F_x/F_m is the corresponding ratio of segmental mobilities. According to Gillham's theory, reaction is arrested due to vitrification as the curing thermoset's glass transition reaches the temperature of polymerization.[17,18] It is therefore possible to calculate the maximum conversion in eq 6 as a function of curing temperature by applying eq 7, with T_g expressing the curing temperature T and α the maximum conversion $\alpha_{\max}$. Figure 3 shows the agreement between experimental data and eq 7 for the resin/amine system using $E_x/E_m = 0.93$ and $F_x/F_m = 0.55$, obtained here by a best fit of the experimental results and which is in good agreement with literature.[18]

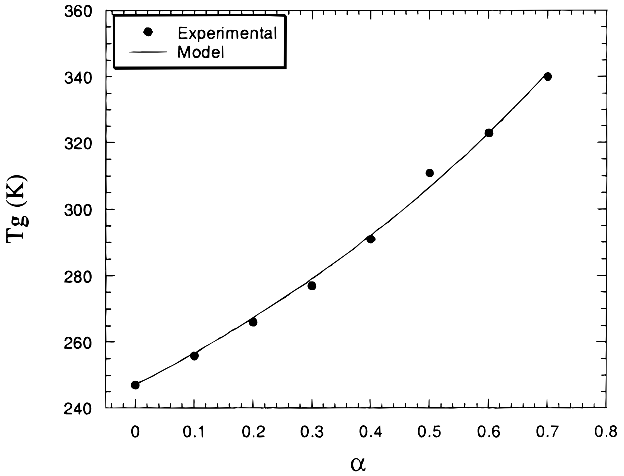

Figure 3. Comparison of experimental data expressing the glass transition temperature as a function of the conversion and the predicted data using the Di Benedetto theory.

The model's agreement with experimental data obtained at 160 °C for the DGEBA−IPD system is shown in Figure 4a, while Figure 4b shows the temperature dependence of the *m* and *n* exponents of eq 6. The curing kinetics analysis of the DGEBA−IPD system clearly identifies the occurrence of both autocatalytic and noncatalytic reactions which is confirmed by the fact that while the *n* exponent increases linearly with temperature, *m* is constant and close to 1, thus identifying the first-order catalysis by hydroxyl groups. A further confirmation is the presence of a maximum in the reaction rate. The rate increase at the onset of polymerization is due to the initially increasing number of hydroxyl groups formed during reaction as the amine opens the epoxy ring. However, as expressed by eq 6, the noncatalytic cure mechanism becomes more important as the conversion increases and takes over at 15% conversion. The autocatalytic and noncatalytic polymerization activation energies are shown in Figure 5. The slopes of the lines yield a value of 47.5 and 52.9 kJ/mol for the activation energies of the noncatalytic and autocatalytic reaction mechanisms, respectively. Although these values are typical for amine−epoxy systems, the general trend of a lower activation energy for the catalyzed mechanism is respected,[5] and the noncatalytic activation energy is close to the average activation energy of the primary−secondary amine−epoxy reaction of 54.4 kJ/mol, previously reported in the literature.[19] Finally, a total enthalpy per bond of 113 kJ/mol was determined, again in agreement with previous works.[5,7,20]

Dendritic Hyperbranched Polymers. The use of eq 2 to follow the curing kinetics of the hyperbranched polymers is complicated by the calculation of the total enthalpy of reaction Q_T. Indeed, for these, a full conversion can hardly be achieved in the temperature range

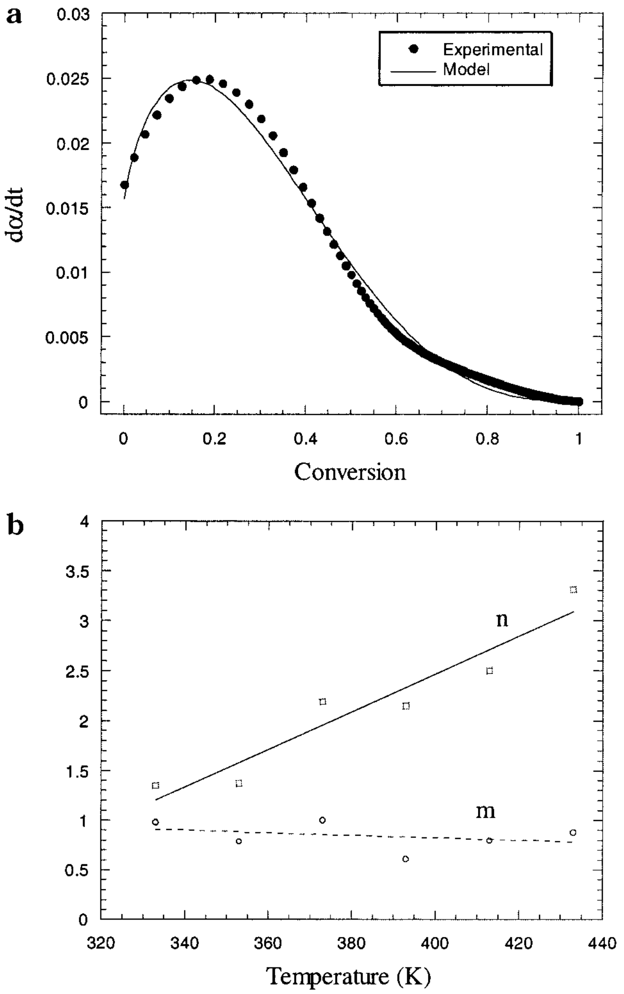

Figure 4. (a) Agreement of the kinetics modified Kamal equation with experimental data as obtained from DSC analysis for the DGEBA−IPD system under isothermal curing temperature at 160 °C. (b) Dependence on temperature of *m* and *n* exponents in Kamal modified equation, as obtained by best-fitting experimental data.

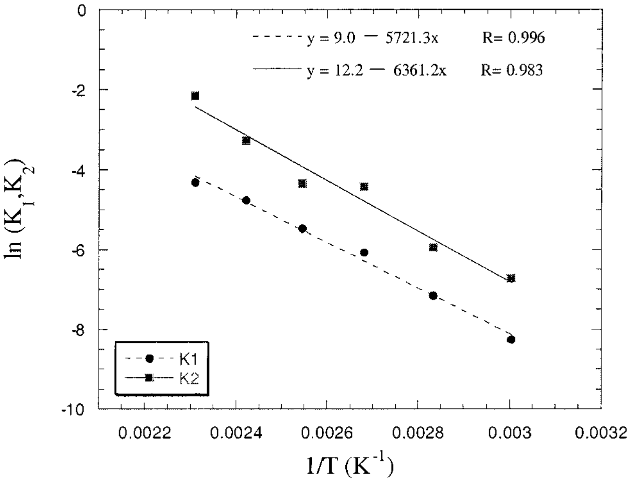

Figure 5. Autocatalytic and noncatalytic polymerization activation energies for DGEBA−IPD system as obtained by linear regression on the polymerization rate constants extracted by best-fitting experimental conversion rates.

80−160 °C, and higher temperatures cannot be used due to the flame point of the isophorone diamine hardener (112 °C for a 99% grade IPD). As a consequence, the total enthalpy of reaction Q_T must be computed with alternative techniques. NIR experiments were used to quantify the final conversions obtained at given curing temperatures. By extrapolating the corresponding reaction enthalpies obtained by DSC to full conversion, Q_T could be determined, allowing one to apply eq 2 to the case of hyperbranched polymers.

Since no maximum of reaction rate versus conversion was experimentally observed, the kinetics model chosen to best fit the experimental data for all HBPs investigated was

$$\frac{d\alpha}{dt} = K_a(\alpha_{max} - \alpha)^n \qquad (8)$$

where α and α_{max} are the conversion and the maximum conversion achievable at a given curing temperature, and K_a is the reaction rate constant. Figure 6 shows the experimental and computed conversion rates versus conversion at 160 °C for the three HBP−IPD systems studied. The absence of a maximum shows that only a noncatalytic reaction occurs.

The linear regression curves of K_a versus temperature yield the activation energy for the three HBP systems, as shown in Figure 7. The activation energy for polymerization is calculated to be 62, 50, and 33 kJ/mol for the HBP40, HBP60, and HBP95, respectively. The polymerization activation energies express a ranking in the reactivity of the HBPs which agrees with the classification of reactivity based on peak temperature for DSC dynamic scans shown in Figure 8. For all HBP−IPD systems, a total enthalpy of 94 ± 10 kJ/mol of epoxy equivalent was found, in good agreement with the dynamic DSC results obtained for model compounds 1 and 2. However, a ±10 kJ/mol of epoxy equivalent error is induced by the deconvolution procedure of the NIR curves used for the quantification of nonreacted epoxy groups on the HBP shells.

Discussion

Evaluation of Solubility and Chemical Composition Effects. Since the two model compounds used differ only by the presence of an ester group on one chain end (see Figure 1), the difference of reactivity observed in Figure 2b between model compound 1 and model compound 2 must be related to the chemistry of this chain end. Part of the reactivity difference could be due to the ester group catalyzing the epoxy amine reaction, although it is generally considered as an inert group for the chemistry of reaction. On the other hand, the solubility of the two model compounds is also strongly affected by the presence of a polar chain end such as an ester group which increases the polarity by a contribution of 490 $J^{1/2}$ $cm^{-1/2}$ mol^{-1} compared to the case of model compound 2.[21] This was experimentally detected by the clouding of the model compound 2−IPD solution, which started as soon as stirring was stopped. The difference in solubility, attributed to the polar asymmetry of model compound 2 without the ester group, would be responsible for the segregation leading to the formation of a phase-separated solution with the polar IPD. As a consequence, the lower reactivity of model compound 2 compared to that of model compound 1, is explained by the entrapment of the reactive groups, which are not left available for the reaction with the amine. In the case of the model compounds, the physical effect of segregation is thus considered to control the final conversion attainable by the amine−epoxy reaction.

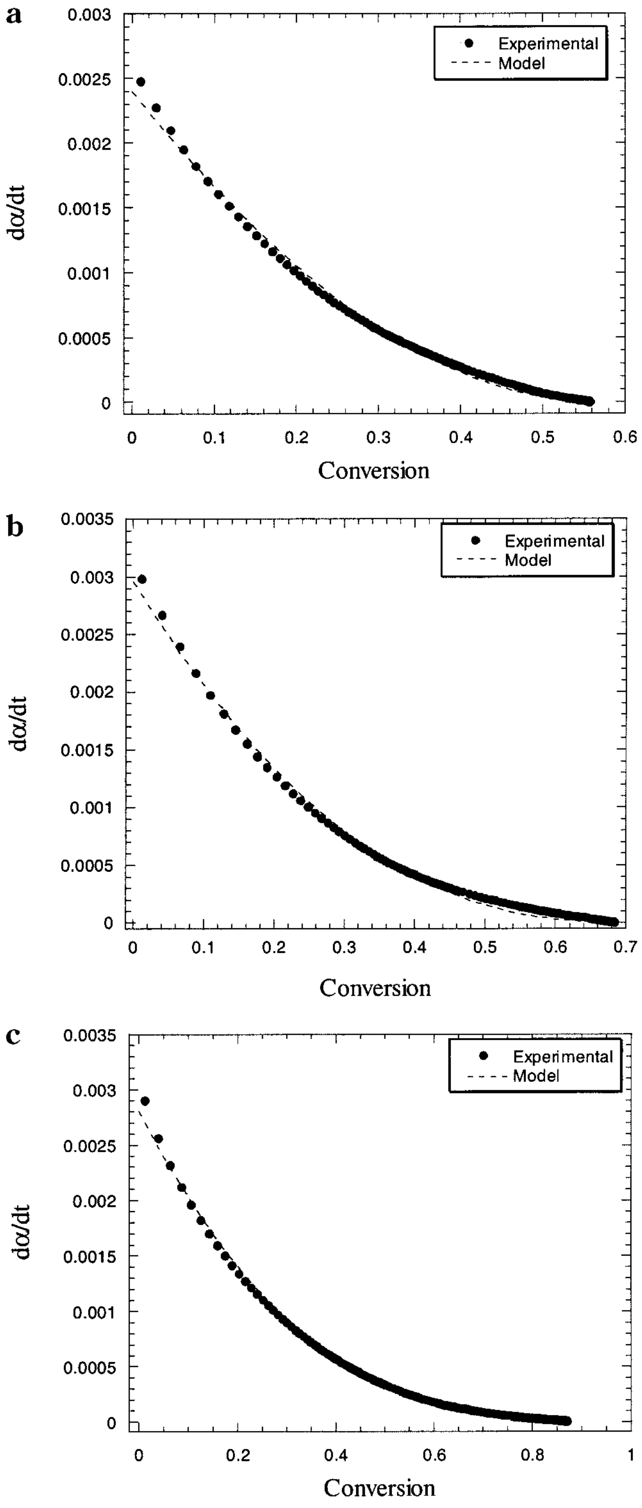

Figure 6. Agreement of the noncatalytic kinetics model with DSC experimental data for the three HBP–IPD systems at 160 °C: (a) HBP40–IPD; (b) HBP60–IPD; (c) HBP95–IPD.

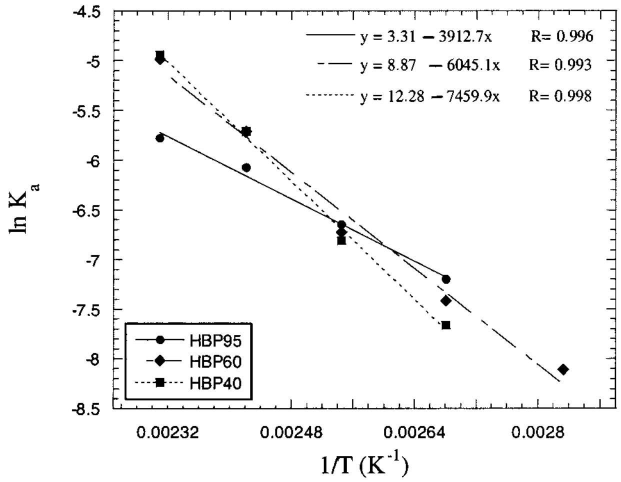

Figure 7. Noncatalytic polymerization activation energies for the three HBP–IPD systems as obtained by linear regression on the polymerization rate constants extracted by best-fitting experimental conversion rates.

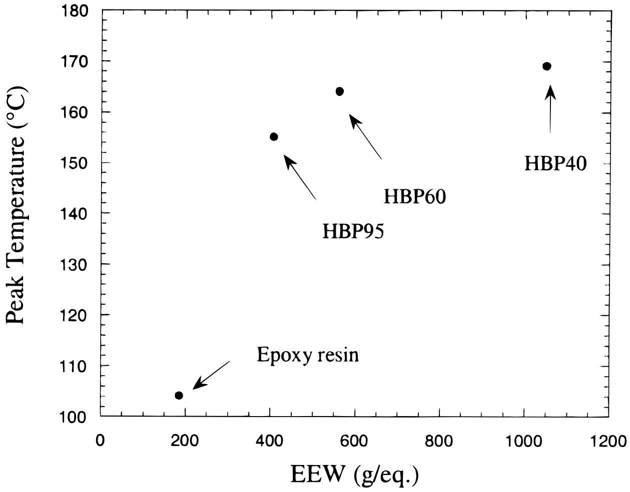

Figure 8. Reactivity peak temperatures obtained by DSC dynamic scans for the DGEBA–IPD and HBP–IPD systems as a function of the EEW of the pure epoxy compounds.

To evaluate the chemical composition effects, the DGEBA and HBP systems, which are both fully soluble, need to be compared. At first, the reaction mechanisms appear to be different, autocatalytic for DGEBA and noncatalytic for HBPs, despite the fact that in both cases catalyzing hydroxyl groups are formed during the epoxy ring opening. This, however, should not be affected by the initial chemical composition and will be discussed in the next section. On the other hand, the enthalpy of reaction can be influenced by the energetic stability of the epoxy groups, which is related to the chemical nature of the epoxy chain. For the DGEBA reference resin, a total enthalpy per bond of 113 kJ/mol was found, in the case of the HBP–IPD systems the total enthalpy per bond was 94 ± 10 kJ/mol, and for the model compounds–IPD systems a value of 91 ± 7 kJ/mol was obtained. The lower values obtained for the HBP and model compounds are thus believed to be due to the absence of ether bonds and aromatic rings in the aliphatic epoxy groups grafted onto the HBP shell, hence lowering their reactivity. Similar trends have been observed comparing reactivity and reaction enthalpies of epoxies cured with aromatic amines of different chemical structures.[3]

Evaluation of Mobility and Reactive Group Spatial Density Effects. The different reaction mechanisms observed for the DGEBA resin and the HBP compounds should not be induced by the chemical nature of the epoxy chains since they are also not influenced by the nature of the hardener.[7,22] The autocatalytic reaction mechanism appears due to the generation of catalyzing chemical units as reaction proceeds. As shown experimentally by NIR, in the case of the HBPs, the epoxy ring reacts with the primary and secondary amine groups, producing hydroxyl groups,

Table 1. Molar Stiffness Calculated with the Bicerano Theory for the Two Model Compounds, DGEBA and HBP95

	molar stiffness
model compound 1	90
model compound 2	79
DGEBA	134
HBP95	1758

similar to the DGEBA case. To provide for an autocatalytic reaction, however, the hydroxyl groups should easily approach the nonreacted epoxy groups. This, in turn, is only possible if the mobility of the molecule carrying the hydroxyl groups is adequate. In the HBP–amine reaction, the hydroxyl groups are shown to be unable to further catalyze the reaction. A rough estimation of the mobility of hydroxyl groups can be done by calculating the molecular diffusivity of a molecule using the Stokes–Einstein equation:[23]

$$D = kT/6\pi R\eta \qquad (9)$$

where R is the hydrodynamic radius of the macromolecule, T is the temperature, and η is the viscosity. Since for the HBPs the term $R\eta$ is much greater than for the corresponding DGEBA, the hydroxyl groups in the HBP shell molecules can be expected not to have the sufficient mobility required for catalyzing the reaction.

To estimate the effect of the molecular mobility for all the compounds used, a predictive semiempirical approach recently developed by Bicerano has been employed.[24] This approach is based on a topological evaluation of the molecular structure, which attributes a weight value to all atoms and chemical bonds considering their position in the macromolecular architecture. This theory allows the evaluation of main polymer properties, such as density, intrinsic viscosity, cohesive properties, solubility parameters, etc. In Table 1, the calculated molar stiffness for the two model compounds, the DGEBA and the HBP95, is presented. The calculated molar stiffness value, whose units are $g^{0.25}$ $cm^{1.5}/mol^{0.75}$, is inversely proportional to molecular mobility. Therefore, model compound 2 appears to be the most mobile, followed by model compound 1 and DGEBA. HBP95, according to the theory, is the less mobile, a factor of more than 13 being calculated for the difference in mobility between DGEBA and HBP95. This is in agreement with the proposed mechanism responsible for the experimentally observed noncatalytic reaction in HBP–IPD systems.

Another trend observed for the HBPs is a decrease in the maximum conversion obtainable at a fixed temperature with the increase of EEW, although a stoichiometric ratio of amine–epoxy is maintained. This is illustrated in Figure 9, where the isothermal conversion curves at 140 °C are plotted for all the compounds investigated. The same level of conversion is impeded for the HBPs because the spatial density of epoxy groups is affected by the epoxy equivalent weight. Since the spatial density of active hydrogen in the amine is constant and the spatial density of the epoxy groups decreases with the EEW, the maximum achievable conversion decreases proportionally to this difference. In other words, some of the epoxy groups are buried in the hyperbranched polymer and inaccessible to the curing agent.

A quantitative theoretical evaluation of the functional group spatial density can be performed by dividing the epoxy equivalent weight by the density of the compound. For simplicity, the compounds can be considered as rigid molecules, and the epoxy group is associated with a fixed volume in space. To easily react, this volume should be comparable with the one associated with the active hydrogen of the amine. If the volume is much larger, steric hindrance would impede the simultaneous bonding of several groups in the same region. The concept is illustrated in Figure 10. In support of this, NIR measurements have confirmed the impediment of secondary amine reaction in HBP–IPD systems. Table 2 expresses for the different compounds the values of the volume associated with a mole of epoxy groups, which is compared to the volume associated with an active hydrogen of the IPD. This approach clearly illustrates the tendency to a decrease in maximum achievable conversion with a decrease in EEW.

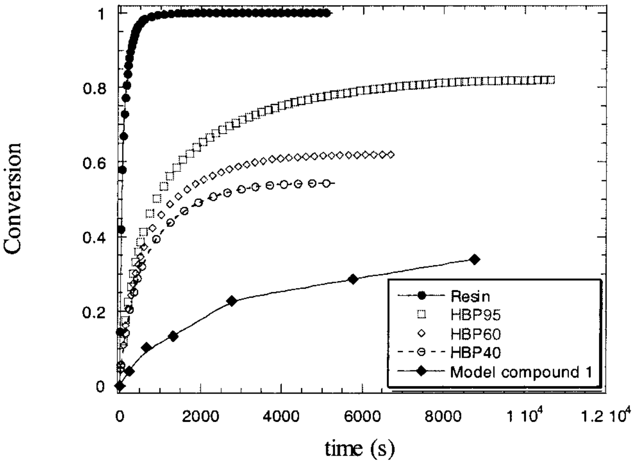

Figure 9. Conversion versus time at 140 °C for all the compounds reacted with IPD.

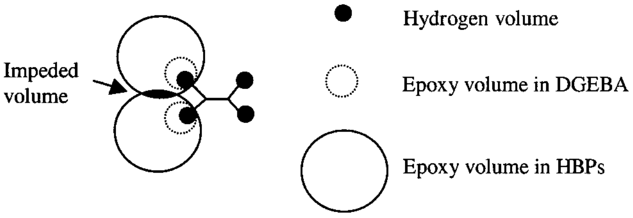

Figure 10. Schematic illustration of the concept of rigid sphere volume associated with reactive groups to take into account the steric hindrance effect.

Table 2. Rigid Volumes in (cm^3/mol) Associated with Reactive Groups as Calculated by Dividing the Reactive Group Equivalent Weight by the Density of Pure Compounds, for IPD, DGEBA, HBP95, HBP60, and HBP40

	volume		volume
IPD	46	HBP60	544
DGEBA	160	HBP40	1016
HBP95	386		

Finally, it should be stated that, for all the systems here investigated, the molecular mobility and reactive group spatial density are closely related, since a reduction in the latter implies an increase of the molecular size of the equivalent epoxy unit, in such reducing its mobility. However, mobility will also be reduced if the nature of the macromolecular backbone is altered, or chain branching is present, which does not necessarily change the EEW. Moreover, a reduction in the reactive group spatial density should merely reduce the intensity of the autocatalytic nature of the epoxy−amine reaction but should not impede it as is the case with a reduced molecular mobility.

Conclusion

Different model compounds have been used to highlight the effects of mobility, chemistry, steric hindrance, and segregation of amine−epoxy curing reactions.

The model compounds used have been shown to have very specific kinetics of reaction. A strong tendency to segregation and formation of micelles was observed in the solutions of both isophorone diamine model compounds, the model compound 2 being the most incompatible. Because of the lack of solubility of the latter, an amine−epoxy reaction is evident only in the case of epoxidized methyl undecenoate.

The DGEBA−IPD system has been shown to follow an autocatalytic reaction mechanism. This is due to the catalytic effect induced by the hydroxyl groups formed by reaction of epoxy with amine and which are considered to have a sufficient mobility to further catalyze the reaction. A modified Kamal model has been successfully used to fit conversion curves experimentally obtained by DSC. On the other hand, HBP−IPD systems show a noncatalytic reaction. The difference in reaction mechanism was partly attributed to the mobility of the hydroxyl groups which is much lower than in the case of the DGEBA resin. This was supported by a topological theory for polymer properties predictions developed by Bicerano.

The effect of volume density of functional groups was investigated using HBPs functionalized to various extents. The EEW was related to the mass associated with a functional group and expressed by the equivalent volume per group calculated from the EEW and the density of the compound. The experimental decrease in maximum achievable conversion could directly be correlated to the increased EEW of the compounds.

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