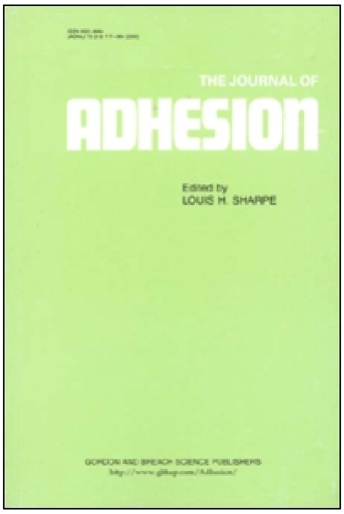

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Engineering Plastics from Lignin. 22. Cure of Lignin Based Epoxy Resins

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The kinetic cure parameters—activation energy, pre-Arrhenius factor, and reaction order—for three lignin copolymer epoxides were determined by multiple heating rate dynamic DSC experiments in accordance with the procedure of Ozawa and Doyle. The three epoxides differed in degree of polyether chain extension (and thereby in lignin content) and in molecular weight. Exothermic cure reactions were observed over a temperature range of between 100 and 240°C. Activation energy, pre-Arrhenius constant, and reaction order ranged between 53 and 66 kJ/mol, 10,000 and 440,000, and 1.21 and 1.28, respectively. Lignin content and molecular weight differences had surprisingly little effect on cure performance. This suggests that there are no steric or mobility obstacles to cure. Whereas the activation energy of the cure reaction is similar to that of commercial epoxy resins (*i.e.*, approximately 60 kJ/mol), the reaction order of the n-th order reaction ranges from 1.21 to 1.28 instead of the expected value of 2. This may be explained by a similar rate of the activation and ring-opening step of the cure reaction.

KEY WORDS epoxides; steam explosion lignin; lignin derivatives; hydroxypropyl lignin; cure kinetics; differential scanning calorimetry (DSC).

INTRODUCTION

In a previous report the epoxidation and fractionation of lignin-poly(alkylene oxide) copolymers were discussed.[1] In contrast to other lignin-based epoxides, these copolymer products contain epoxy groups which are not attached directly to the polyphenolic lignin, but they are separated from it by a poly(propylene/ethylene oxide) chain (Fig. 1). It was shown that these lignin copolymer-based epoxides can be crosslinked with an aromatic diamine to form strong thermosets which, depending on lignin content and polyether chain length, have glass transition temperatures ranging from 0°C to well above 100°C. However, preliminary to the formation of thermosetting networks it was of interest to investigate the influence of lignin content and/or molecular weight on cure kinetics and network formation. Although the epoxidation of lignins and lignin derivatives has been the subject of numerous studies (see Reference 1), no cure kinetic studies of these resins have been reported so far.

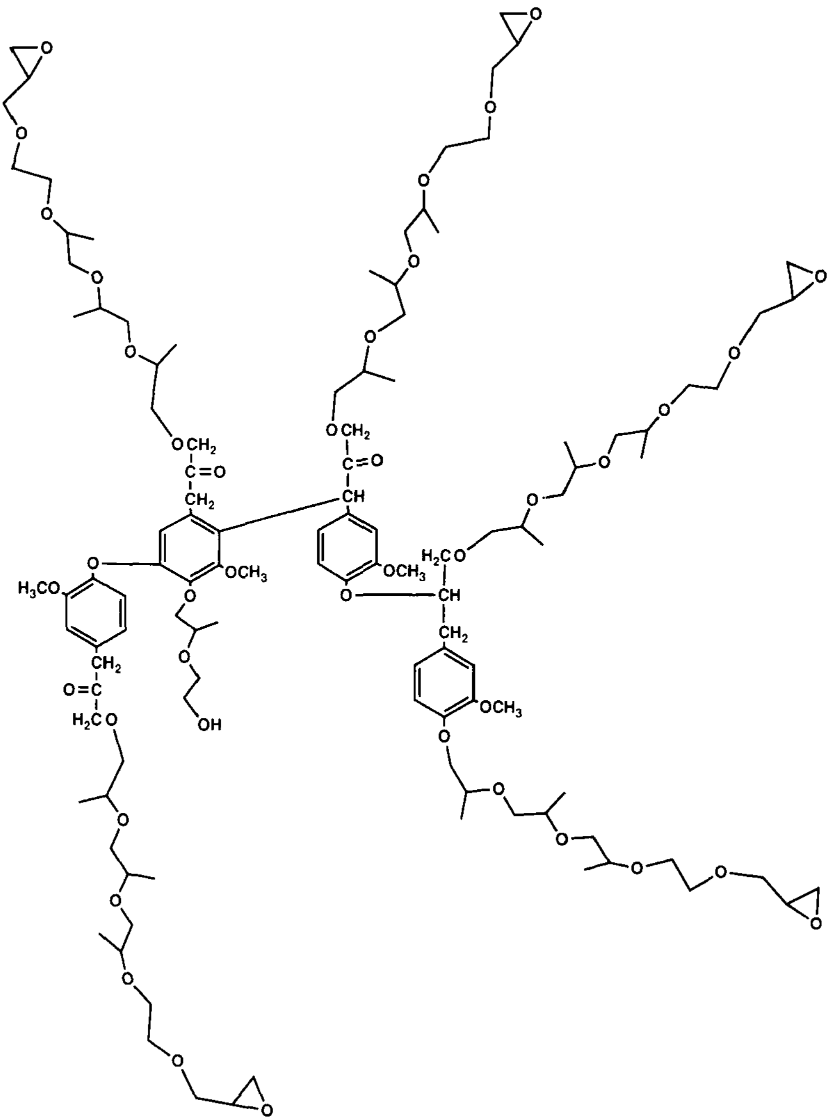


FIGURE 1 Schematic representation of a lignin-polyether copolymer epoxide.

When studying the kinetics of thermosetting systems one can distinguish two stages, roughly divided by the onset of diffusion control which is very often in the vicinity of the gel-point. Thus, the cure in the first stage is only a function of the chemical reaction kinetics while it also becomes influenced by the mobility of the reactants in the second stage. It has been shown, for instance, that commercial diglycidylether of bisphenol-A/meta-phenylene diamine (DGEBA-mPDA) systems change the order and type of reaction after the onset of gelation.[2]

Based on the model of Horie *et al.*,[3] stoichiometric epoxy-amine reactions are two-step processes whereby the primary amine initially reacts with an epoxy group to form a secondary amine which subsequently (second step) reacts with another oxirane to form the final tertiary amine crosslink. Both steps are catalyzed by hydrogen bond donating species which very often are hydroxyl groups that either are initially present, or that are formed during the reaction. The latter reaction, often referred to as "of autocatalytic nature," has its maximum rate of conversion at a conversion level of between 30 and 40%. On the other hand, if the catalyst is present initially in sufficient quantities, the reaction follows n-th order kinetics with the highest rate of reaction at very low conversion. The reaction is usually a second order process since the bi-molecular ring opening and addition step is rate determining (see Fig. 2).[4]

Differential scanning calorimetry (DSC) has become a convenient method to study the cure of thermosetting resins assuming that the rate of exothermic heat released during the course of the reaction is proportional to the rate of conversion.[5] Principally, DSC can be carried out in isothermal and scanning modes, and kinetic data can be obtained from both techniques. Nevertheless, the isothermal method

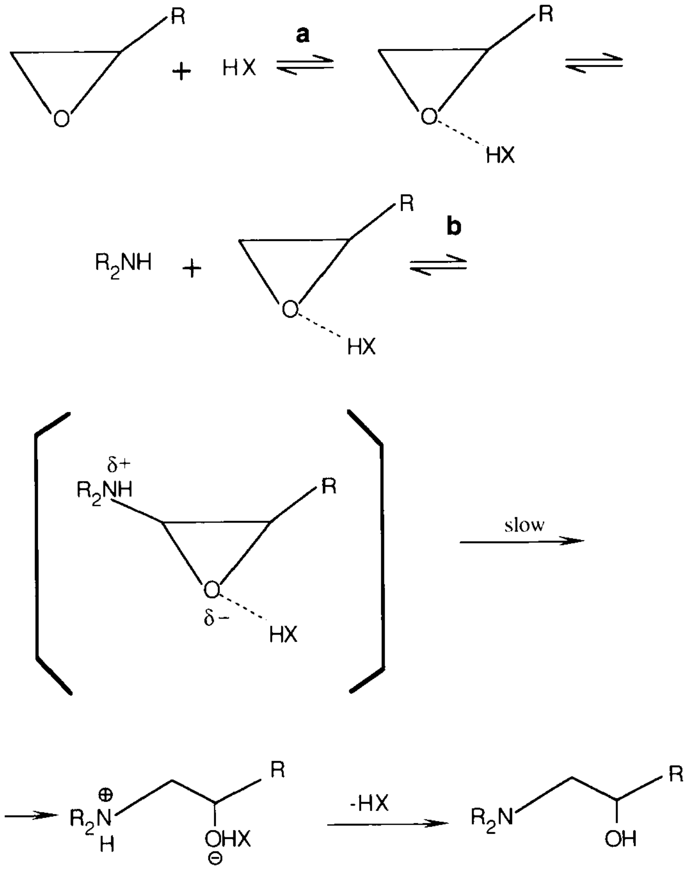


FIGURE 2 Mechanism of epoxy-amine reaction (Ref. 4): a) Formation of activated oxirane ring, hydrogen bonding between ring oxygen and [HX]; and b) Formation of transition stage and ring-opening.

is more straightforward, since rate and extent of reaction are recorded only as a function of time, while in dynamic mode these parameters are simultaneously functions of time and temperature. Since it has been shown that, in epoxy-amine reactions, the conversion up to the peak temperature is a constant which is independent of the scan rate[5] it is possible to calculate activation energies from results of multiple heating rate experiments using DSC in the scanning mode in accordance with the method of Ozawa[6] and Doyle.[7] Subsequently, the order of reaction can be determined from the slope of $\ln(d\alpha/dt)_T + E_a/RT$ *versus* $\ln(1-\alpha_T)$, and the intercept of this plot yields the natural log of the pre-Arrhenius frequency constant since the basic rate equation $(d\alpha/dt) = k\ f(\alpha)$ can be rewritten as:

$$\ln[A\,f(\alpha)] = \ln\left(\frac{d\alpha}{dt}\right)_T + \frac{E_a}{RT} \qquad (1)$$

where α = extent of reaction
E_a = activation energy
A = pre-Arrhenius constant
$f(\alpha)$ = function of reactant conc.

It was the objective of the present study to determine the kinetic cure characteristics of lignin polyether copolymer-based epoxides in relation to chemical structure parameters.

EXPERIMENTAL

I. Materials

Steam explosion lignin from yellow poplar wood *(liriodendron tulipifera)* was chain-extended with 12 moles of propylene oxide (PO) and 4 moles of ethylene oxide (EO) per kg of lignin. Subsequently, the lignin-polyether copolymer was epoxidized (Figure 1) with epichlorohydrin and fractionated by solvent precipitation. Chain-extension, epoxidation, and fractionation were carried out in accordance with earlier work.[1] Three fractions distinguished by varying lignin content and molecular weight (Table I) were used in this study. Meta-phenylene diamine (mPDA) was

TABLE I
Compilation of molecular weight, epoxy equivalent weight (EEW), and lignin content for three lignin based epoxy fractions

Sample designation	Mn[1] ($\times 10^3$)	M[1] ($\times 10^3$)	EEW[2] (grams/epoxy eq.)	Lignin content[3] (%)
A1	0.63	3.0	231	16
A2	1.9	28.0	399	37
A3	93.8	214.0	439	42

[1]By GPC.
[2]By HBr titration.
[3]By UV-spectroscopy.

chosen as crosslinking agent. This was purchased from Aldrich Chemical Company and used as received. Opened bottles were stored under nitrogen at -20°C. The low lignin content epoxide fraction was sufficiently liquid at room temperature to be mixed with the crosslinking agent in neat form. The procedure involved weighing the resin into a wide-mouth amber storage bottle and heating it in an oil bath to 80°C while being stirred. The stoichiometric amount of mPDA (with an amine equivalent weight of 27 g/eq.) was weighed into a small open glass dish and brought to a melt (*ca.* 70°C). The low-viscosity melt was added to the epoxy and stirring continued for five minutes. While reaction during mixing never can be completely avoided, the conversion during the procedure is small since, from this and earlier studies, it was found that the reaction does not significantly start before the temperature surpasses 100°C. The bottle was flushed with argon, sealed and stored at -70°C.

The two higher lignin content epoxy fractions were not suited to this method of mixing since they were either a highly viscous tar or a solid. To ensure intimate mixing of epoxy and hardener, it was necessary to blend them in solution and recover the solid or tarry blend by vacuum evaporation of the solvent at ambient temperature.

II. Methods

Differential Scanning Calorimetry Throughout this study, a DSC-4 instrument (Perkin Elmer, Inc.) connected to a temperature controller and interfaced to a Perkin Elmer computer (TADS) was used. All DSC experiments were conducted with the DSC head cooled to -70°C. The entire ensemble was covered by a transparent enclosure and flushed with dry nitrogen to avoid condensation. Dynamic experiments were carried out at four different heating rates (10, 20, 30, and 40° min^{-1}). All scans were done under simultaneous correction of the signals with a prerecorded baseline. Temperature calibration based on the melting endotherm of indium was carried out for all four rates. Two types of sample pans were used: sealed steel pans for the liquid resin and crimped aluminum pans for the solid samples. Total heat of reaction, H_{RXN}, was calculated by drawing a straight baseline from the beginning to the end of the exotherm and integrating the peak area. This value was taken as equivalent to 100% conversion. The peak temperature, T_p, was chosen as the point of maximum ($d\Delta H/dt$). Furthermore, the exotherm was divided into 30 degree wide slices and the partial heat of reaction, ΔH_T, and the individual temperature rates of enthalpy generation, $(d\Delta H/dt)_T$, were determined (Fig. 3). The conversion, α_T, and the rate of reaction, $(d\alpha/dt)_T$ were calculated as follows:

$$\left(\frac{d\alpha}{dt}\right)_T = \frac{\left(\frac{d\Delta H}{dt}\right)_T}{\Delta H_{RXN}} \tag{2}$$

$$\alpha_T = \frac{\Delta H_T}{\Delta H_{RXN}}$$

More specific experimental details are given elsewhere.[8]

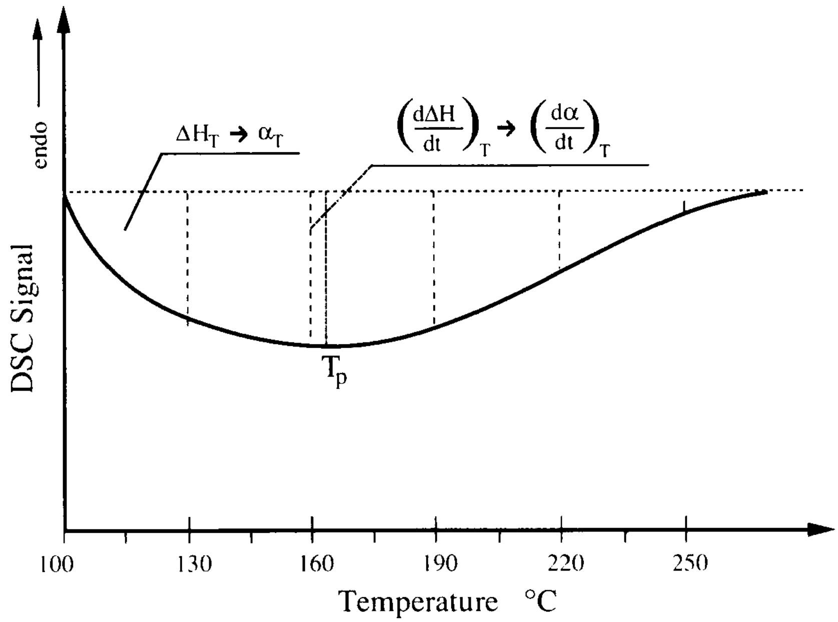
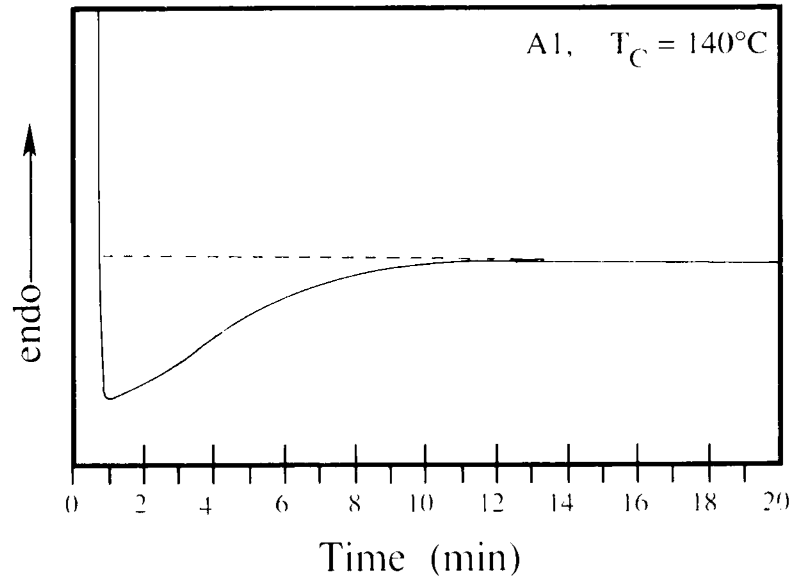


FIGURE 3 Determination of partial extent of conversion, α_T, and rate of conversion, $(d\alpha/dt)_T$, at specified temperatures T. (See equations 2 and 3 in text).

RESULTS AND DISCUSSION

The reaction of lignin polyether copolymer epoxides with meta-phenylene diamine (mPDA) follows n-th order cure kinetics where the maximum rate of conversion takes place at the beginning of the reaction (Fig. 4). This makes kinetic investigation by isothermal DSC impossible. It was, therefore, necessary to resort to multiheating dynamic DSC experiments in order to determine parameters for the rate equations.

Table II lists the total heat of reaction, ΔH_{RXN}, the peak temperature, T_p, and the conversion at peak temperature, α_{Tp}, for the three epoxide fractions. The values of the total heat of reaction and the conversion at peak temperature are fairly independent of heating rate, although α_{Tp} shows some scatter. However, it has to be taken into account that this variable is very sensitive to small errors in the determination of the peak temperature. The cure activation energies, E_a, of the three systems were obtained from the slopes of plots of the logarithmic scan rate, log ϕ, *vs.* the inverse peak temperature, T_p^{-1}, (Ozawa plot, Fig. 5). From the linear least square fits the activation energies (in kJ/mol) were calculated (Table III). The values are in good agreement with the overall range of activation energies reported for other epoxy-aromatic amine systems.[9] The activation energies show a consistent positive correlation with lignin content and/or molecular weight of the copolymer. Aside from the nature of E_a as a measure of energy barrier to reactions, it also can be considered a time-temperature shift factor which gives information about the



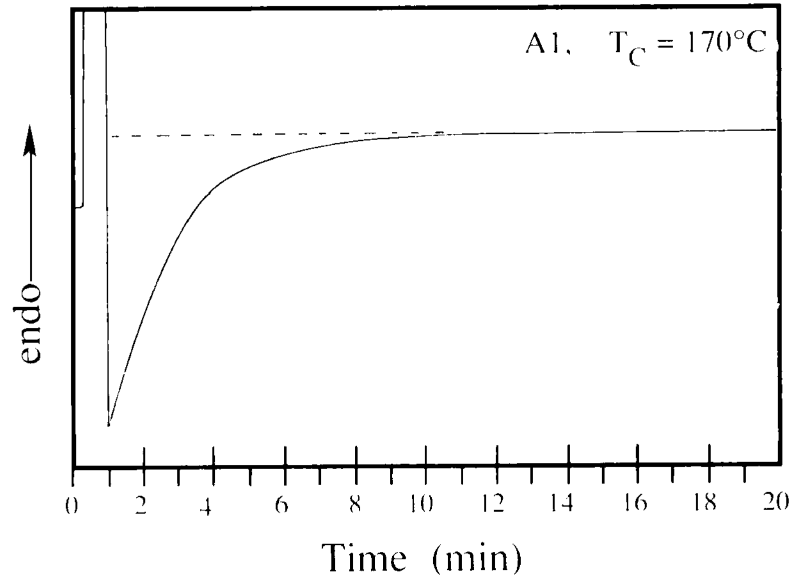


FIGURE 4 Isothermal DSC traces of cure exotherms, T_c, taken at 140°C and 170°C (fraction A1). The reaction exotherm clearly reveals n-th order characteristics since the maximum rate of conversion is at the start of the reaction.

TABLE II

Peak temperature, total exothermic heat, and conversion up to peak temperature for three lignin epoxy fractions

	Heating rate (°min^{-1})											
	10			20			30			40		
Sample	T_p[1]	H_{RXN}[2]	α_{Tp}[3]	T_p	H_{RXN}	α_{Tp}	T_p	H_{RXN}	α_{Tp}	T_p	H_{RXN}	α_{Tp}
A1	157.8	500	0.36	176.8	503	0.45	190.2	547	0.47	200.3	537	0.46
A2	166.6	434	0.51	187.7	448	0.56	193.7	416	0.50	206.8	428	0.52
A3	158.3	—	—	172.2	228	0.47	181.7	—	—	192.7	278	0.41

[1] Temperature of $(d\Delta H/dt)_{max}$(°C)

[2] Total Heat of Reaction (J/g)

[3] Conversion at Peak Temperature

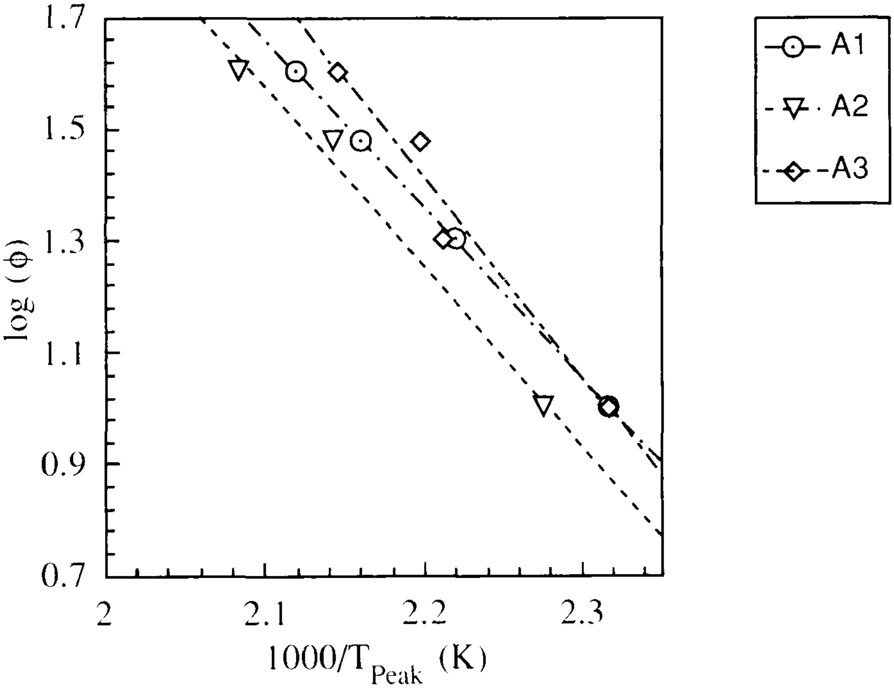


FIGURE 5 Relationship between the logarithmic heating rate (log ϕ) and the inverse peak temperature for three lignin epoxy fractions cured with mPDA (Ozawa plot).

TABLE III
Activation energies, pre-Arrhenius factors, and orders of reaction of three lignin based epoxide fractions cured with mPDA

Sample	Lignin content (%)	Activation energy (kJ/mol)	Reaction order	Nat. log of pre-Arrhenius constant
A1	16	52.7	1.21	9.2
A2	37	59.1	1.23	11.2
A3	42	65.6	1.28	13.0

magnitude of the temperature-dependent rate constant. However, to make absolute assessments about the time needed to reach a fixed extent of conversion, it is necessary to have knowledge of the reaction order and the Arrhenius factor. For this purpose, the extent and rate of reaction were calculated for each exotherm in 30 degree intervals from the partial area and the ordinate of the DSC trace, respectively (Fig. 3). From these data it was possible to determine the reaction order n and the pre-Arrhenius factor A by plotting $\ln(A\ f(\alpha))_T$ which is the sum of $(d\alpha/dt)_T$ and E_a/RT *vs.* $\ln(1-\alpha_T)$ (Fig. 6). The intercept at $\ln(1-\alpha_T)=0$ gives ln(A), and the slope is equivalent to the reaction order n. Indeed, examining the respective plots (Fig. 6) for the three fractional resin systems reveals that not only is the relationship highly linear, but the data also overlap for all scan rates. Only in the limits of low

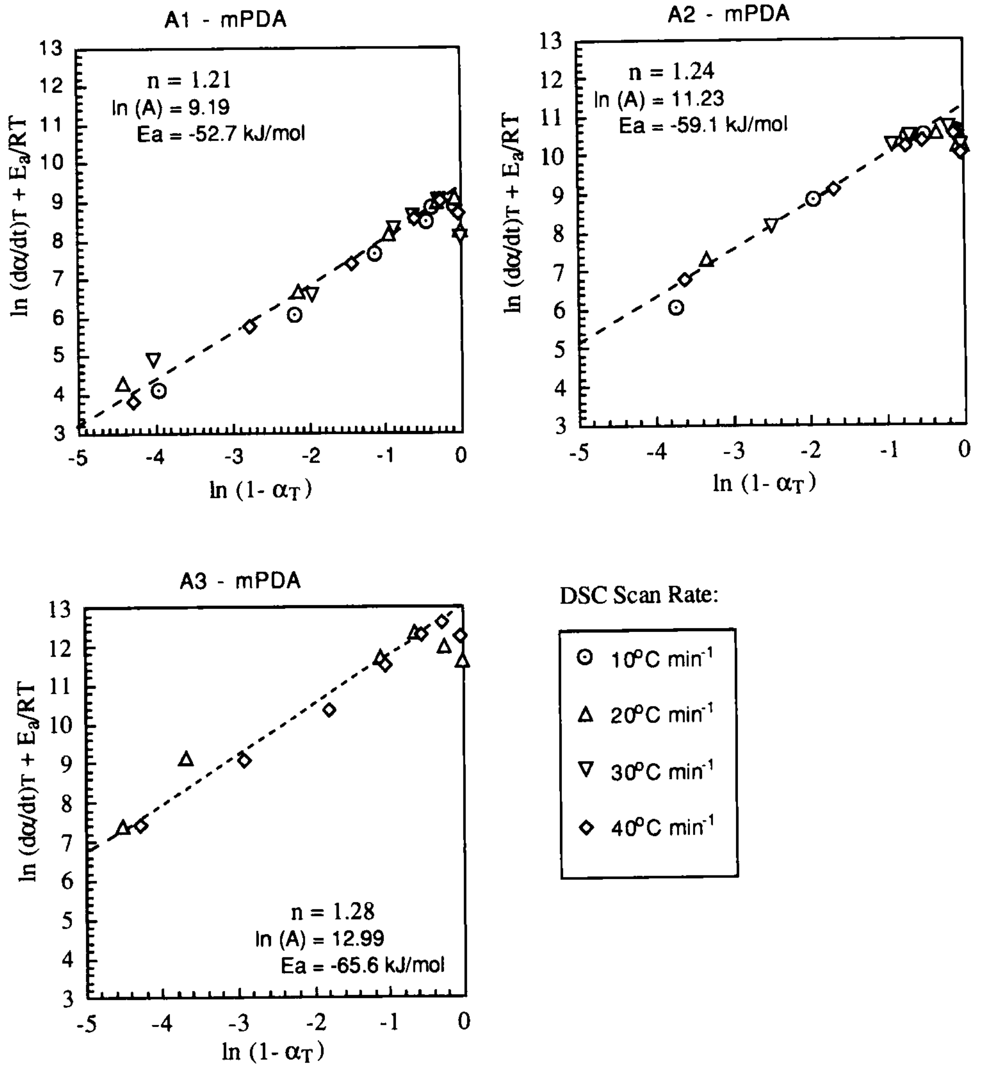


FIGURE 6 Determination of the rate of reaction and the pre-Arrhenius frequency factor for three lignin epoxy fractions cured with mPDA.

conversion ($\alpha<10\%$) do the data deviate from a straight line. This indicates a slight initial autocatalytic character of the cure. However, this deviation is much smaller, and the independence from the chosen heating rates higher, than similar results reported for an n-th order epoxy-novolac system.[10] The order of reaction, n, and ln(A) are compiled in Table III. Both the reaction order and the frequency factor increase with lignin content and/or molecular weight. It is so far not clear whether these trends together with the simultaneous increase in activation energy are genuine and significant, or whether they are merely due to compensation effects since the determination of A is based upon the activation energies.

It is now possible to write the overall isothermal rate equation for the three epoxy-amine systems as follows:

$$A1\text{: } \frac{d\alpha}{dt} = 9900\, e^{-(52670/RT)} (1-\alpha)^{1.21}$$

$$A2\text{: } \frac{d\alpha}{dt} = 73100\, e^{-(59050/RT)} (1-\alpha)^{1.24}$$

$$A3\text{: } \frac{d\alpha}{dt} = 442000\, e^{-(65580/RT)} (1-\alpha)^{1.28}$$

and from this to calculate the extent and rate of conversion as a function of time. These relationships were evaluated using three cure temperatures, 100°, 150°, and 200°C (Fig. 7). It is obvious that there is only little influence of lignin content or

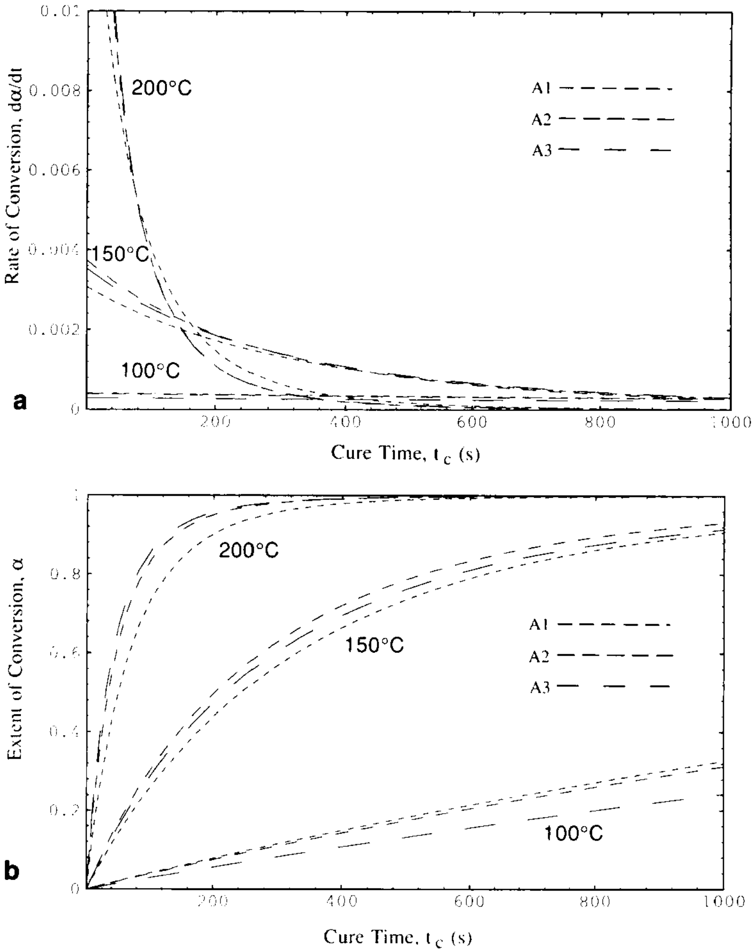


FIGURE 7 Theoretical isothermal extent of conversion (a) and rate of conversion (b), for three lignin epoxy fractions cured with mPDA, as function of cure time and cure temperature (calculated from dynamic DSC data).

TABLE IV
Reaction half times of three lignin based epoxide fractions cured with mPDA

Sample	Reaction half times (in sec) at cure temperature (°C) 100	150	200	Lignin content (%)	M_n of copolymer ($\times 10^3$)
A1	1810	243	50	16	0.63
A2	1872	197	33	37	1.9
A3	2680	220	31	42	93.8

molecular weight of the epoxy copolymer on the kinetics of the epoxy-amine cure reaction. The rates and extents of conversion as a function of cure time are almost identical for the three fractions. Very often it is convenient to compare reactions by calculating the half times where 50% of the reactants are depleted. The respective values are compiled in Table IV. Although most likely not significant, a slight influence of lignin content is detectable since the reaction is relatively faster for the low lignin-content resin at low temperatures. However, at high cure temperatures, where mobility constraints are reduced, the trend is reversed. As will be shown in a subsequent report,[11] lignin content plays a significant role once the reaction becomes diffusion-controlled, and the mobility of the functional groups becomes rate-determining.[8]

The reaction order of the three fractions is a fractional number close to one in each case. n-th order reactions where n is equal to one have been reported[5] but this would be in conflict with the basic underlying reaction mechanism (Fig. 2).[12] Only if one assumes that the bi-molecular oxirane ring, opening and addition step (Fig. 2b), which is usually much slower than the activation step and thus rate-determining, has a rate constant in the order of the uni-molecular oxirane activation step (Fig. 2a) is it possible to arrive at reaction orders closer to 1 than to 2. It was possible to show that the same reactions change to a reaction order equal to two once the system becomes diffusion-controlled, *e.g.* the mobility of the epoxy group is reduced and therefore, step b (Fig. 2) becomes rate-determining.[12]

CONCLUSIONS

The cure kinetics of epoxidized chain-extended lignin copolymer fractions with meta-phenylene diamine could be investigated by dynamic DSC. Due to their n-th order curing characteristics, isothermal experiments did not yield the necessary information, and multiple heating rate dynamic DSC experiments needed to be conducted. The exotherms typically started at 100°C and lasted to 240°C. They were analyzed according to the procedure developed by Ozawa and Doyle. Thereby it was found that the lignin content did not have a significant influence on the chemical kinetics of the curing reaction as long as the reaction was not diffusion-controlled. The reaction orders were fractional numbers close to one (1.21–1.28), which is in disagreement with the normally-observed, second-order mechanism for epoxy-amine reactions. An explanation for this phenomenon may lie in the assumption that the rate of the bi-molecular oxirane ring opening reaction is of the same magnitude as the uni-molecular activation phase.

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