DSC Study on the Effect of Cure Reagents on the Lignin Base Epoxy Cure Reaction

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ABSTRACT: The cure reactions of liquid lignin base epoxy resin (LEPL) with three different curing agents, viz., methylhexahydrophthalic anhydride, maleic anhydride, and 2-methyl-4-methylimidazole (EMI-2,4), were investigated by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry. Cure kinetics was evaluated using the multiple heating rate Kissinger method. The reactivities of the three curing agents were compared based on kinetics results obtained by DSC. FTIR spectra of these curing systems were also studied. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2332–2338, 2007

Key words: cure kinetics; DSC; epoxy; anhydride; imidazole

INTRODUCTION

Lignin is a kind of abundant biomass resource. Its utilization has drawn attention for more than a century; however, only small portion of lignin and its derivatives has found application.[1] A large amount of lignin is modified into all kind of derivatives in pulp and paper industry and poured as part of wastewater, which results in great harm to environment. Based on the point of environment protection and sustainable development, it has been looked important to utilize these lignin derivatives. In recent decades, lignin-based polymer has been more and more considered as potential way to use lignin reasonably in large scale.[2–5] Some researchers have also noticed lignin-based epoxy. Zhao[6] synthesized liquid lignin base epoxy resin (LEPL) by modifying lignin derivative to improve its reactional ability, followed by epoxidization.

Generally, the physical, electrical, transports, and ultimate mechanical properties of epoxy resin depend strongly upon the curing agents and curing process. The curing agents plan an important role in epoxy resin properties.[7] Imidazole are commonly used curing agents for epoxy cure. Imidazole-cured resins show good heat resistance, high modulus, and wide range of temperature. Besides, the imidazole, a further, widely employed family of epoxy curing agents is that of carboxylic dianhydrides.[8] These are generally less reactive than imidazole, but also less toxic and yield resins with a reduced tendency to absorb atmosphere moisture. So knowledge of the rate and kinetics of cure of LEPL with various curing agents is of utmost important to predict and to control the end properties of the crosslinked material.

Kinetic investigations are one of the most important applications of thermal analysis. The differential scanning calorimetry (DSC) technique finds more applicability since the epoxy is exothermic process. The kinetics of epoxy curing system has been widely studied by using isothermal or dynamic DSC technologies.[9–11] The curing agents and process of epoxy are very important to its possibility and performance. In this study, cure kinetics of lignin base epoxy resin cured with three cure reagents, MATHPA, MA, and EMI, is studied by using DSC. The rate and kinetics of different curing agents cured system are obtained and evaluated.

EXPERIMENTAL

Calcium lignosulfonate (lignin derivatives) was provided by Guangzhou Pulp and Paper industry, Guangzhou, People's Republic of China. Methylhexahydrophthalic anhydride (MTHPA) (m. p. −15°C, $d = 1.21$ g/cm^3), maleic anhydride (MA) (m. p. 53°C, $d = 1.50009$ g/cm^3), 2-methyl-4-methylimidazole (EMI-2,4) (m. p. 45°C, $d = 0.975$ g/cm^3), benzyldimethylamine (BDMA) (m. p. −75°C, $d = 0.900$ g/cm^3), and other reagents were analytically pure grade and purchased from Shanghai Chemical. The LEPL was synthesized by Zhao's[6] method. Calcium lignosulfonate was pretreated by sulfuric acid solution

and turned into lignosulfonic acid solution. Excess phenol was then added into the stirred lignosulfonic acid solution, followed by sulfuric acid solution being added at 80°C. The weight of phenol and sulfuric acid solution both were 40% of calcium lignosulfonate by weight, and the concentration of phenol and sulfuric acid solution were 99.5% and 50%, respectively. After the system had reacted at 95°C for 3 h, two phases were formed: an upper dark organic layer and a lower light acid solution layer. The dark organic layer was neutralized first and then distillated to remove phenol and get a kind of black gel. The black gel can be divided into water-soluble part and water-insoluble part. The water-soluble part was applied as monomer to synthesize lignin based epoxy resin. The water-soluble part was mixed with epichlorohydrin and 20 wt % sodium hydroxide water solution as catalyst was added. The deep brown-red liquid epoxy resin (LEPL) was acquired. The important properties of LEPL are epoxy value of 0.47 mol/100 g and $M_n = 365$.

The components of LEPL-MTHPA curing system were mixed in the ratio LEPL:MTHPA:BDMA = 10:8:0.3 by weight. The components of LEPL-MA curing system were mixed in the ratio LEPL:MA: BDMA = 10:4:0.3 by weight. The components of LEPL-EMI-2,4 curing system were mixed in the ratio LEPL:EMI-2,4 = 10:8 by weight. Curing studies were conducted on a TA Instruments DSC Q-10 in standard DSC mode under nitrogen atmosphere at a flow rate of 50 mL/min. After mixing the epoxy components the samples (7–9 mg) were sealed in an aluminum DSC sample pan and then covered with an aluminum lid and equilibrated at 50°C. The heat flow of the sample was recorded when it heated form 50 to 200°C in a constant heating experiment. The DSC measurements were performed at different heating rates of 2.5, 5, 7.5, and 10°C/min. The reaction was considered to be complete when the rate curve leveled off to a baseline. The DSC instrument was calibrated for temperature and heat flow using indium and lead metal standard. The Fourier transform infrared spectroscopy (FTIR) measurements were carried out with a EQUNOX 55 (BRUKER, Germany). The wavelength of spectrum was from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The uncured liquid sample was dabbed into a KBr pellet for tests directly. The cured epoxy was milled into powder. Took a small amount of powder (1–2% of the KBr amount) mixed with KBr powder grind the mixture for 3–5 min. Then press the mixture for 2 min to form a pellet.

THEORETICAL ANALYSIS

The DSC exothermic curves were used to evaluate the heat of cure (ΔH) and kinetic parameter of the cure reaction.
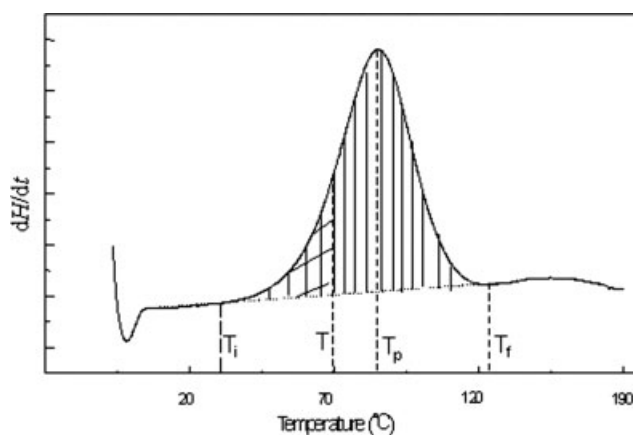

Figure 1 Representative dynamic DSC curve of the thermosetting resin.

The representative DSC curve displaying heat flow dH/dt against temperature T is shown in Figure 1. The onset temperature T_i, the peak temperature T_p, the terminal temperature T_f, and the values of dH/dt of the point on the curve can be got directly from the curve. The line between T_i and T_f is baseline. The whole area S of the exothermal peak is in direct proportion to the total quantity of heat ΔH released during the cure reaction completed, then S can be gained:

$$S = m\Delta H/\xi$$

where m is the mass of reactive sample, and ξ is the calibration coefficient that is independent of temperature.[12]

The FTIR spectra, as shown in Figure 2, indicates that the epoxy groups' absorption disappear after cure. This means the curing reaction is completed. That is to say the heat of ΔH is approximately the total heat of the curing reaction. Thus, ΔH can be considered as a constant over the whole cure
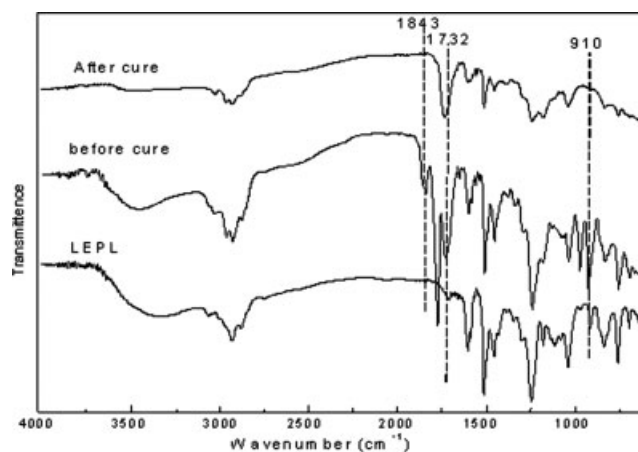

Figure 2 FTIR spectra of LEPL-MTHPA curing systems.

reaction. The heat of cure is directly proportional to the area under the DSC cure. The fractional conversion α calculated from the fractional and total areas under the DSC curve was used for the computation of the kinetic parameters.

The fractional extent of conversion at a given temperature T can be expressed as

$$\alpha = S_T/S = \Delta H_T/\Delta H$$

where ΔH_T is the heat of reaction of partially cured samples heated up to the temperature T. Then, the rate of the cure reaction is $d\alpha/dt = (dH/dt)/\Delta H$, where dH/dt is the heat flow above the baseline.

All kinetic studies start with a basic rate equation, which relates $d\alpha/dt$ to a function of the concentrations of the reactants [$f(\alpha)$] through a rate constant (k):

$$d\alpha/dt = kf(\alpha) \tag{1}$$

where α is the chemical conversion or extent of reaction and $f(\alpha)$ is assumed to be independent of temperature. k is assumed to follow an Arrhenius equation, thus $d\alpha/dt$ is expressed as:

$$d\alpha/dt = Ae^{-E/RT}f(\alpha) \tag{2}$$

where E is the activation energy, R is the gas constant (8.314 J/mol K), T is the absolute temperature, A is the pre-exponential of frequency factor, and $f(\alpha)$ is a function of the fractional extent of conversion α.

It has been demonstrated that some epoxy-anhydride systems follow nth-order autocatalytic kinetics, while others follow autocatylytic kinetics.[13–15] It also has been demonstrated that epoxy-EMI-2,4 system follows autocatalytic kinetics.[16]

No matter what the kinetics is, the function $f(\alpha)$ can be expressed in the form of one equation:

$$f(\alpha) = (1-\alpha)^n \alpha^m \tag{3}$$

where $n + m$ is the overall order of reaction.

Therefore, the objective of the kinetic study of the curing process is to determine the reaction equation, the reaction orders (m and n), E, and A. If $m = 0$, the reaction follows nth-order kinetics; if $m \neq 0$, the reaction follows autocatalytic kinetics.

RESULTS AND DISCUSSION

Heating FTIR spectra analysis

The FTIR spectra of LEPL-MTHPA, LEPL-MA, and LEPL-EMI-2,4 are shown in Figures 2–4, respectively. The curing mechanism of LEPL-anhydride and
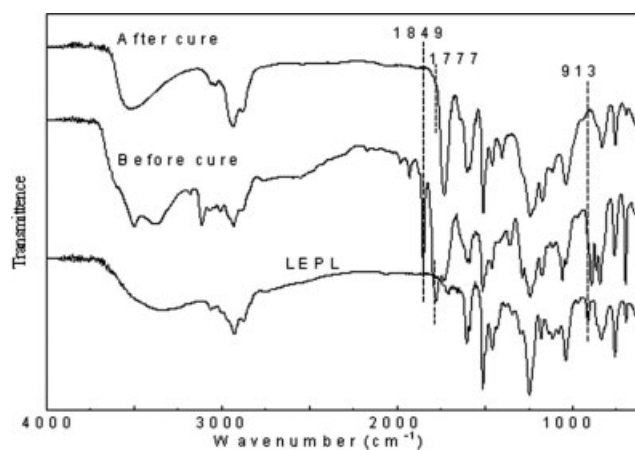
Figure 3 FTIR spectra of LEPL-MA curing systems.

LEPL-EMI-2,4 are shown in Figures 5 and 6, respectively. The FTIR spectra analysis is based on the band intensity change of functional groups during the reaction period. The LEPL-anhydride curing reaction is the reaction between epoxy and the anhydride (esterification). As shown in Figures 2 and 3, in the reaction between epoxy and anhydride, epoxy can be considered as a tetra-functional monomer while anhydride is bi-functional. This reaction produces ester linkage in the cured resins. FTIR was used to observe the change of the functional groups during the LEPL-anhydride process.

The analysis of FTIR spectra is based on the peak intensity variation of the epoxy groups' absorption at 910 cm^{-1}. For FTIR spectra of the LEPL-MTHPA system, the continual decreasing of epoxy band intensity at 910 cm^{-1} and that of the anhydride at 1775 cm^{-1} shows that there is progressive consumption of the epoxy and anhydride during the curing reaction. In the band at 1243 cm^{-1} and its vicinity there is an
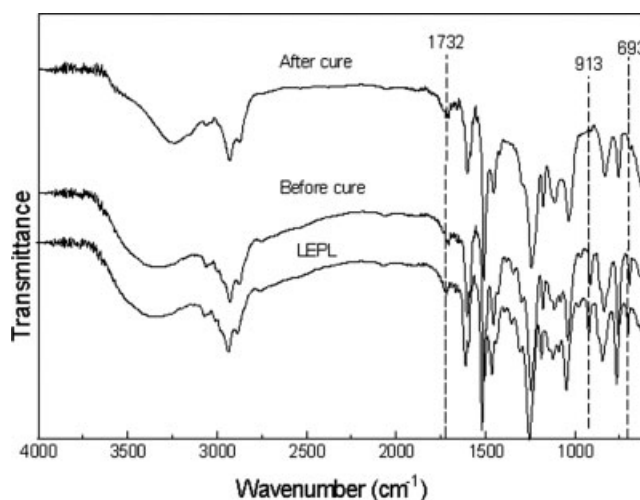

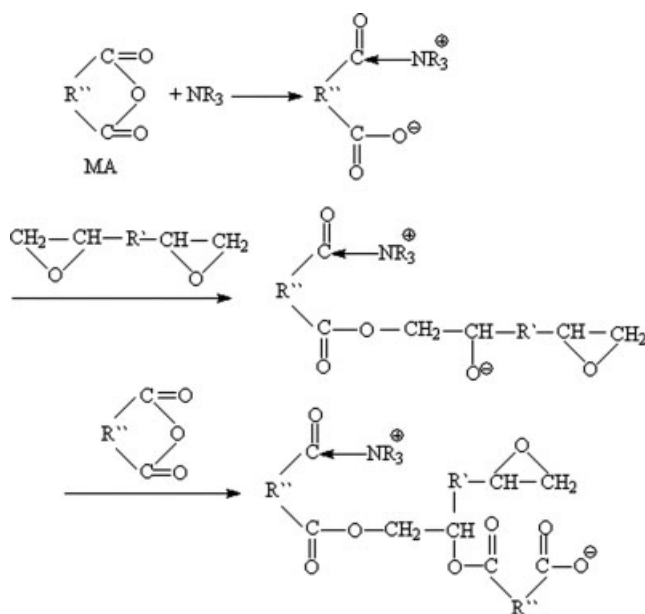**Figure 4** FTIR spectra of LEPL-EMI-2,4 curing systems.

Figure 5 Curing mechanism for the LEPL-anhydride system.

overlapping of the vibration of epoxy ring, the stretching vibration of C—O anhydride, changes are observed within this band during the heating process. Decreasing of both the epoxy and anhydride absorption bands can be observed due to their consumption by the curing reaction. Bands at 910 and 1243 cm^{-1} corresponding to epoxy groups disappear after the curing process while the intensity of the band at 1843 cm^{-1}, characteristic of anhydride groups, decreases. In addition, an increase of the intensity of the ester band at 1732 cm^{-1} is observed. All these changes indicate that the main reaction of curing is a polyaddition esterification reaction, which is accordance with the mechanism shown in Figure 5.

As can be seen in Figures 2 and 3, the mechanism of LEPL-MA curing system is similar to LEPL-MTHPA except two differences. One is that the band intensity at 1979, 1927, and 690 cm^{-1} disappeared, which attribute to unsaturated carbon atoms of MA,
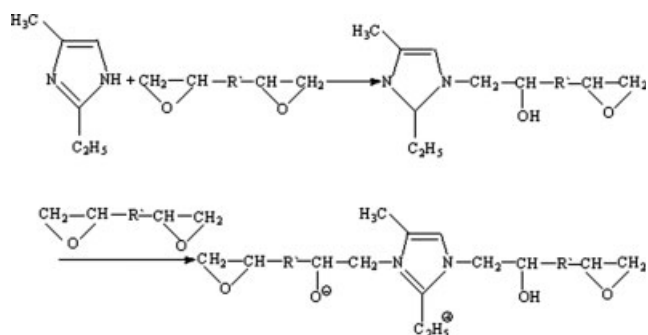

Figure 6 Curing mechanism for the LEPL-EMI-2,4 system.

during the LEPL-MA curing process. This indicated that unsaturated carbon atoms of MA were consumed in the process. Another difference is the continued presence of the hydroxyl band at 3650–3100 cm^{-1}. This change indicates there has been an addition esterification reaction with a parallel etherification reaction.

Figure 4 illustrates the variation in the FTIR spectra of LEPL-EMI-2,4 system before and after cure. The main changes appear to be the reduction of magnitude of the absorption peaks associated epoxy (913 cm^{-1}) groups, hydrogen bonds (3500–3200 cm^{-1}), and 693 cm^{-1}. The peak of epoxy groups disappears after cure. The peak of hydrogen bonds becomes sharper. The peak intensity at 693 cm^{-1}, owing to the vibration of substituted benzene ring structure, also decreases. It suggests the peak at 693 cm^{-1} is associated with the molecular weight or steric hindrance of benzene ring structure. Thus, it can be seen the main reaction of LEPL-EMI-2,4 curing system is the epoxy groups' consumption, while other groups have no variation. This mode of cure can hold the molecular structure except epoxy group. From the general mechanism of epoxy resin cured by imidazole, as shown in Figure 6, the variation of groups during the cure reaction is accordance with the mechanism illustrated in Figure 6.

Analysis of dynamic DSC data

The multiple heating rate Kissinger method,[17] which makes possible the determination of the activation energy regardless of reaction order by making differential thermal analysis at a number of heating rates, was used to calculate the kinetic parameters. The Kissinger method is based on the assumption that the conversion at the peak during exotherm is constant and independent of the heating rate. The reactions were conducted at four different heating rates: 2.5, 5.0, 7.5, and 10.0°C/min. Table I lists peak (T_p) temperature of the LEPL-MTHPA, LEPL-MA, and LEPL-EMI-2,4 cure systems at different heating rates. Cure temperatures can be considered as an indicator of reactivity. Based on the cure temperature reactivities for the cure reactions are in the order LEPL-EMI-2,4≫LEPL-MA≫LEPL-MTHPA.

TABLE I
Peak Temperatures at Different Heating Rates of Different Curing System

System	Peak temperature at different heating rate (K)			
Heating rate (°C/min)	2.5	5.0	7.5	10.0
LEPL-MTHPA	380.49	390.94	397.11	401.73
LEPL-MA	373.99	388.15	395.92	401.45
LEPL-EMI-2,4	359.28	375.95	384.52	388.39

On the basis of Kissinger method, E can be calculated with the peak temperature (T_p) and heating rate β as follows:

$$d[\ln(\beta/T_p^2)]/d(1/T_p) = -E/R$$

where β is the heating rate in $^\circ$C/min, R is the gas constant (8.314 J/mol K).

Figure 7 shows the plot of $\ln(\beta/T_p^2)$ versus $1000/T_p$ of the LEPL-MTHPA cure system. A linear regression suggests that, to a good agreement ($R = 0.99998$), the activation energy E calculated by Kissinger method is 76.54 kJ/mol.

For the thermosetting resins we have

$$\ln(d\alpha/dt) = \ln A - E/RT + n\ln(1 - \alpha) + m\ln\alpha \quad (4)$$

then $\ln[d(1 - \alpha)/dt] = \ln A - E/RT + n\ln\alpha$
$$+ m\ln(1 - \alpha) \quad (5)$$

Equation (4) − Eq. (5)

Value I $= \ln(d\alpha/dt) + E/RT - \ln[d(1 - \alpha)/dt]$
$$- E/RT = (n - m)\ln[(1 - \alpha)/\alpha] \quad (6)$$

Equation (4) + Eq. (5)

Value II $= \ln(d\alpha/dt) + E/RT + \ln[d(1 - \alpha)/dt]$
$$+ E/RT$$
$$= 2\ln A + (n + m)\ln[\alpha(1 - \alpha)] \quad (7)$$

DSC curing curve with the heating rate of 10°C/min was studied. The value of $n - m$ determined from the slope of the plot of Value I versus $\ln[(1 - \alpha)/\alpha]$, as shown in Figure 8, is 0.92; the values of $n + m$ and $2\ln A$ obtained from the slope and intercept of the plot of Value II versus $\ln[\alpha(1 - \alpha)]$, as shown in Figure 9, are 0.98 and 50.5 respectively.
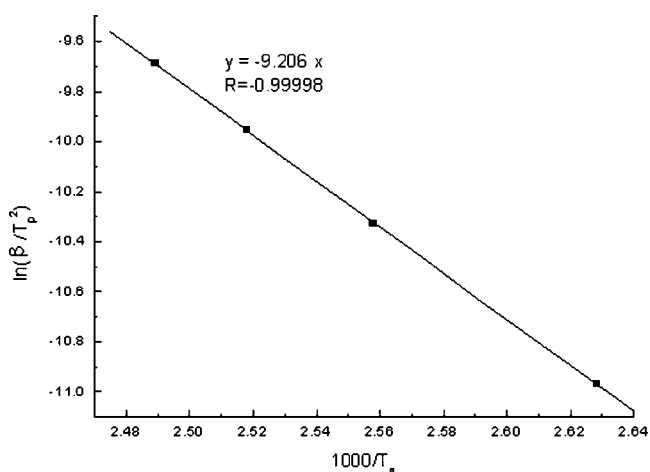

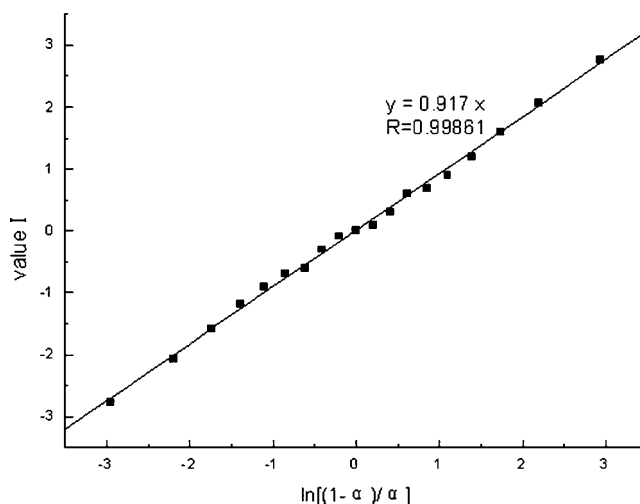**Figure 8** Plot of Value I versus $\ln[(1 - \alpha)/\alpha]$ (heating rate of 10°C/min).

Then we have

$$n \approx 0.95; \quad m \approx 0.03; \quad A = e^{25.3}$$

the parameter m is near 0, and so it can be ignored.

Thus, the curing kinetic equation of the LEPL-MTHPA system with Kissinger method can be expressed as

$$d\alpha/dt = e^{25.3}e^{(-76.54/RT)}(1 - \alpha)^{0.95}, \qquad \alpha \in [0, 1]$$

With the same method, the activation energies and kinetics parameters of LEPL-MA and LEPL-EMI-2,4 cure system were obtained and listed in Table II.

For the epoxy-anhydride system, as shown in Table II, the activation energy of LEPL-MTHPA is bigger than that of LEPL-MA system. The lower reactivity of MTHPA owing to the methyl in the
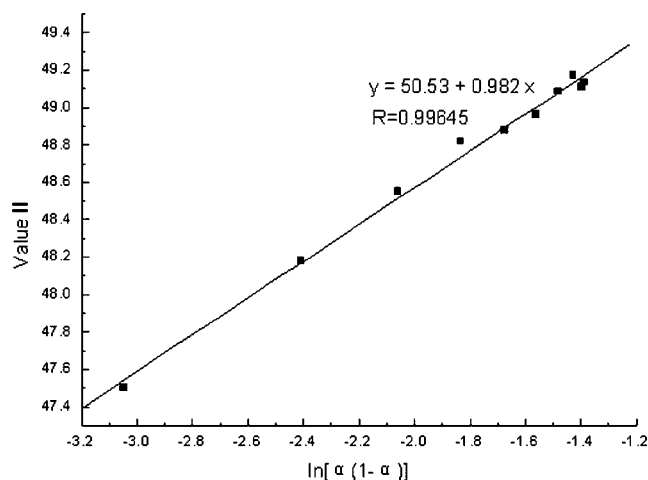

Figure 7 Plot of $\ln(\beta/T_p^2)$ versus $1000/T_p$.

Figure 9 Plot of Value II versus $\ln[\alpha(1 - \alpha)]$ (heating rate of 10°C/min).

System			E (KJmol^{-1})					Correlation coefficient
Cure reaction activation energy system								
LEPL-MTHPA			76.54					0.99998
LEPL-MA			56.35					0.99921
LEPL-EMI-2,4			47.22					0.99214

System	$n + m$	$2\ln A$	Correlation coefficient	$n - m$	Correlation coefficient	n	m	A
Order of reaction and frequency factor system								
LEPL-MTHPA	0.981	50.532	0.99861	0.917	0.99645	0.95	0.03	$e^{25.3}$
LEPL-MA	1.474	39.206	0.99950	1.004	0.99968	1.00	0.47	$e^{19.6}$
LEPL-EMI-2,4	1.148	33.157	0.99960	0.635	0.9964	0.89	0.26	$e^{16.58}$

System	Curing kinetic equation
Curing kinetic equation system	
LEPL-MTHPA	$d\alpha/dt = e^{25.3}e^{(-76.54/RT)}(1 - \alpha)^{0.95}\alpha^{0.03}, \quad \alpha \in [0,1]$
LEPL-MA	$d\alpha/dt = e^{19.60}e^{(-56.35/RT)}(1 - \alpha)^{1.00}\alpha^{0.47}, \quad \alpha \in [0,1]$
LEPL-EMI-2,4	$d\alpha/dt = e^{16.58}e^{(-47.22/RT)}(1 - \alpha)^{0.89}\alpha^{0.26}, \quad \alpha \in [0,1]$

molecular structure, the steric hindrance and inductive effect of methyl decrease the electrophilic reactivity of carbon of carboxylic acid, thus lower the reactivity of anhydride of MTHPA. The activation energy of LEPL-EMI-2,4 system is lower than LEPL-MTHPA and LEPL-MA system. This suggests EMI-2,4 react faster than MTHPA or MA with LEPL. The activation energy of LEPL-MTHPA system is 76.54 kJ/mol. Similar values have been report by Montserrat et al.[14] (64–75 kJ/mol), which the epoxy used is DGEBA. The activation energy of LEPL-MA system is 56.35 kJ/mol, much smaller than that reported by Taratorin et al.[15] (100 kJ/mol), and the activation energy of LEPL-EMI-2,4 system 47.22 kJ/mol, similar to the result obtained by Zhou et al.,[18] whose activation energy is 49.03 kJ/mol.

For LEPL-MTHPA system, $n = 0.95$, $m = 0.03 \approx 0$, and so the system follows nth order kinetics; for LEPL-MA system, $n = 1.00$, $m = 0.49$, and so the system follows autocatalytic kinetics; for LEPL-EMI-2,4 system, $n = 0.89$, $m = 0.26$, and so the system follow autocatalytic kinetics. As indicates in Table II, the overall reaction order $n + m$ of LEPL-MA system is 1.474, while the LEPL-MTHPA system is 0.981. It suggests the cure reaction of LEPL-MA system is more complex than LEPL-MTHPA system. The result is accordance with the FTIR spectra, which indicated the unsaturated carbon atoms of MA were consumed in the process. The frequency factor A and overall reaction order of LEPL-EMI-2,4 system is $e^{16.58}$ and 1.148, respectively. Similar results obtained by Zhou et al. are $e^{14.5}$ and 1.22, respectively. The pre-exponential factor of the two systems shows a large difference. This may be attributed to the difference in molecular structure of LEPL and DGEBA. From the apparent activation energy and reaction order points of view, it suggests the reaction of LEPL with EMI-2,4 is similar to the reaction of DGEBA with EMI-2,4.

CONCLUSIONS

The reaction kinetics of LEPL cured with three curing agents were studied by DSC and FTIR. The kinetics parameters including frequency A, activation energy, and overall reaction order were obtained and evaluated. With Kissinger method, a simple and effective method in qualitative comparison among different curing systems, the cure reaction apparent activation energy of the LEPL-MTHPA, LEPL-MA, and LEPL-EMI-2,4 system is 76.54, 56.35, and 47.22 kJ/mol, respectively. The value of ln A of the LEPL-MTHPA, LEPL-MA, and LEPL-EMI-2,4 system is 25.3, 19.6, and 16.58, respectively. The $m + n$ of the LEPL-MTHPA, LEPL-MA, and LEPL-EMI-2,4 system is 0.95, 1.47, and 1.148, respectively. Furthermore, the LEPL-MTHPA system follows nth order kinetics, and the LEPL-MA and LEPL-EMI-2,4 system follow autocatalytic kinetics. FTIR spectra indicate the reactions are completed when the cure process is over. Thus the MTHPA, MA, and EMI-2,4 are reliable curing agents for LEPL cure.

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