

Effects of Modifiers in Organoclays on the Curing Reaction of Liquid-Crystalline Epoxy Resin

Min-Min Shen,^{1,2} Man-Geng Lu,¹ Yong-Lie Chen,² Cheng-Yong Ha¹

¹Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China

²Sun Yat-Sen (Zhongshan) University, Guangzhou 510275, China

Received 5 March 2004; accepted 10 October 2004

DOI 10.1002/app.21443

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effects of three organoclays (Cloisite 10A, 93A, and 30B) with different modifiers on the curing reaction of a liquid-crystalline epoxy (LCE) resin based on 4,4'-diglycidylxybiphenyl and the curing agent sulfanilamide were studied. The curing kinetics of the LCE and clay composites were analyzed with differential scanning calorimetry. The Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose methods were used to calculate the activation energies at different conversions. All three alkylammonium ions

lowered the reaction activation energy and catalyzed the epoxy ring-opening reaction with the diamine curing agent. 30B, with two hydroxy groups of quaternary ammonium, showed the highest catalysis because the hydroxy groups facilitated the curing process. 10A and 93A had similar catalytic abilities. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1329–1334, 2005

Key words: organoclay; liquid-crystalline polymer

INTRODUCTION

Epoxides constitute an important class of thermosetting polymers. The properties of epoxy resins can be improved by the addition of mesogenic units to the network, which results in liquid-crystalline thermosets.^{1–8} Improvements in liquid-crystalline epoxy (LCE) networks have been described previously and include greater thermal and orientational stability, low shrinkage upon curing, low thermal expansion coefficients, high moduli, and enhanced reaction rates.^{9–16} These improvements make LCEs potentially useful for a number of applications, such as electronics, advanced composites, and nonlinear optics.

The study of LCE composites has attracted much attention in the past years. The effect of coreacting a conventional epoxy resin with LCEs was investigated by Carfagna et al.^{17,18} and Sue et al.¹⁹ Some articles have reported LCE composites based on carbon fibers^{20–22} and carbon nanotubes.²³ Because many rigid-rod monomers require very expensive raw materials for synthesis, their blends with cheaper components can extend the market for LCEs toward new applications.

Clays have long been used as fillers in polymer systems because of their low cost and the improved mechanical properties in the resulting polymer composites due to their high aspect ratio and platy mor-

phology. All other parameters being equal, the efficiency of a filler at improving the physicomechanical properties of a polymer system is sensitive to its degree of dispersion in the polymer matrix. Clay consists of hundreds of individual platy layers that are held together by electrostatic forces between two adjacent particles. The electrostatic forces are very strong, and it is difficult to break the layers down to the scale of individual particles with no apparent interaction in the dispersion process to obtain a true nanocomposite: the exfoliated nanocomposite. A faster intragallery polymerization produces an exfoliated clay structure. The individual clay layers are pushed out of the tactoids by the gradual diffusion of monomeric epoxy into the clay gallery. It has been argued that faster intragallery polymerization results from the catalytic activity of the organic modifier, quaternary alkylammonium ions, present inside the clay gallery. Conventional polymer–clay composites containing aggregated nanolayer tactoids commonly have improved rigidity, but often at the expense of strength, elongation, and toughness. Until recently, clay particles could be dispersed on the nanoscale, typically in the range of 1–100 nm. Clay-based nanocomposites exhibit markedly improved properties in comparison with the pure polymers or conventional composites. The use of organoclays as precursors to nanocomposite formation has been extended to various polymer systems, including epoxies, polyurethanes, polyimides, nitrile rubber, polyesters, polypropylene, polystyrene, and polysiloxanes. Much work has been done on nanocomposites based on conventional epoxy resins.^{24–29}

Correspondence to: M.-G. Lu (mglu@mail.gic.ac.cn).

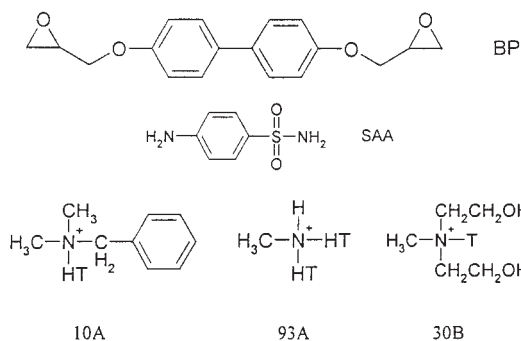


Figure 1 Chemical structures of BP, SAA, and the three organoclay modifiers (10A, 93A, and 30B). HT denotes hydrogenated tallow (~65% C18, ~30% C16, and ~5% C14).

In this study, three organoclays (Cloisite 10A, 93A, and 30B) with different modifiers were selected to investigate which chemical structure of the organic modifiers had the highest catalytic activity with respect to 4,4'-diglycidyloxybiphenyl (BP) and the curing agent sulfanilamide (SAA), which is widely used in LCE systems. The three modifiers were all quaternary alkylammonium ions with at least one long alkyl chain. 10A had a phenyl group that was more compatible with the LCE resin and diamine curing agent, and so the monomeric epoxy and curing agent could more easily diffuse into the clay gallery. 93A had a proton, and 30B had two hydroxy groups, which were supposed to catalyze the epoxy ring-opening reaction with amine curing agents. The kinetic parameters were obtained by an isoconversional method.

THEORETICAL

This study started with the basic equation for nonisothermal conditions:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where T is the temperature, α is the reaction conversion, A is the pre-exponential factor in the Arrhenius equation, $\beta = dT/dt$ is the heating rate, E is the activation energy, R is the gas constant, and $f(\alpha)$ is a model function that depends on the reaction mechanism.

The integral form of eq. (1) is

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT$$

If we suppose $G(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)}$ and $u = E/(RT)$, then trivial arrangement yields

$$G(\alpha) = \frac{AE}{\beta R} \int_{\infty}^u \frac{-e^{-u}}{u^2} du = \frac{AE}{\beta R} P(u) \quad (2)$$

Differential scanning calorimetry (DSC) is an effective method for monitoring curing kinetics. The fractional conversion (α) can be defined as follows:

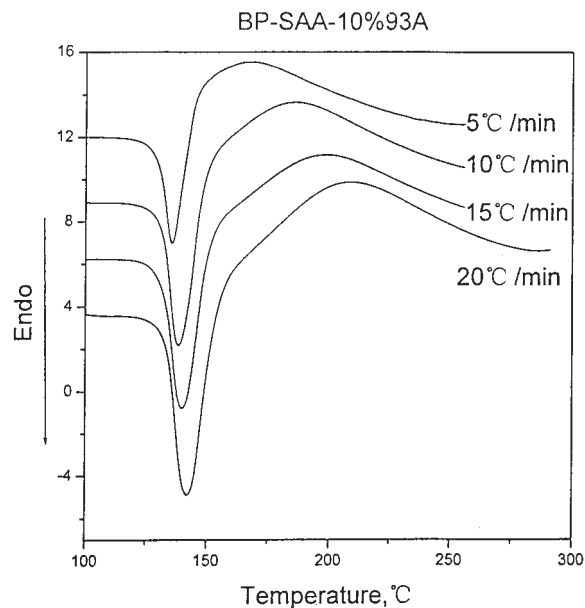
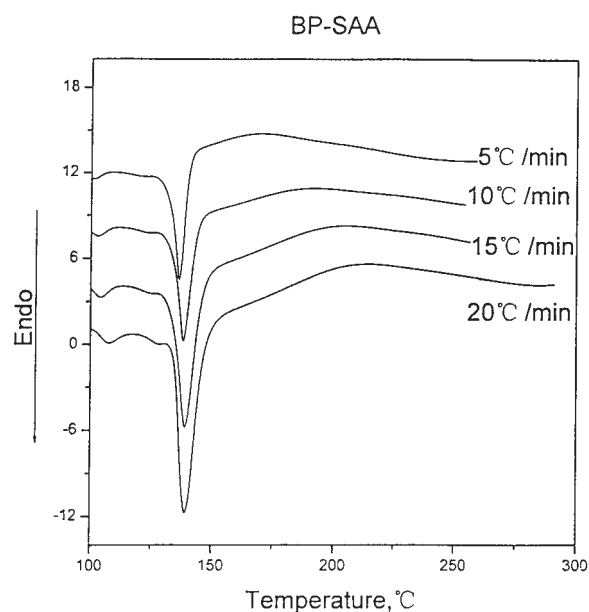


Figure 2 DSC scans at different heating rates.

TABLE I
T_p for BP-SAA

Sample	T _p (°C)			
	20°C/min	15°C/min	10°C/min	5°C/min
No clay	215.6	207.0	194.2	173.7
10% 10A	205.2	196.9	186.4	164.0
10% 93A	204.6	195.6	184.4	164.2
10% 30B	202.4	193.8	184.0	163

$$\alpha = \frac{1}{Q_{rxn}} \int_0^t \frac{dQ}{dt} dt \quad (3)$$

where dQ/dt is the specific heat flow and Q_{rxn} is the total heat released when an uncured material is completely cured. The value of Q_{rxn} was determined by the integration of a DSC peak:

$$Q_{rxn} = \int_0^{t_f} \frac{dQ}{dt} dt \quad (4)$$

where t_f is the time to the completion of the cure. In fact, t_f is the time at which the heat flow drops below the sensitivity of a DSC instrument.

From eqs. (1) and (2), $f(\alpha)$ had to be known for the calculation of E and A . Different models have been developed to describe the curing reactions of epox-

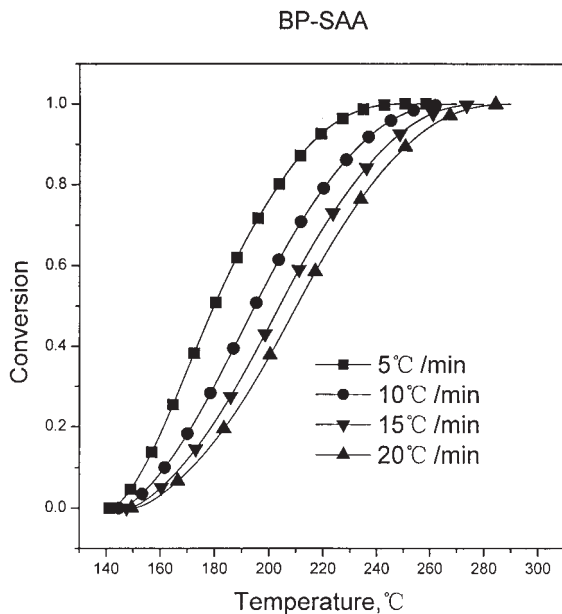


Figure 3 α as a function of the temperature at various heating rates.

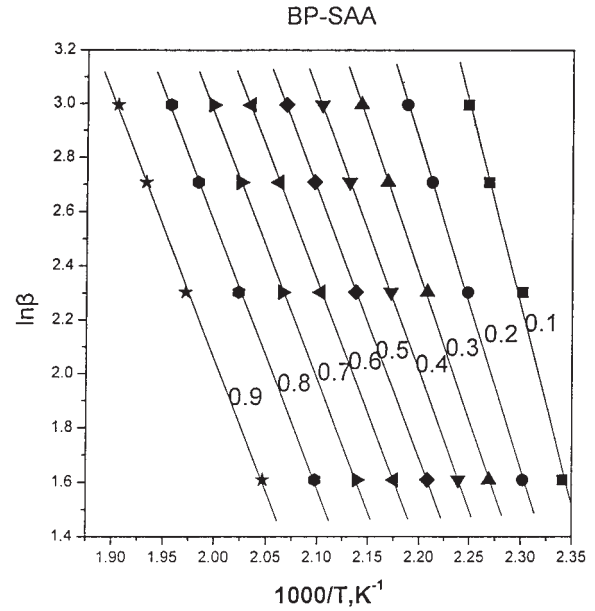


Figure 4 Plots of $\ln \beta_i$ versus $1000/T_{\alpha,i}$ according to the FWO method.

ides, including the n th-order reaction model, the autocatalytic reaction model, and the diffusion-control model.³⁰ Recently, isoconversional models have been widely used to analyze the curing process of epoxy resins, for which it is not necessary to assume a particular form of a reaction model to evaluate the curing kinetics.^{31,32}

According to the Doyle equation,³³ $P(u)$ was $0.00484e^{-1.0516u}$. The Ozawa equation was obtained from eq. (2) after natural logarithms were taken:

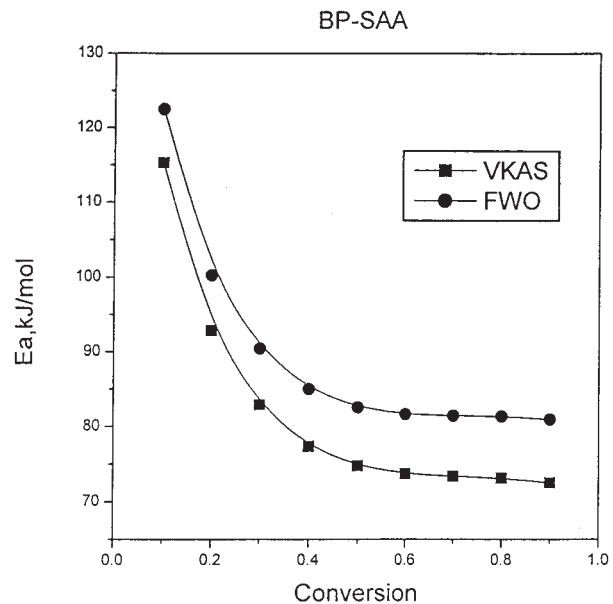


Figure 5 E as a function of the conversion.

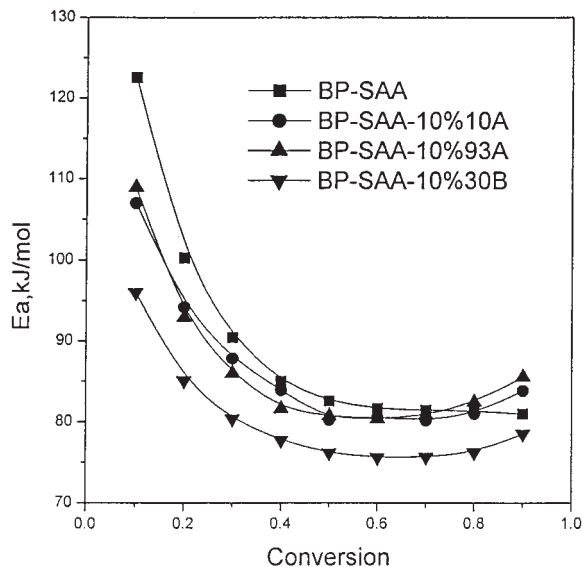


Figure 6 E as a function of the conversion according to the FWO method.

$$\ln \beta = -1.0516 \frac{E}{RT} + \ln 0.00484 \frac{AE}{G(\alpha)R} \quad (5)$$

The Flynn–Wall–Ozawa (FWO)^{34,35} method is an integral method that can be used to determine E and A without knowledge of the reaction mechanism. It was used to determine E and A for given values of the conversion. E for different conversion values was calculated from $\ln \beta_r - 1000/T_{\alpha,i}$ plots.

The Kissinger–Akahira–Sunose (KAS) method³⁶ is another kinetic method for determining E from the relationship between the conversion and the reaction temperature without a precise knowledge of the reaction mechanism. At the maximum reaction rate ($T = T_p$),

$$\frac{d}{dT} \left(\frac{d\alpha}{dT} \right)_{T_p} = 0$$

was 0. Therefore, the Kissinger function was obtained from eq. (1) as follows:

$$\ln \frac{\beta}{T_p^2} = -\frac{E}{RT_p} + \ln \frac{AE}{R} + \ln \left[\frac{-df(\alpha)}{d\alpha} \right]_{\alpha} \quad (6)$$

The variational Kissinger–Akahira–Sunose (VKAS) method is like the FWO method and was used to determine E for given values of the conversion from $\ln \frac{\beta_i}{T_{p,i}^2}$ plots.

EXPERIMENTAL

Materials

The LCE monomer, BP, was synthesized according to a method reported in the literature.³⁷ SAA was pur-

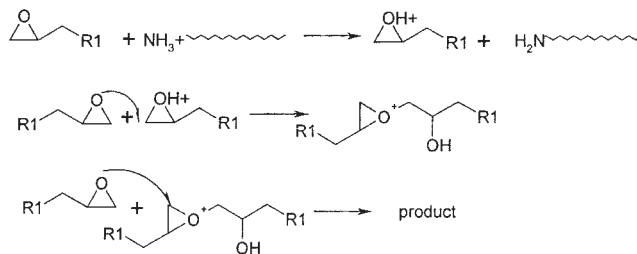


Figure 7 Mechanism of the homopolymerization of epoxy induced by proton transfer.

chased from Alfa. Cloisite 10A, 93A, and 30B nanoclays were supplied by Southern Clay Products (Gonzales, TX). The chemical structures of the three modifiers are shown in Figure 1.

Sample preparation

BP, 10% organoclay, and a stoichiometric amount of SAA were mixed with solvents (ethanol/chloroform = 9:1) via stirring at 70°C for 2 h, and then the solvents were removed and dried *in vacuo* at room temperature. A plain, white powder was obtained and stored in a freezer.

DSC measurements

An approximately 5-mg sample was weighed accurately. Nonisothermal scans were performed in a TA 2910 DSC instrument at different heating rates (from 5 to 20°C/min) under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Nonisothermal curing

The curing kinetics of LCE with diamine curing agents were evaluated with DSC. Figure 2 shows the dynamic scans of two samples at different heating rates. Similar results were obtained for samples with 10A and 30B modifiers. As shown in Figure 2, there are a sharp endothermic peak and an exothermic peak in each DSC curve for all the samples. The endothermic peak corresponds to the melting of BP, but it is a little lower than the pure BP melting point (157°C at 10°C/

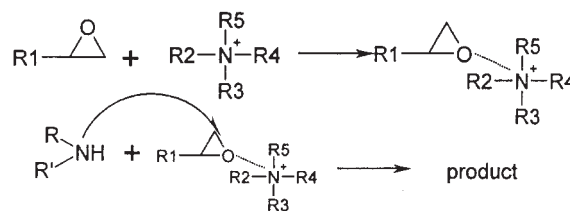


Figure 8 Mechanism of the epoxy ring-opening reaction catalyzed by ammonium ions.

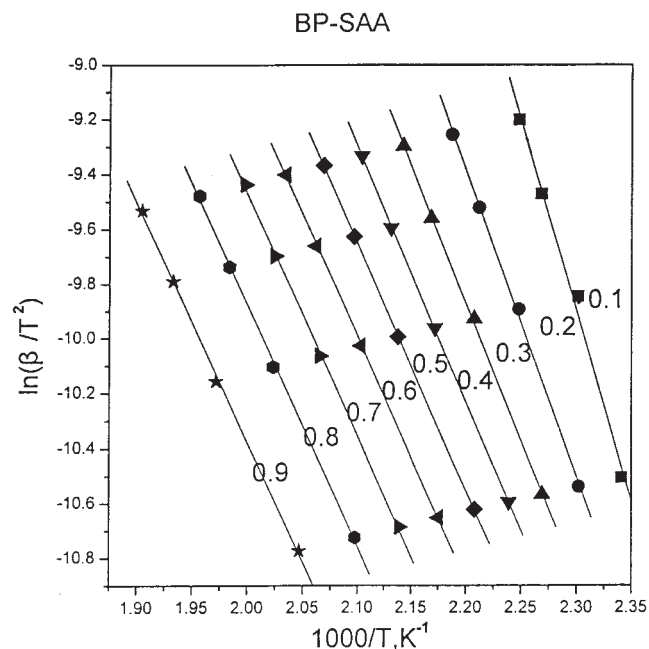


Figure 9 Plots of $\ln(\beta_i/T_{\alpha,i}^2)$ versus $1000/T_{\alpha,i}$ according to the VKAS method.

min). The reduction of the BP melting point may be caused by mixing with SAA, or the curing reaction partly occurred before the melting (e.g., noncrystallized BP cured at a low temperature). The curing reaction mainly took place after the melting of the LCE monomers. Its wide temperature range proved that postcuring at a higher temperature was necessary. The peak temperature increased with an increase in the heating rate. For the sample with organoclay, the exothermal peaks shifted toward a lower temperature (Table I), and this indicated that the organoclay could catalyze the curing reaction of BP and SAA.

Kinetic analysis

α at different heating rates was calculated by the integration of the heat release according to eq. (3). The

relationship between the conversion and curing temperature for BP/SAA samples is shown in Figure 3. Isoconversional plots based on the FWO method are presented in Figure 4, and the dependence of E on α is presented in Figure 5. The values of E were not constant, as supposed in many works throughout the entire curing process. During the early stage of the curing reaction, E first was high, then decreased sharply, and finally remained practically constant.

The dependence of E on the conversion clearly revealed the autocatalytic reaction occurring in these systems. During the initial stage of curing, the primary amine addition was predominant. Etherification occurred only at elevated temperatures once all the primary amine was exhausted. Therefore, a high E value at a lower conversion (122.5 kJ/mol at $\alpha = 0.1$) was attributed to the primary amine addition. This value was markedly higher than the average one, which was supposed to be constant throughout the entire curing process.³⁸ Because the hydroxyl groups formed during the curing facilitated ring opening, it was reasonable to expect a reduction in E in comparison with that at the very beginning of the cure. Therefore, the constant E value of 84 kJ/mol was associated with the autocatalytic reaction. It started at a conversion of approximately 0.4 and lasted until a high conversion. These results were different from those of a conventional epoxy system, for which the change in E was observed as the curing reached a conversion of 0.6.³⁹ It must be associated with the formation of the liquid-crystalline phase. It has been reported that the liquid-crystalline phase facilitates the reduction of the viscosity (e.g., retarding gelification).⁴⁰

The relationships between the reactivation energy and the conversion of three samples with 10A, 93A, and 30B are shown according to the FWO method in Figure 6. The changing tendency of E , with or without organoclays, was the same in the conversion range of 0–0.7. Therefore, the addition of organoclays did not change the curing process. During the initial stage of curing, the addition of the primary amine and the

TABLE II
Activation Energy (E_a) as Calculated by the FWO and VKAS Methods

Conversion	No clay		10% 10A		10% 93A		10% 30B	
	E_{aFWO} (kJ/mol)	E_{aVKAS} (kJ/mol)	E_{aFWO} (kJ/mol)	E_{aVKAS} (kJ/mol)	E_{aFWO} (kJ/mol)	E_{aVKAS} (kJ/mol)	E_{aFWO} (kJ/mol)	E_{aVKAS} (kJ/mol)
0.1	122.5	115.3	107.0	99.8	108.9	101.6	96.0	88.8
0.2	100.2	92.8	94.2	86.9	92.9	85.5	85.1	77.7
0.3	90.4	82.9	87.8	80.4	83.0	78.4	80.4	72.9
0.4	85.0	77.3	83.9	76.4	81.6	74.0	77.7	70.1
0.5	82.4	74.8	80.2	72.6	80.7	73.0	76.1	68.4
0.6	81.6	73.7	80.6	72.9	80.4	72.5	75.6	67.8
0.7	81.4	73.4	80.2	72.3	80.8	72.8	75.6	67.7
0.8	81.3	73.2	81.0	73.0	82.4	74.3	76.2	68.1
0.9	81.0	72.6	83.8	75.6	85.5	77.2	78.5	70.2

epoxy group took place. After the primary amine was exhausted, the addition of the second amine followed, and the hydroxy group that formed during epoxy ring opening reduced *E*. During the final stage of curing, the reaction became practically diffusion-controlled. The organoclay could further retard the movement of reaction groups and the orderly arrangement of mesogens.⁴¹ It is not clear why *E* increased slightly at this stage.

Figure 6 shows that *E* of three samples with organoclays was lower than that of the pure resin, and this suggested that all three alkylammonium ions could catalyze the curing reaction. Pinnavaia and coworkers^{42,43} found that the organic ion of a modifier in the clay galleries could induce the homopolymerization of epoxy groups. The mechanism involved a transfer of the modifier to the epoxy group, which caused homopolymerization, as shown in Figure 7.

As for the three organoclays with different modifiers, their catalytic activities were different. As expected, 30B had the lowest activation and highest catalytic activities because the hydroxy groups of the modifier in the 30B clay facilitated the epoxy ring-opening reaction, as mentioned previously. 10A and 93A showed similar catalytic activities, although 93A had a proton in the organomodifier. However, the transfer of the proton in the ternary ammonium salts was difficult, and the epoxy ring-opening reaction was only catalyzed by the ammonium ion, as shown in Figure 8.

Plots by the VKAS method are presented in Figure 9, and the values of *E* at certain conversions, obtained by the VKAS and FWO methods, are presented in Table II. Table II shows the same changing tendency of *E* obtained from both methods. For a given conversion, the *E* value determined by the FWO method was greater than that determined by the VKAS method, and the difference was caused by the differences of the two methods.

CONCLUSIONS

The kinetic results showed that the curing process of the LCE monomer/diamine with and without organoclays could be described with the FWO and KAS methods. The organoclays did not change the curing reaction mechanism. During the early stage of the curing process, the reaction was mainly controlled by the addition of the primary amine and epoxy group; an autocatalytic process followed, and the reaction finally became diffusion-controlled. However, the organoclays could catalyze the epoxy ring-opening reaction. 30B with two hydroxy groups had the highest catalytic ability because the hydroxy groups facilitated the curing process. 10A and 93A had similar catalytic abilities.

References

- Robinson, A. A.; McName, S. G.; Freidzon, Y. Z.; Ober, C. K. *Polym Prepr* 1993, 34, 743.
- Lin, P. H.; Yee, A. F.; Earls, J. D.; Hefner, R. E., Jr.; Sue, H. J. *Polymer* 1994, 35, 2679.
- Lee, J. Y.; Jang, J. *J Polym Sci Part A: Polym Chem* 1998, 36, 911.
- Mormann, W.; Brocher, M. *Polymer* 1998, 39, 4905.
- Mormann, W.; Brocher, M. *Polymer* 1998, 39, 6597.
- Lee, J. Y.; Jang, J.; Hong, S. M.; Hwang, S. S.; Kim, K. U. *Polymer* 1999, 40, 3197.
- Liu, W. C.; Carfagna, C. *Macromol Rapid Commun* 2001, 22, 1058.
- Castell, P.; Serra, A.; Galia, M.; Giamberini, M.; Carfagna, C. *J Polym Sci Part A: Polym Chem* 2003, 41, 1.
- Jahromi, S.; Kuipers, W. A. G.; Norder, B.; Mijs, W. J. *Macromolecules* 1995, 28, 2201.
- Carfagna, C.; Amendola, E.; Giamberini, M.; Mensitieri, G.; Nobile, M. A. D. *Polym Eng Sci* 1995, 35, 137.
- Sue, H. J.; Earls, J. D.; Hefner, R. E., Jr. *J Mater Sci* 1997, 32, 4031.
- Benicewicz, B. C.; Smith, M. E.; Earls, J. D.; Rriester, R. D., Jr. *Macromolecules* 1998, 31, 4730.
- Ortiz, C.; Kim, R.; Rodighiero, E.; Ober, C. K.; Kramer, E. J. *Macromolecules* 1998, 31, 4074.
- Tan, C.; Sun, H.; Fung, B. M.; Grady, B. P. *Macromolecules* 2000, 33, 6249.
- Ortiz, C.; Belenky, L.; Ober, C. K.; Kramer, E. J. *J Mater Sci* 2000, 35, 2079.
- Lee, J. Y.; Song, Y. W.; Kim, S. W.; Lee, H. K. *Mater Chem Phys* 2002, 77, 455.
- Punchaipetch, P.; Ambrogi, V.; Giambeini, M.; Brostow, W.; Carfagna, C.; Souza, N. A. D. *Polymer* 2001, 42, 2067.
- Punchaipetch, P.; Ambrogi, V.; Giambeini, M.; Brostow, W.; Carfagna, C.; Souza, N. A. D. *Polymer* 2002, 43, 839.
- Sue, H. J.; Earls, J. D.; Hefner, R. E., Jr. *J Mater Sci* 1997, 32, 4039.
- Sue, H. J.; Earls, J. D.; Hefner, R. E., Jr. *Polymer* 1998, 39, 4707.
- Carfagna, C.; Acierno, D.; Palma, V. D.; Amendola, E.; Giamberini, M. *Mater Chem Phys* 2000, 201, 2631.
- Carfagna, C.; Meo, G.; Nicolais, L.; Giamberini, M.; Priola, A.; Malucelli, G. *Mater Chem Phys* 2000, 201, 2639.
- Bae, J.; Jang, J.; Yoon, S. H. *Mater Chem Phys* 2002, 203, 2196.
- Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *J Phys Chem Solids* 1996, 57, 1005.
- Kornmann, X.; Lindberg, H.; Berglund, L. A. *Polymer* 2001, 42, 1303.
- Kornmann, X.; Lindberg, H.; Berglund, L. A. *Polymer* 2001, 42, 4493.
- Chin, I.-J.; Albercht, T. T.; Kim, H. C.; Russell, T. P.; Wang, J. *Polymer* 2001, 42, 5947.
- Becher, O.; Varley, R.; Simon, G. *Polymer* 2002, 43, 4365.
- Xu, W.; He, P.; Chen, D. *Eur Polym J* 2003, 39, 617.
- Lu, M. G.; Shim, M. J.; Kim, S. W. *Polym Eng Sci* 1999, 39, 274.
- Kim, S. W.; Lu, M. G.; Shim, M. J. *J Appl Polym Sci* 2001, 82, 1495.
- Lu, M. G.; Shim, M. J.; Kim, S. W. *Macromol Chem Phys* 2001, 202, 223.
- Doyle, C. D. *J Appl Polym Sci* 1961, 5, 285.
- Ozawa, T. *Bull Chem Soc Jpn* 1965, 38, 1881.
- Flynn, J. H.; Wal, L. A. *J Polym Sci Part B: Polym Lett* 1996, 4, 323.
- Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
- Carfagna, C.; Acierno, D.; Palma, V. D.; Amendola, E.; Giamberini, M. *Macromol Chem Phys* 2000, 201, 2631.
- Mijovic, J.; Fishbain, A.; Wijaya, J. *Macromolecules* 1992, 25, 986.
- Lu, M. G.; Kim, S. W. *J Appl Polym Sci* 1999, 71, 2401.
- Mallon, J. J.; Adams, P. M. *J Polym Sci Part A: Polym Chem* 1993, 31, 3349.
- Shen, M. M.; Lu, M. G.; Chen, Y. L.; Ha, C. Y. *Polym Int*, to appear.
- Pinnavaia, T. J.; Lan, T.; Wang, Z.; Shi, H.; Kaviratna, P. D. *Am Chem Soc Polym Mater Sci Eng Proc* 1995, 73, 250.
- Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *J Phys Chem Solids* 1996, 57, 1005.