# Curing Behavior and Rheology Properties of Alkyl-Imidazolium-Treated Rectorite/Epoxy Nanocomposites

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A novel organic rectorite (OREC) was prepared by treating the natural sodium rectorite (Na-REC) with ionic liquid 1-hexadecyl-3-methylimidazolium bromide ([C16mim]Br). The curing behaviors of nanocomposites were quantitatively studied according to the differential scanning calorimetry (DSC) and rheology methods. It was shown by DSC that the activation energies of epoxy system decreased when OREC with reactive imidazole groups were incorporated. The viscosity and viscous flow activation energy were obtained by rheology during the curing reaction. The curing kinetics of the nanocomposites was also deduced from dynamic viscosity analysis and isotherm viscosity analysis. Better dispersion states of the filler can decrease the curing reaction activation energy. The best processing conditions of the nanocomposites were found. POLYM. ENG. SCI., 53:2470-2477, 2013. © 2013 Society of Plastics Engineers

## INTRODUCTION

Epoxy resins have played a very important role in polymer matrix composite materials because of their superior mechanical, adhesive properties and chemical resistance. Incorporating layered silicate clay into the epoxy matrix can obtain excellent performances compared with traditional composites [1–3]. Among the layer silicate clays, rectorite (REC) is a kind of regular interstratified clay consisting of a muscovite-like layer and a montmorillonitelike layer in the ratio of 1:1 [4]. It is worth further investigation in view of its many particular properties such as good dispersion, cation exchange performance, high tem-

Published online in Wiley Online Library (wileyonlinelibrary.com). © 2013 Society of Plastics Engineers perature resistance, and good gas barrier property. But untreated clay cannot be dispersed well in polymer matrix because of its natural hydrophilicity and incompatibility with polymer chains. In our previous work [5], the natural sodium rectorite (Na-REC) was treated with ionic liquid 1hexadecyl-3-methylimidazolium bromide ([C16mim]Br). The ionic liquid can greatly increase the spacing of the layer that can result in the exfoliated dispersion after curing with tung oil anhydride (TOA). The mechanical and thermal properties of the product were improved.

Curing of a resin system is a critical and productivitycontrolling step in the fabrication of thermosetting-matrix composites. The cure process of an epoxy resin is the crosslinking of linear macromolecules with a complicated mechanism. As soon as the crosslinking forms, the resin cannot be softened and melted, thus making it difficult to study [6]. It is reported that the curing process of an epoxy resin will be affected by the incorporation of a smectite clay. The kinetics of the curing reaction can help us to know more about the exfoliation process of the filler [7]. For example, even when the epoxy resin and the hardener system are the same, diglycidyl ether of bisphenol-A epoxy cured with an amine, and the nanoclay is an organically modified montmorillonite, the kinetics of the curing reaction can vary significantly and can display a number of different features depending upon the conditions of the cure process [8-10]. As a result, the fully or partially exfoliated or not-exfoliated-at-all nanocomposites have corresponding effect on the properties of the cured nanocomposite. Many equations have been developed to investigate the cure kinetics of the epoxy system, including the nth-order reaction model, the autocatalytic reaction model, and the diffusion control model [11, 12]. All kinetic studies can start with the basic equation that relates the rate of conversion at constant temperature to some

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function of the concentration of reactants. Kenny et al. [13] used Raman spectroscopy and thermal analysis to investigate the curing kinetics of diglycidyl ether resin. They observed a catalytic effect caused by the high thermal conductivity of the carbon nanotubes (CNTs). Tao et al. [14] used DSC to study the effect of CNT types on the cure behavior of epoxy. From dynamic DSC studies, all single-walled carbon nanotubes initiated curing at a lower temperature relative to the neat resin, whereas the overall degree of cure was lower. Isothermal DSC studies only showed discernable differences in cure behavior during the early stages (20 min) of cure. Dean and coworkers [6] used DSC and rheology to investigate the effect of carboxyl- and fluorine-modified multi-wall carbon nanotubes on the curing behavior of epoxy resin. Activation energy and rate constants were obtained from isothermal DSC. Comparison of the activation energies and rate constant suggests that the cure mechanisms of the neat resin and fluorinated sample are similar but different from carboxylated sample. This difference in reaction mechanism can be attributed to differences in nanotube dispersion.

To the best of our knowledge, DSC methods are widely used in the study of curing kinetics. However, DSC method only gives the overall cure kinetics by measuring the rate of produced heat and requires assumptions about enthalpies of elementary reactions. One can utilize rheological methods to investigate the curing process more successfully in order to overcome these impediments. The kinetic analysis of the isothermal curing followed by storage modulus obtained from the rheometry experiments have been shown to be an effective rheological characteristic to investigate the cure behavior. The techniques are not only crucial for optimization of the processing cycle, but also can be applied to achieve a fundamental understanding of the crosslinking between kinetics and the mechanical behavior of the system [15, 16].

In our previous work [5], we obtained exfoliated organic rectorite (OREC)/EP nanocomposites. The feature of the nanocomposites could be attributed to the nanofiller, which was treated by [C16mim]Br. Although the compatibility of the nanofiller was improved after being modified by ionic liquid, the chemistry structure of the filler may make the exfoliated process and curing behavior more compatible. Thus, it is very important to know more in detail about the curing behavior of OREC/EP nanocomposites for further industrialization. In this study, we aimed to study the curing kinetics of the exfoliated OREC/EP nanocomposites, which was obtained in the previous work using the DSC and rheology methods. The rheology properties were also investigated.

# **EXPERIMENTS**

## Materials

TABLE 1. The structure of organic modifier, epoxy resin, and curing agents.



was purchased from Lanzhou Institute of Chemical Physics. Industrial grade EP was diglycidyl ether of bisphenol A, with an average molecular weight of 390 and equivalent of 0.48–0.54 eq/100 g, obtained from Chemical plant in Wuxi Adjani. Industrial grade TOA was provided by Yangzhou Chemical. Chemically pure 2-E-4-MI was import-packing. The structures of the organic modifier, resin, and curing agents are illustrated in Table 1.

# Preparation of the Nanocomposites

The preparation of the nanocomposites followed the same method as in our previous work [5]. The OREC/TP nanocomposites were obtained after curing with TOA. The same amount of TOA was maintained in the four samples. The TGA results showed that the content of OREC in the nanocomposites was 1%, 3%, and 5%, respectively.

## Characterization

Differential Scanning Calorimetry Thermal characterization was performed using EXSTAR 6300 (NSK Ltd., Japan) under nitrogen atmosphere. The heating rate was 5°C/min, 10°C/min, 20°C/min, and 30°C/min. The scanning range was from 50°C to 250°C.

The rheology was measured using HAAKE Rheo Stress 1. Dynamic viscosity measurement was conducted with  $1 \text{ s}^{-1}$  of shear rate,  $1^{\circ}\text{C/min}$  of heating rate starting from 50°C. Isothermal viscosity measurement was conducted at 85°C, 100°C, and 115°C. The shear rate was maintained at  $1 \text{ s}^{-1}$ . The viscosity at variable shear rate was measured at 40°C, 65°C, and 100°C. The range of shear rate was 1–100 s<sup>-1</sup>. The curves of viscosity *versus* shear rate and viscosity *versus* time were recorded.



FIG. 1. DSC cures of EP/ TOA system at different temperature rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

## **RESULTS AND DISCUSSION**

#### Dynamic DSC Thermograms Analysis

The change of a specific physical property, which can be directly related to the chemical conversion of a thermoset resin system, can be easily monitored by an instrument during curing process and used to investigate curing kinetics of the epoxy nanocomposites. Therefore, DSC was used to study the curing kinetics of the epoxy/ OREC/TOA system based on the change of heat of the exothermic reaction during the curing. Kissinger's method [17] or the method suggested by Ozawa [18] and Foun [19] was used to study the curing kinetics of thermoset resin systems. In this section, we use this method to record the curing kinetics of the nanocomposites. Figure 1 shows the dynamic DSC thermogram for the epoxy/OREC/TOA nanocomposites measured at different heating rate. The curing reaction parameters are analyzed as follows:

Following Kissinger model

$$\ln\left(\frac{\beta}{T_{\rm p}^2}\right) = \ln\left(\frac{A\cdot R}{E_1}\right) - \frac{E_1}{R} \cdot \frac{1}{T_{\rm P}}$$
(1)

After derivation:

$$\frac{d\left[\ln\left(\beta/T_{\rm P}^2\right)\right]}{d\left(1/T_{\rm P}\right)} = -\frac{E_1}{R} \tag{2}$$

Flynn–Wall–Ozawa equation:

$$\frac{d[\ln\beta]}{d(1/T_{\rm p})} = -\frac{1.052E_2}{R}$$
(3)

Then based on the crane equation:

$$\frac{d[\ln\beta]}{d(1/T_{\rm p})} = -\left(\frac{\Delta E}{nR} + 2T_{\rm p}\right) \tag{4}$$

When  $\Delta E/nR >> 2T_p$ , the Crane equation can be simplified to

$$\frac{d[\ln\beta]}{d(1/T_{\rm p})} = -\frac{\Delta E}{nR} \tag{5}$$

where  $\beta$ -heating rate is in K/min;  $T_p$  is the melting point in K; R = 8.3144 J/(mol·K);  $E_1$ ,  $E_2$ ,  $\Delta E$  are the apparent activation energy in J/mol; A is the frequency factor in s<sup>-1</sup>; and n is the reaction order.

Plotting the ln  $(\beta/T_p^2)$  with  $1000/T_p$  can obtain a straight line (line 1). Using the value of slope and intercept, the value of  $E_1$  and A can be obtained. Plotting the ln  $\beta$  with  $1000/T_p$  can obtain another straight line (line 2). Using the value of slope and intercept of this line, the value of  $E_2$  can be obtained. Then,  $\Delta E$  is equal to  $(E_1 + E_2)/2$ . The slope of line 2 can be substituted to Eq. 5, thus the reaction order *n* can be calculated.

The basic information of the DSC thermoset is listed in Table 2. The values of the curing kinetic parameters,  $E_1, E_2, \Delta E, n$ , and ln A, determined by the fitting methods are listed in Table 3. The activation energies of epoxy decrease when the OREC with reactive imidazole groups are incorporated. This kind of decrease in activation energies has also been reported for the epoxy nanocomposite systems comprising nanocarbon tube treated with imidazole [20]. However, activation energies increase when the OREC content reaches 5%. It was reported in the previous work [5] that the dispersion of EP5 changed to an intercalated state compared with other exfoliated nanocomposites. The introduction of OREC may take two parts of influence to the curing reaction. On the one hand, introduction of OREC can lead to a decrease of viscosity

TABLE 2. The basic information analysis from the DSC thermoset.

Samples	$\beta(^{\circ}C \cdot min^{-1})$	$\ln\beta$	$T_{\rm p}$ /K	$1/T_{\rm p}~(\times~10^3)$	$-\ln(\beta/T_p^2)$
EP/TOA	5	1.609	415.54	2.41	10.45
	10	2.303	430.92	2.32	9.83
	20	2.996	445.02	2.247	9.2
	30	3.401	453.29	2.206	8.832
1%	5	1.609	416.53	2.4	10.45
	10	2.303	431.07	2.32	9.83
	20	2.996	446.49	2.24	9.2
	30	3.401	455.97	2.19	8.84
3%	5	1.609	415.96	2.4	10.452
	10	2.303	431.73	2.316	9.833
	20	2.996	447.42	2.235	9.2
	30	3.401	457.41	2.186	8.85
5%	5	1.609	415.3	2.41	10.45
	10	2.303	430.1	2.33	9.83
	20	2.996	445.9	2.24	9.2
	30	3.401	454.1	2.2	8.34

TABLE 3. Curing kinetics parameters calculated with different methods.

Samples	Filler content (%)	$E_1/(\text{KJ}\cdot\text{mol}^{-1})$ Kissinger	$E_2/(\text{KJ}\cdot\text{mol}^{-1})$ Flynn-Wall-Ozawa	$\Delta E/(\mathrm{KJ}\cdot\mathrm{mol}^{-1})$	n	ln A
EP0	0%	67.134	70.66	68.9	0.927	11.04
EP1	1%	64.446	68.141	66.29	0.925	10.21
EP3	3%	61.344	64.4	62.87	0.928	9.27
EP5	5%	64.618	68.284	66.45	0.925	10.3

in the system, which will be verified later. This will decrease the collision possibility between each thermoactivated molecules and result in higher apparent activation energy [15]. On the other hand, when the OREC present the exfoliated dispersion state in the nanocomposites, the surface of the filler can get more opportunity to touch with the epoxy chains. The imidazole groups on the OREC surface may participate in the curing reaction as well. This can improve the curing reaction, thus leading to a decrease of the activation energy. However, if the dispersion state changes to intercalated state, the layer structure of OREC may not fully open during the curing reaction [21]. As a result, some functional groups on the surface of OREC are shielded to react with epoxy chains, which leads to a higher activation energy. Furthermore, the reactor order is almost the same (around 0.92-0.93). It indicates that the mechanism of the curing reaction is not changed when the OREC filler is introduced [13, 14]. The reactor order is not the integral number, which indicates that the curing reactor is complex [21].

# Rheology Analysis

The cure process of the epoxy-clay system is the crosslinking of linear macromolecules. The rheology properties can successfully reflect the process of cosslinking. Thus, many important parameters, such as viscosity and viscous flow activation energy, can be obtained. It is helpful to know more details about the manufacturing process.

#### Dynamic Viscosity Analysis

Figure 2 shows the dependence of viscosity on the temperature in the nanocomposites. The viscosity curves present a "U" shape. In the initial stage, the dynamic of epoxy molecules was improved because of the increased temperature and thus a decrease in the viscosity. As the curing reaction occurs, the crosslinking network gradually forms, which will increase the molecular chain length [14]. This will hinder the viscosity to increase further. Thus, the variance of viscosity becomes smoother. Finally, the system turns to solid state because of the crosslinking behavior. The molecular dynamics is hindered leading to an increased viscosity. The inflection point of the curves (around 140°C) reflects the curing point [15]. In the nanocomposites, a small increase in the viscosity can be seen after the curing point when intro-

ducing more OREC clay. It may indicate the composition of the clay (especially, imidazole group on the surface of OREC clay) can slightly enhance the curing reaction. Furthermore, It can be observed that the viscosity is the lowest between  $80^{\circ}$ C and  $140^{\circ}$ C, which means that this temperature range is more suitable for the manufacturing process.

#### Isotherm Viscosity Analysis

Three temperature points ( $85^{\circ}$ C,  $100^{\circ}$ C, and  $115^{\circ}$ C) were chosen to conduct isothermal experiment based on the results of dynamic viscosity. In these temperatures, the viscosity of the system is low and the curing point does not reach. Figure 3 shows the isotherm viscosity curves of nanocomposites. The curing curves at different temperatures have similar shape, but obvious differences in their gel times and curing rate. It is evident from Fig. 3 that with increasing temperature the gel time decreases, and the curing rate is accelerated.

The cure behavior can be further studied based on the isothermal viscosity curves [17–19]. The relationship between viscosity and time can be described by Roller semi-empirical model:

$$\eta_{\rm t} = \eta_0 \exp(kt) \tag{6}$$



FIG. 2. Viscosity verse cure time at different temperatures with 1 °C/ min of heating rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIG. 3. The viscosity curves of the EP/TOA systems with different OREC content at static temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where  $\eta_0$  is the viscosity in the initial stage; *k* is the reaction rate constant; and *t* is the curing time. After taking logarithm, the Eq. 6 changes as:

$$\ln \eta_{\rm t} = \ln \eta_0 + kt \tag{7}$$

After linear fitting the  $\ln \eta_t - t$  curves, the parameters  $\eta_0$  and k can be obtained. The relation between  $\eta_0$  and k follows Arrhenius equation:

$$\eta_0 = \eta_\infty \exp\left(\frac{E_\eta}{\mathrm{RT}}\right) \tag{8}$$

$$k = k_{\infty} \exp\left(-\frac{E_k}{RT}\right) \tag{9}$$

where  $\eta_{\infty}$  and  $k_{\infty}$  are pre-exponential factors,  $E_{\eta}$  is the viscous flow activation energy, and  $E_{\rm k}$  is the activation energy of curing reaction.

The equation can change to the following after taking logarithm with Eqs. 8 and 9.

$$\ln \eta_0 = \ln \eta_\infty + \frac{E_\eta}{RT} \tag{10}$$

$$\ln k = \ln k_{\infty} - \frac{E_k}{RT} \tag{11}$$

After linear fitting the  $\ln \eta_0 - 1/T$  and  $\ln k - 1/T$  curves, the parameters of  $E_{\eta}$  and  $E_k$  can be obtained.

Table 4 shows parameters calculated with Roller equation. Viscous flow activation energy of the systems increases when more clay is introduced into the matrix. It indicates that the viscosity of the nanocomposite is sensitive to the OREC content. It may be attributed to the reason that the confinement of the intercalated polymer chains within the OREC clay galleries prevents the segmental motions of the polymer chains [16] causing the reduction in the free volume of the matrix. Consequently, deceases the chain dynamics of epoxy chains and

TABLE 4. Parameters calculated with Roller equation.

Samples	$\ln \eta_{\infty}$	$E_{\eta}$ (kJ/mol)	$\ln k_{\infty}$	$E_{\rm k}$ (kJ/mol)
EP	-23.16458	84.1	27.98324	93.2
1% OREC	-24.47664	87.56	27.18185	90.76
3% OREC	-30.26066	105	26.0324	87.8
5% OREC	-32.7426	112.7	27.66	91.9



FIG. 4. Viscosity-shear rate curve of the resin at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases the viscous flow activation energy. Moreover, the activation of curing reaction slightly decreases and then increases as the clay loading increases. This shows a great correspondence with the results of DSC.

## The Viscosity Analysis Upon Changing the Shear Rate

The shear viscosity data of the nanocomposites measured at different temperature with different shear rate is shown in Fig. 4. All the viscosity curves show that the nanocomposites present obvious non-Newtonian behaviors. The addition of filler to the EP significantly increases the shear viscosity at low shear rate and as the shear rate increases, the shear viscosity decreases asymptotically. An obvious shear thinning property can be observed at lower temperature (40°C, 65°C).

Interesting data can be found upon increased temperature. When measured at 45°C, the shear viscosities of all the samples decrease first and then stabilize the shear viscosity with increase in the shear rate. However, the shear viscosity shows a small increase after it reaches a stable point with increase in the shear rate at 65°C, whereas, when the temperature reaches 100°C, the shear viscosity increases as the shear rate is raised. At 45°C, epoxy molecules physically entangled each other at the beginning of viscosity measurement, thus indicating highest viscosity. With increase in the shear rate, the molecules began to disentangle leading to reduced viscosity. The disentanglement tended to complete at a specific shear rate and since then the viscosity remained constant [12]. It also indicates that the curing reaction does not happen. However, a slightly increase of the viscosity indicates that the curing reaction can slightly occur on this relative low temperature ( $65^{\circ}$ C). Moreover, the shear rate can greatly enhance the curing reaction on  $100^{\circ}$ C, although the resins are still in the gel state [13].

Figure 5 shows the viscosity–time curves measured at 100°C. The increased viscosity range is accelerated when the filler amount increases. It further indicates that the OREC can improve the curing reaction.

#### Curing Reaction Mechanism

From the following results, we suppose that both the curing agent (TOA) and clay filler can enhance the curing behavior. Here, we propose that two curing reactions may happen in the EP/TOA/OREC system, including imidazole curing reaction [22, 23] and TOA curing reaction [24–26]. The possible scheme of the curing reaction is shown in Fig. 6.

Imidazole group are typical functional groups of the ionic liquid, which is the modifier of the OREC. Thus,



FIG. 5. Viscosity-time curve of the different system at 100°C.

the imidazole curing reaction may occur on the clay layer. Some reports have proved that the imidazole curing reaction occurs on low temperature, whereas anhydride curing reaction happens on high temperature. In our results, the viscosity data upon changing the shear rate showed that the curing reaction of the gel polymer occurred on low temperature ( $65^{\circ}$ C), which was far from the curing point. This curing reaction may indicate the imidazole curing reaction. Although a large increase of the viscosity when the shear rate was increased at 100°C indicated the TOA curing reaction occurred. We can observe the slight increase of viscosity at  $65^{\circ}$ C and a large increase of viscosity at  $100^{\circ}$ C, as the amount of imidazole was too less compared with TOA content.

Furthermore, the curing reaction also showed dependence on the dispersion state of the clay. As was illustrated in the previous work [5], the compatibility between OREC and epoxy chains were excellent. The interface interaction of OREC and epoxy chains was strong according to the organic chains [C16Br<sub>min</sub>] [5]. As the curing reaction occurred, the exothermic heat accelerated the destroying process of the OREC layer structure. Thus, more epoxy chains and the reaction molecular (TOA and 2-E-4-M) entered into the gallery of the OREC layer. This further pushed the curing reaction. More reaction molecules could enter into the gap of the filler, leading to an improvment of curing reaction. As a result, the activation energy was decrease. The data of activation energy measured by DSC and rheology can verify this deduction.

# CONCLUSION

In this work, we studied the kinetics of the cure reaction of nanocomposites based on the epoxy resin with ionic liquid-modified REC clay and cured with a TOA crosslinking agent. The kinetic parameters detected by DSC were showed that the activation energies of epoxy system decreased when OREC with reactive imidazole



FIG. 6. Proposed curing reaction mechanism. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

groups were incorporated in. It was showed by rheology that the viscosity of the nanocomposites increased as the filler amount increased. The OREC filler can slightly improve the curing reaction according to chemistry and physical interaction. Combined with the results of rheology, we demonstrated that the mainly curing reaction was TOA curing reaction as the content of imidazole was relatively low compared with TOA. The results of rheology also showed that the best melting flow ability of the nanocomposite can be achieved from 80°C to 140°C.

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