

Curing Behavior of Epoxy Resin/Tung Oil Anhydride Exfoliated Nanocomposite by Differential Scanning Calorimetry

Suping Bao,¹ Shijun Shen,² Guodong Liang,³ Hongbo Zhai,² Weibing Xu,^{2,4} Pingsheng He⁵

¹Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

²Department of Polymer Science and Engineering, Hefei University of Technology, Hefei 230009, Anhui, China

³Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310000, Zhejiang, China

⁴Material Characterization Center, Department of Chemistry, Western Kentucky University, Bowling Green, Kentucky 42101

⁵Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, Anhui, China

Received 15 July 2003; accepted 4 November 2003

ABSTRACT: The nanocomposite of epoxy resin/tung oil anhydride/organic montmorillonite was prepared by casting and curing. The distance of the clay gallery rose and the exfoliated nanocomposite was formed. The exfoliation behaviors of the nanocomposite had been investigated by X-ray diffraction (XRD). The curing mechanism and kinetics of epoxy resin with the different amounts of organic montmorillonite were studied using isothermal and dynamic methods by differential scanning calorimetry (DSC). Some parameters, the activation energy and reaction orders, were calculated by the modified Avrami equation in analysis of the isothermal experiment. The total curing mechanism and

kinetics of curing reaction were also analyzed by the Flynn–Wall–Ozawa method. It was noted that the instantaneous activity energy during the curing process could be obtained by the Flynn–Wall–Ozawa method and the trend of the results was in agreement with those obtained from the modified Avrami equation. These results show that the activity energy decreases with the addition of organic montmorillonite. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3822–3829, 2004

Key words: resins; differential scanning calorimetry (DSC); Curing of polymers; nanocomposites

INTRODUCTION

Nanocomposite^{1–4} is a new class of composites, in which at least one dimension of the dispersed particles is in the nanometer range. Most polymer nanocomposites are characterized by only one dimension in the nanometer range, which is called polymer-layered nanocomposite, in which the filler is present in the form of sheets of one to a few nanometers thick to hundreds or thousands nanometers long. Now more and more researchers are focusing on the preparation of polymer-layered nanocomposites and the improved properties^{5–9} of those materials. Several methods^{10–14} are used to obtain the polymer-layered nanocomposites, including exfoliation–adsorption, *in situ* intercalative polymerization, melt interaction, and the *sol-gel* method. Two techniques,¹⁵ X-ray diffraction (XRD) and transmission electron microscopy (TEM), are used to characterize the structure of nanocomposites and identify the type of composites. Recently, great attention has been paid to the study of the intercalation and

exfoliation of polymer-layered composites. As far as the intercalated nanocomposites are concerned, the interlayer spacing is increased in comparison with the organic clay, leading to a shift of the diffraction peak toward a lower angle. It is noted that angle and layer spacing are related through Bragg's relation: $2d\sin\theta = n\lambda$, where λ corresponds to the wave length of the X-ray diffraction used in the experiment, d the interclay spacing, and θ the measured diffraction angle. However, no diffraction peaks can be observed in the XRD of exfoliated nanocomposite because the large spacing between the layers exceeds 8 nm so that the peak cannot be observed in the angle range of the experiment. A few studies have been carried out on the synthesis and reaction process, especially for the nanocomposite on the basis of thermosetting resin. It is important to understand the mechanism and kinetics of resin curing with the rapid application of resin and composite systems. Some kinetic models are used to accurately fit the curing process in order to determine the curing mechanism and kinetic parameters, including the reaction order, activation energy, and frequency factors of the curing reaction. The curing behaviors of thermosetting resin under different

Correspondence to: S. Bao (bao_suping1030@sina.com.cn).

curing conditions have been discussed with different curing models.

Although different thermosetting resins are cured with different curing agents, fillers, and additives under isothermal and dynamic conditions, it is well known that differential scanning calorimetry (DSC) is useful for the rapid analysis of curing process. In addition, other techniques, such as dynamic measure analyzer (DMA), thermomechanical analysis (TMA), and Fourier-transform infrared (FTIR), have also been employed to study the curing kinetics. Liu et al.¹⁶ calculated the degree of reaction and the kinetics parameters according to the change of the absorbing peak with the time by the FTIP spectroscopy results. Laza et al.¹⁷ focused their work on the effect of amine concentration on the kinetics of epoxy resin, the rheologic characteristics during the crosslink process, and the dynamic-mechanical properties of the system by means of a dynamic measure thermal analyzer (DMTA). From those articles, we find that the methods described above were mainly used to describe the cure kinetics of epoxy resin with amine as a curing agent. It is well known that the curing kinetics of thermosetting resin are very complex and there are several reactive processes of crosslink and the vitrification phenomena. In general, in those methods described above, under some hypotheses the main curing reaction^{18–20} can be studied to describe the curing process of the system and some dynamic parameters obtained, such as activation energy and frequency factor, are apparent parameters of the whole curing process that comprises the behavior before the occurrence of vitrification and after the crosslink phenomenon.

In our previous work,²¹ the exfoliated nanocomposites of epoxy resin were obtained with tung oil anhydride as curing agent and the structure and behavior of nanocomposites were studied by XRD and DMTA. In this article, DSC testing was used to study the curing process of an epoxy resin system with tung oil anhydride (TOA) as the curing agent in two modes (isothermal condition and dynamic condition). A variety of kinetic models, modified Avrami equations, and Flynn–Wall–Ozawa, were used to characterize the kinetics of the curing reactions.

EXPERIMENTAL

Materials

The diglycidyl ether of biphenyl A, epoxy resin E-51, with weight per epoxy equivalent of 191.1 g eq^{-1} , was obtained from Shanghai Resin Factory, China. Tung oil anhydride, the curing agent of epoxy resin, and tri(dimethylamino-methyl)phenol(DMP-30), the curing accelerant, were from the Corporation of Hefei Baofeng Chemistry. Organic montmorillonite²¹ (Org-MMT), which was made in our laboratory by the ion

exchange of organic ammonium using the inorganic montmorillonite, which was bought from Qingsan Chemistry Agent Factory in Lin'an and $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$, the surfactant of clay, which was purchased from the Research Institute of Xinhua Active Material in Changzhou.

Sample preparation

Epoxy resin was well mixed with both 160 phr of TOA, 3 phr of DMP-30, and various contents of organic montmorillonite, where the phr is an abbreviation of "part per one hundred base resin". Epoxy resin/TOA/Org-MMT mixtures were obtained and poured into a poly(tetrafluoroethylene)(PTFE) mold. After being cast into small bars, they were degassed simultaneously and then cured at 100°C for 2 h. The type of nanocomposite of curing products was determined by XRD analysis.

X-ray diffraction analysis

The change of lattice spacing of montmorillonite was measured by using a Japanese Rigaku-D/max- γB rotating anionod X-ray diffractometer equipped with $\text{Cu}\alpha$ radiation, with wavelength of 0.154 nm, acceleration voltage of 40 kV, and electric flow of 100 mA. The scanning range was from 1.2° to 10° with a rate of $1^\circ/\text{min}$.

DSC testing

In this experiment, the DSC testing was performed in two modes: isothermal and dynamic conditions. The experiments on DSC were conducted with a Mettler Toledo DSC-821E under nitrogen atmosphere at a flow of 80 ml/min. Under the isothermal condition, the sample of 5–6 mg of epoxy resin/tung oil anhydride with 0, 5, and 10 phr of Org-MMT was placed into the aluminum crucible. Isothermal experiments were conducted at four temperatures: 145, 150, 155, and 160°C . The reaction was not considered complete while the signal leveled off the baseline. Thus, the dynamic measurement was observed using the heating rate of $10^\circ\text{C}/\text{min}$ from 50 to 250°C after each isothermal measurement. Under the dynamic condition, the sample of 5–6 mg of the mixture of epoxy and curing agent with 0, 3, 5, 7, and 10 phr of Org-MMT was placed into the aluminum crucible in order to obtain the instantaneous activation energy. Dynamic scans were conducted at the heating rate of 5, 10, 15, 20, and $30^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

X-ray diffraction analysis

Depending on the nature of layered silicate and polymer matrix, the exfoliated nanocomposite²² was ob-

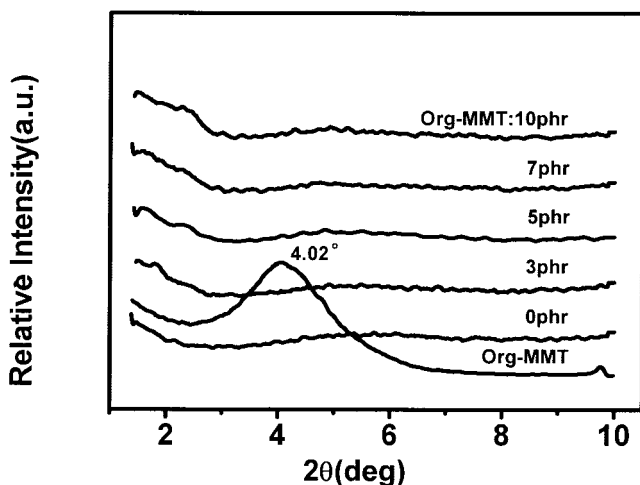


Figure 1 XRD patterns of Org-MMT and epoxy resin/TOA/Org-MMT nanocomposites.

tained when the individual 1~2-nm-thick silicate layers were dispersed in the polymer matrix and segregated from one other. Then no diffraction peak was visible in the XRD diffractograms. Figure 1 shows XRD patterns of epoxy resin/TOA/Org-MMT nanocomposites containing various contents of clay with the results of Org-MMT for comparison. The (001) peak of Org-MMT ($2\theta = 4.02^\circ$) disappeared and the interlayer spacing of Org-MMT is 2.19 nm according to $2d\sin\theta = n\lambda$ [$n = 1$ and $n = 2$ corresponding to the (001) peak and (002) peak, respectively]. Compared to the peak of Org-MMT, the (001) peak disappeared and did not shift to a lower angle, indicating that the clay was exfoliated without a regular repeat distance between the layers. It is considered that the cure reaction occurs at high temperature with TOA agent, a large amount of epoxy resin monomer can enter the gallery because the pliability of curing agent molecule is helpful to the intergallery and extragallery polymerization of epoxy resin. Consequently, a sufficient amount of epoxy resin molecules penetrate the gallery space and

the galleries continue to expand with the increase of the degree of polymerization until an exfoliated nanocomposite is formed. Messersmith and Giannelis²³ also found it possible for epoxy resin to penetrate into the clay basal spacing and the exfoliated nanocomposites to be obtained with anhydride as the curing agent.

DSC studies on epoxy resin/DETA/Org-MMT nanocomposite

It is well known that the curing of epoxy resin is complex, including several reaction processes. The phenomenology²⁴ compared with the dynamic mechanical model may be used to characterize the curing behavior for the attainment of some parameters, including reaction activity energy, frequency factor, and reaction order. The modified Avrami expression was attributed to evaluate the curing behavior of epoxy resin in an isothermal mode. Under isothermal conditions the curing temperature is constant before the dynamic scanning of measuring the residual heat. It is reported²⁵ that the curing kinetics of thermosetting resins in an isothermal mode can be obtained by the modified Avrami expression and the results are in agreement with those from other analytical methods.

DSC experiments under isothermal conditions yield data on heat flow versus time for epoxy resin/TOA/Org-MMT at four curing temperatures shown in Figure 2, which can be used to evaluate kinetic parameters with a series of dynamic models. During the curing reaction, the degree of cure, α , at time t is defined as

$$\alpha = \frac{H_t}{H_T + H_s} \quad (1)$$

where H_t denotes the heat under the isothermal exotherm curve at time t , H_T is the total heat under the isotherm curve during the circle of isothermal experiment and H_s is the residual heat under the exotherm

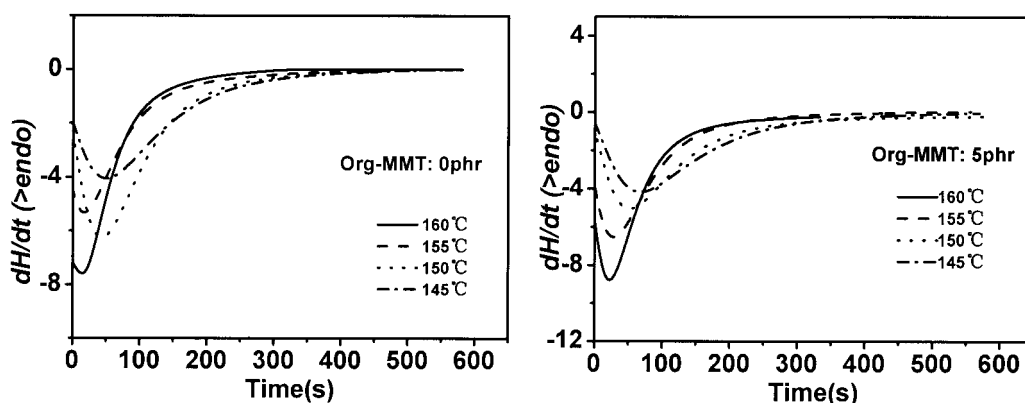


Figure 2 Isothermal DSC curing curves for pure epoxy system and epoxy resin/TOA/Org-MMT nanocomposites.

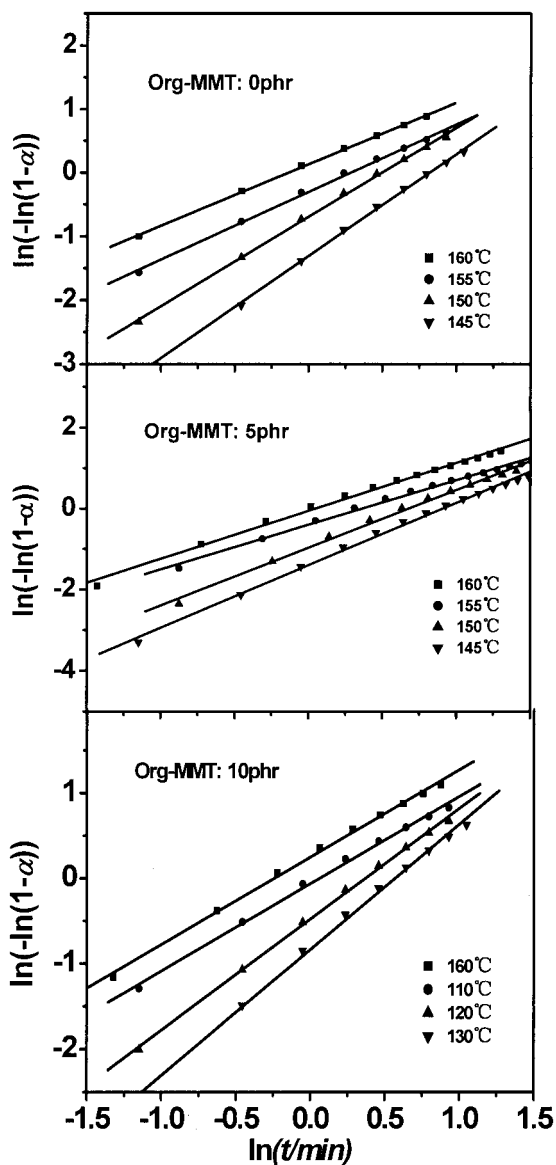


Figure 3 Plots of $\ln[-\ln(1 - \alpha)]$ versus $\ln(t/\text{min})$ of epoxy resin/TOA/Org-MMT nanocomposites with different contents of Org-MMT at various isothermal curing temperature.

heat in the subsequent dynamic scanning. In some documents,^{26,27} there was a resume that for thermo-setting resin with a single reaction and no other enthalpic events, such as the evaporation of solvent or volatile components, enthalpy relaxation, or significant changes in the heat capacity with conversion, the measured heat flow (dH_t/dt) is proportional to the conversion rate, $d\alpha/dt$, in a cure process. Thus, the conversion rate or the reaction rate can be defined as:

$$\frac{d\alpha}{dt} = \frac{dH_t/dt}{H_T + H_s} \quad (2)$$

There are usually several general categories of the modeling equations, such as the n th-order and the

modified Avrami equation used to characterize the isothermal cure kinetics. The n th-order kinetics model is the most simple model to represent the overall curing process:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (3)$$

where n is the reaction order and k denotes the temperature-dependent rate constant obeying an Arrhenius temperature dependency:

$$k = A \exp(-E/RT) \quad (4)$$

where A is the preexponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

The modified Avrami equation that was revised from the crystallization kinetics model [eq. (5)], was applied in the analysis of curing kinetics under the isothermal condition.

$$\alpha(t) = 1 - \exp(-kt^n) \quad (5)$$

where $\alpha(t)$ is the degree of crystallization at time t , k is the Avrami rate constant, and n is the Avrami exponent. In the analysis of the isothermal curing, $\alpha(t)$ is the degree of cure at time t and n is the curing reaction order. It changed into the logarithmic expression:

$$\ln[-\ln(1 - \alpha)] = \ln k + n \ln t \quad (6)$$

For n th-order reactions, based on eq. (6) a plot of $\ln[-\ln(1 - \alpha)]$ against $\ln t$ (min) should yield a linear relationship. The slope and the intercept are n and $\ln k$, respectively, under each isothermal temperature.

TABLE I
Values of n , k , and E_a Obtained from the Avrami Equation at Different Isothermal Temperatures for Epoxy Resin/TOA/Org-MMT Nanocomposites

Org-MMT (phr)	T (°C)	n	k	E_a (kJ/mol)
0	145	1.60	0.2712	92.6
	150	1.40	0.5006	
	155	1.06	0.7401	
	160	0.97	1.1434	
5	145	1.54	0.2464	87.9
	150	1.42	0.3817	
	155	1.15	0.6434	
	160	1.16	0.9637	
10	145	1.47	0.4334	82.5
	150	1.30	0.6200	
	155	1.02	0.9394	
	160	1.02	1.2827	

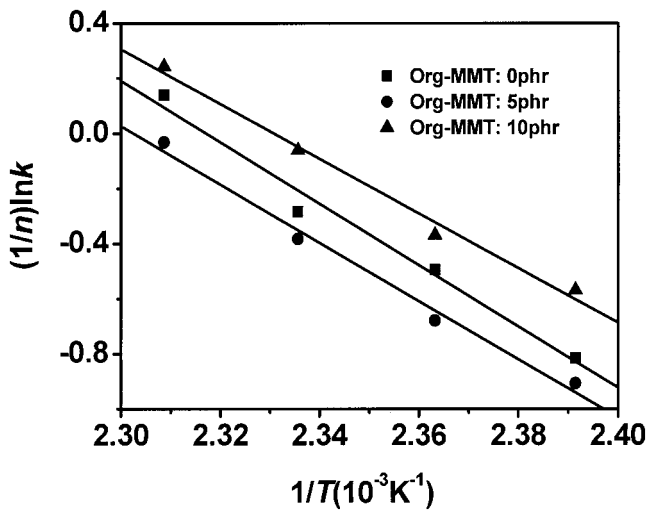


Figure 4 Plots of $(1/n)\ln k$ versus $1/T(10^{-3}\text{K}^{-1})$ of epoxy resin/TOA/Org-MMT nanocomposites with different contents of Org-MMT.

The line then can be obtained between the reciprocal of temperature ($1/T$) and $(\ln k)/n$.

$$\frac{\ln k}{n} = \ln A - \frac{E}{RT} \quad (7)$$

The activation energy E and frequency factor A can be obtained from the slope and the intercept, respectively. The linear lines of $\ln[-\ln(1-\alpha)]$ against $\ln t$ (min) at different temperatures are given in Figure 3 and good linearity during the process of curing lead to the estimation of k and n for all epoxy resin/TOA/Org-MMT nanocomposites. According to the Avrami expression, the relation between the reciprocal of temperature ($1/T$) and $(\ln k)/n$ is used to obtain the parameters for the systems at different isothermal temperatures and the results are listed in Table I.

From Table I, the rate constant k is sensitive to curing temperature and the values increased with rising temperature. The value of reaction order, n , decreased at the lower temperatures (145 and 150°C) with the addition of Org-MMT, and n changed only slightly at higher temperatures between neat system and epoxy resin/TOA/Org-MMT systems. It is noted that the values of n are about 1.5 at lower temperatures (145 and 150°C), but about 1.0 at temperatures of 155 and 160°C. The obvious difference of curing reaction orders between two different temperatures cannot be observed in our previous work²⁶ on the epoxy system with diethylenetriamine as the curing agent. It may be explained that because of the special structure of TOA with two long chains and the existence of void of crosslink, the change of temperature had a great effect on the velocity of epoxy molecular and curing agent molecular moving into the gallery of organic clay. The activation energy in Table I decreased corresponding to the addition of the organic montmorillonite. The activation energy calculated from the line [in Fig. (4)] of the pure system was 92.6 kJ/mol, and the values of 82.5 kJ/mol from the systems with 10 phr Org-MMT were reported using the same modified Avrami equation. It showed that the cure process of the system of epoxy resin and TOA was affected by the addition of Org-MMT. It was considered that the viscosity of the system increased with the addition of filler and the activity energy was improved. But it was a failure that the opinion was applied in this experiment. Because of the special gallery structure of Org-MMT, there are intergallery and extragallery polymerizations and the moving of epoxy resin into the gallery of Org-MMT. As a result, the exfoliated nanocomposite was obtained corresponding to the XRD patterns in Figure 1. The gallery of Org-MMT played an important role during the curing process of the epoxy resin system. The gallery continued to expand and the in-

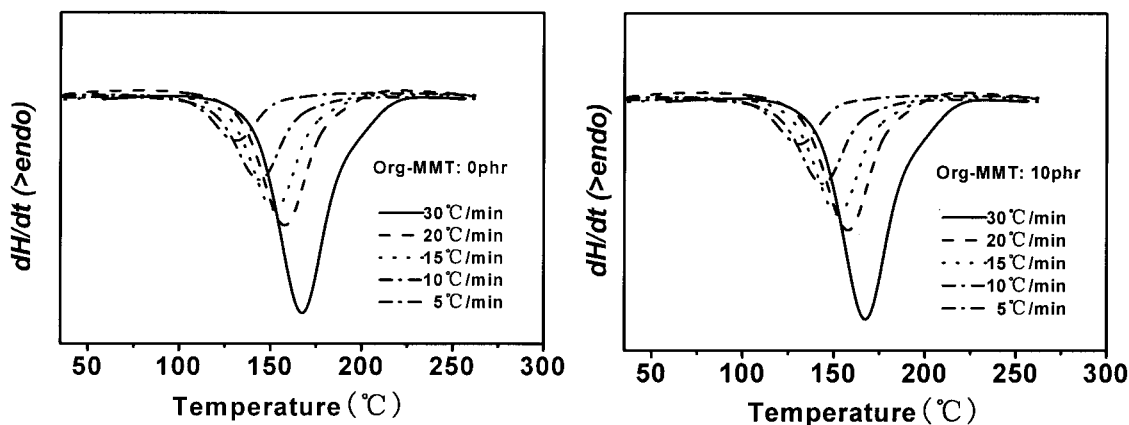


Figure 5 Nonisothermal dynamic DSC curing curves of epoxy resin/TOA/Org-MMT nanocomposites with different contents of Org-MMT.

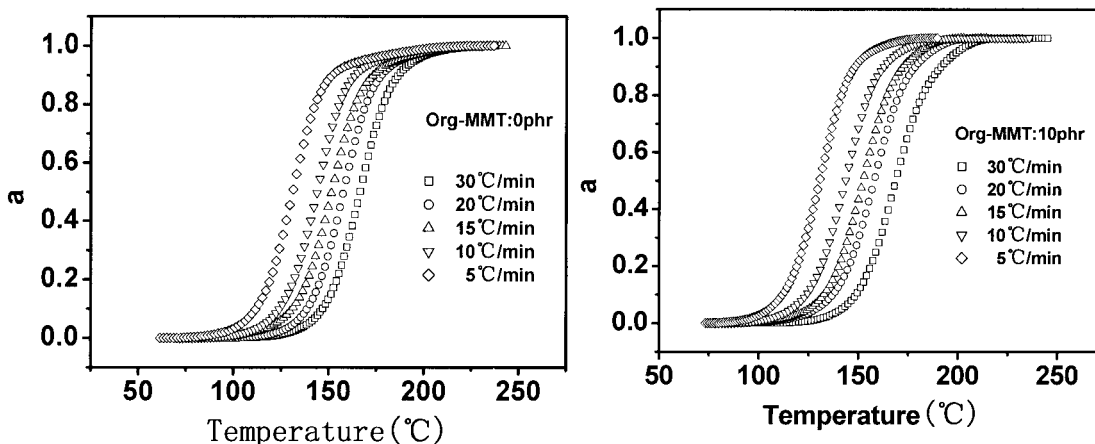


Figure 6 Relationship between the degree of curing α versus T for epoxy resin/TOA/Org-MMT nanocomposites with various contents of Org-MMT during the dynamic curing process.

tergally provided room for collision of activated molecules and polymerization of epoxy resin while the degree of curing increased. Thus it is reasonable that the polymerization was accelerated by the occurrence of Org-MMT.

Compared with the Avrami equation, the Flynn-Wall-Ozawa²⁸ equation can provide a method to evaluate the instantaneous activate energy of the cure reaction during the curing process:

$$\lg(\beta) = \lg \left[\frac{AE}{g(\alpha)R} \right] - 2.315 - \frac{0.457E}{RT} \quad (8)$$

where $\beta = dT/dt$ denotes the heating rate (K/min), T is the temperature (K) during the curing process, E is the phenomenological activation energy (J/mol), R is the ideal gas constant, 8.314J/(mol · K), and $g(\alpha)$ is the function of the degree of cure α .

In this study, the curves of the epoxy resin systems with 0, 3, 5, 7, and 10 phr of Org-MMT tested at five heating rates carried out in the dynamic DSC are shown in Figure 5. The curves of the relationship between the degree of curing α that was obtained by eq. (1) versus temperature are plotted in Figure 6. From eq. (8), the lines of $\lg(\beta)$ against the reciprocal of temperature ($1/T$) are given in Figure 7 and the values of the instantaneous activity energy are listed in Table II. The values of activation energy increase with the accrual of the degree of curing in the pure epoxy system. The crosslink density and the viscosity of the system increased and the probability of collision of activated molecules decreased with the curing reaction. The values of the instantaneous phenomenological activation energy then increased with the increment of the degree of curing, α . However, there is no trend like this in the epoxy resin/TOA/Org-MMT

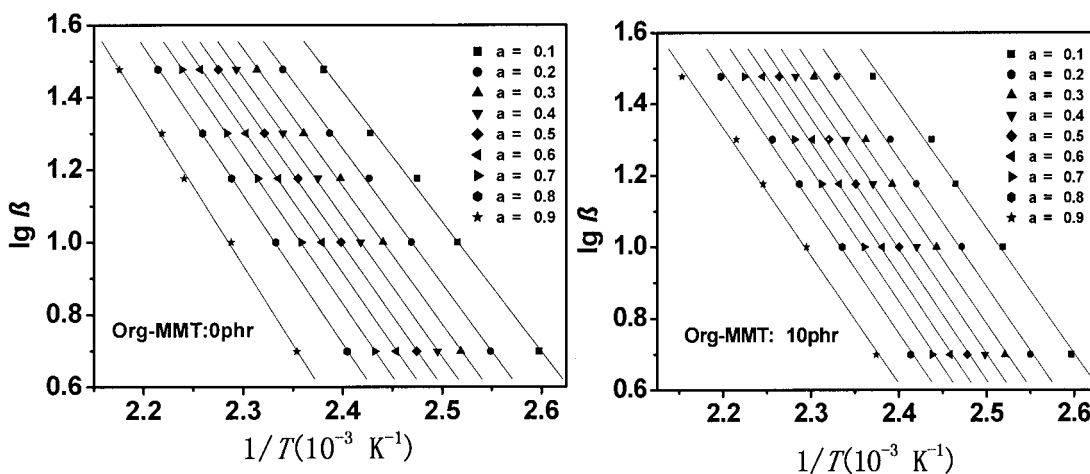


Figure 7 Relationship between $\lg\beta$ versus T^{-1} of epoxy resin/TOA/Org-MMT nanocomposites with various contents of Org-MMT during the dynamic curing process.

TABLE II
Values of the Instantaneous Activation Energy for Epoxy Resin/TOA/Org-MMT Nanocomposites with Different Content of Org-MMT During the Dynamic Curing Process

Degree of curing (α)	Instantaneous activity energy during dynamic curing process (kJ/mol)				
	Org-MMT : 0 phr	Org-MMT : 3 phr	Org-MMT : 5 phr	Org-MMT : 7 phr	Org-MMT : 10 phr
0.1	64.97	65.90	66.91	62.18	63.23
0.2	67.76	66.58	67.24	62.47	64.81
0.3	69.15	66.98	67.46	62.83	65.58
0.4	70.14	67.22	67.72	63.13	66.13
0.5	71.08	67.42	67.98	63.36	66.58
0.6	72.05	67.41	68.13	63.52	66.86
0.7	73.12	66.88	67.93	63.45	66.85
0.8	74.55	65.05	66.73	62.89	66.13
0.9	79.13	59.85	63.50	61.19	64.77

system. The activation energy was relative to many factors, such as viscosity of system, curing temperature, degree of crosslink, and curing time. Generally speaking, owing to the increment of viscosity of the system coming from crosslinking during curing process, the activation energy of the system increases with the increment of the degree of cure. In the epoxy resin/TOA/Org-MMT system, for one thing, the instantaneous activation energy was enhanced by the occurrence of crosslink; on the other hand, the existence of Org-MMT has an effect on the change of the instantaneous activation energy during the curing process. At the early stage of curing process, Org-MMT had not been fully exfoliated and Org-MMT existing at the millimeter scale had little effect on the curing process. However, most of galleries of Org-MMT were exfoliated when the curing process had progressed and layers of Org-MMT were dispersed evenly in the epoxy resin base. The intergallery of Org-MMT provided space for epoxy resin molecules to react with the curing agent, TOA, and then to accelerate the curing process that conquers the effect by the change of crosslinking. That is, introduction of Org-MMT shielded the effect of crosslink degree on the instantaneous activation energy to some extent during the later stage of the curing process. As a result, when the instantaneous activation energy increased during the curing reaction process, the instantaneous activation energy of the epoxy resin/TOA/Org-MMT system changed little with the increment of curing degree and even decreased when the curing degree of the nanocomposites was above 0.6.

CONCLUSION

XRD patterns showed that the exfoliated nanocomposite of epoxy resin/tung oil anhydride/organic montmorillonite was obtained. In this experiment, good linearity of the lines of $\ln[-\ln(1-\alpha)]$ against $\ln t$ was plotted when the modified Avrami equation was applied to characterize the isothermal curing reaction

of the epoxy resin/TOA/Org-MMT system. The values of k shift to higher values with the increase of isothermal temperature and the phenomenological activation energy obtained by the modified Avrami equation is lower than that of pure resin, which may be explained in that the exfoliation of galleries of Org-MMT played a role in the curing reaction. To describe the change of phenomenological activation energy at different curing degrees during the curing process, the Flynn-Wall-Ozawa method was applied to calculate the instantaneous activation energy. It then can be concluded that the results can be taken as a proof that the appearance of exfoliated structure has an effect on the curing reaction of epoxy resin and TOA. The instantaneous activation energy of the epoxy resin/TOA/Org-MMT system changed little with the increment of curing degree and even decreased when the curing degree of the nanocomposites was above 0.6, while the instantaneous activation energy increased during the curing reaction process in the pure system.

The authors gratefully appreciate the financial support of this work by the Nature Science Foundation of Anhui Province, China.

References

- Alexandre, M.; Dubois, P. *Mater Sci Eng A* 2000, 28, 1.
- Wu, J.; Lerner, M. M. *Chem Mater* 1993, 5, 835.
- Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A. *J Mater Res* 1993, 6, 1185.
- Akelah, A.; Moer, A. *J Mater Sci* 1996, 31, 3589.
- Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 1755.
- Messersmith, P. B.; Giannelis, E. P. *J Polym Sci, Part A: Polym Chem* 1995, 33, 1047.
- Vaia, R. A.; Vasudevan, S.; Krawiec, W.; Giannelis, E. P. *Adv Mater* 1995, 7, 154.
- Doh, J. G.; Cho, I. *Polym Bull* 1998, 41, 511.
- Tyan, H. L.; Liu, Y. C.; Wei, K. H.; *Polymer* 1999, 40, 4877.
- Neoh, K. G.; Tan, K. K.; Goh, P. L.; Huang, S. W.; Kang, E. T.; Tan, K. L. *Polymer* 1999, 40, 887.

11. Rong, M. Z.; Zhang, M. Q.; Liu, H. *Polymer* 1999, 40, 6169.
12. Lu, J.; Liu, B.; Yang, H. *J Mater Sci Lett* 1998, 36, 1605.
13. Balazs, A. C.; Singh, C.; Zhulina, E. *Macromolecules* 1998, 31, 8370.
14. Vaia, R. A.; Giannelis, E. P. *Macromolecules* 1997, 30, 7990.
15. Giannelis, E. P.; Manias, E. *Adv Polym Sci* 1999, 118, 108.
16. Liu, J.; Zhao, M.; Zhang, R. Z.; *Chinese J Funct Polym* 2000, 13, 207.
17. Laza, J. M.; Julian, C. A.; Larreun, E.; Rodriguez, M.; Leon, L. M. *Polymer* 1998, 40, 35.
18. Hourston, D. J.; Lane, J. M.; Zhang, H. X. *Polym Int* 1997, 42, 349.
19. Gomez, C. M.; Bucknall, C. B. *Polymer* 1993, 34, 2111.
20. Barral, L.; Cano, J.; Lopez, J.; Lopez-Bueno, I.; Nogueira, P.; Abad, M. J.; Ramirez, C. *J Polym Sci Part B* 2000, 38, 351.
21. Xu, W. B.; Bao, S. P.; He, P. S. *J Appl Polym Sci* 2002, 84, 842.
22. Lan, T.; Kaviratna, P. D.; Pinnavania, T. J. *Chem Mater* 1995, 7, 2144.
23. Messersmith, P. B.; Giannelis, E. P. *Chem Mater* 1994, 6, 1719.
24. Yousefi, A.; Lafleur, P. G.; Gauoin, R. *Polym Comp* 1997, 18, 157.
25. Lu, M. G.; Shim, M. J.; Kim, S. M. *Thermochim Acta* 1998, 323, 37.
26. Xu, W. B.; Bao, S. P.; Shen, S. J.; Wang, W.; He, P. S. *J Polym Sci Part B* 2003, 41, 378.
27. Boey, F. Y. C.; Qiang, W. *Polymer* 2000, 41, 2081.
28. Lopez, J.; Lopez-Bueno, I.; Nogueira, P.; Ramirez, C.; Abad, M. J.; Barral, L.; Cano, J. *Polymer* 2001, 42, 1669.