Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Effect of functionalized kaolinite on the curing kinetics of cycloaliphatic epoxy/anhydride system

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ARTICLE INFO

ABSTRACT

Silane grafted kaolinite (K_{GS}) was prepared through grinding kaolinite and then grafting with 3-aminopropyltriethoxysilane. The influence of K_{GS} on the curing kinetics of cycloaliphatic epoxy resin was studied by non-isothermal differential scanning calorimetry at different heating rates. The reaction activation energy (E_a) was determined based on the Flynn–Wall–Ozawa method. The results of dynamic differential scanning calorimetry (DSC) kinetic analysis show that the surface hydroxyl groups of clay decreases the E_a from 70.6 kJ mol^{-1} to 62.8 kJ mol^{-1} and accelerates the curing reaction of the epoxy resin. The silane grafting reactions consume the surface hydroxyl groups of kaolinite and lead to a decrease in the catalytic efficiency of K_{GS} in the curing of epoxy resin.

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1. Introduction

Epoxy resins are widely used in industry due to their superior characteristics such as good mechanical properties, thermal stability, flame retardant, and chemical resistance. These properties can be greatly improved by the addition of clay fillers. However, compatibility issues will be encountered between the hydrophilic clays and the hydrophobic polymer when clays are dispersed into a polymer matrix (Becker et al., 2002; Chen et al., 2008; González-Domínguez et al., 2011; Wang et al., 2008). One way of overcoming this problem is to modify the clay surface with organic surfactants or/and coupling agents to change the hydrophilic surface to a hydrophobic one. The incorporation of organic modified fillers, such as organoclays, into polymers often improves the affinity and at the same time improves the mechanical, thermal, and physicochemical properties compared with unreacted polymers (Becker et al., 2002; Ha et al., 2007; Park et al., 2009; Wang et al., 2006; Wang et al., 2008).

The properties of the epoxy resin strongly depend on their chemical structure, the extent of curing, the clay mineral–polymer compatibility, as well as the curing conditions (Balabanovich et al., 2004; Cizmecioglu et al., 1986; McIntyre et al., 2005; Naito and Todd, 2002). Therefore, in order to understand and control better the cure process, and optimization of the properties of the final product, it is essential to trace exactly

the relationship between structure and properties of the epoxy resin system. The literatures showed that clays may accelerate the curing reaction of the epoxy resin (Erdoğan et al., 2008; Lee et al., 1997), especially those have been modified by organoclays (Román et al., 2007; Xu et al., 2003). Thus, the effect of organoclays on the curing kinetics is necessarily understood for the optimization of the processing conditions and final product properties.

Differential scanning calorimetry (DSC) is an effective method for the determination of the curing kinetics of epoxy resin systems with organoclays (Brnardic et al., 2006; Ivankovic et al., 2006; Montserrat et al., 2008; Román et al., 2007; Saad et al., 2011; Xu et al., 2003). However, previous investigations realized a number of inconsistent reaction mechanisms and conclusions for the epoxy resins modified with organoclays. Some reports claimed that organoclays could accelerate the curing of the epoxy systems (Montserrat et al., 2008; Román et al., 2007), while others showed little impact (Ivankovic et al., 2006; Saad et al., 2011). Significantly more research is required to increase our fundamental knowledge and understanding of the curing process. On the other hand, most previous studies of the curing of epoxy resins have focused on the effect of montmorillonite due to its high cation exchange capacity (CEC). Very little attention has been paid to the influence of modified kaolinite on the cure behavior of epoxy resins.

In the present study, the ball-milled kaolinite was silanated with 3-aminopropyltriethoxysilane (APTES). The effect of the silylated kaolinite (K_{GS}) on the curing kinetics of cycloaliphatic epoxy resins was investigated, based upon the results of dynamic DSC

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tests. Methylhexahydrophthalic anhydride (MHHPA) and 2-ethyl-4-methylimidazole (EMI) were used as curing agent and activator, respectively. The experimental findings provided detailed information on the understanding of the curing mechanisms of the kaolinite modified epoxy resins and hence are of practical and industrial importance for the application of clay minerals.

2. Experimental

2.1. Materials

The epoxy resin was 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (≥97%, Tetrachem, China) with an epoxy equivalent mass of 127.0 g mol^{-1}. The curing agent used was MHHPA (≥98%, Bangcheng, China) and activator was EMI (99%, Bangcheng, China). The raw kaolinite was obtained from Maoming, China, and used as received without further purification. APTES was purchased from Aldrich (≥98%) and was used as received. The chemical structures of the cycloaliphatic epoxy resin, the curing agent and activator are shown in Fig. 1.

2.2. Kaolinite grinding and silylation

A selected amount of kaolinite was ground for 6 h (denoted as K_G) using a Fritsch pulverisette 5/2-type laboratory planetary mill at a rate of 370 rpm. Both grinding bowl (with a diameter of 7.5 cm and a volume of 300 cm^{-3}) and balls (with a diameter of 2 cm) are made of corundum. 4.0 g of as-prepared K_G was dispersed in 40 cm^3 of cyclohexane. With stirring, 4.0 g of APTES was slowly dropped into the clay suspension. The mixture was then stirred at 80 °C for 24 h. The reaction product was collected by centrifugation and washed with cyclohexane in order to remove the excess silane. After drying at 80 °C for 24 h, the grafted product was collected for further reaction (designated as K_{GS}).

2.3. Preparation of the epoxy/clay nanocomposites

Cycloaliphatic epoxy resin and curing agent were mixed in a 100:132 mass ratio. The amount of activator was set at 1% (mass percent, the same hereinafter) of the epoxy system. A specific amount of K_G and K_{GS} (5% of the epoxy system) were mixed with the epoxy at room temperature, and stirred with a rotation rate of 1000 rpm using a planetary gravity mixer (RM200S, SINO Science & Technology Co., Ltd). The samples were designated as epoxy (epoxy/MHHPA), epoxy/K_G (ground kaolinite filled epoxy), and epoxy/K_{GS} (silylated ground kaolinite filled epoxy).

2.4. Characterization

Thermogravimetric analysis (TG) was performed on a Netzsch STA 409 PC/PG instrument, with a heating rate of 10 °C min^{-1} from

3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate
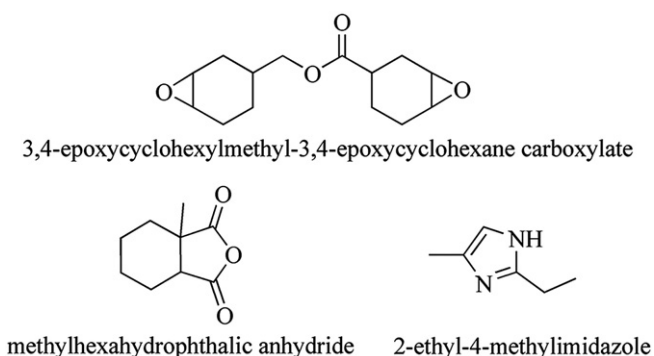
methylhexahydrophthalic anhydride   2-ethyl-4-methylimidazole

Fig. 1. The chemical structure of raw materials.
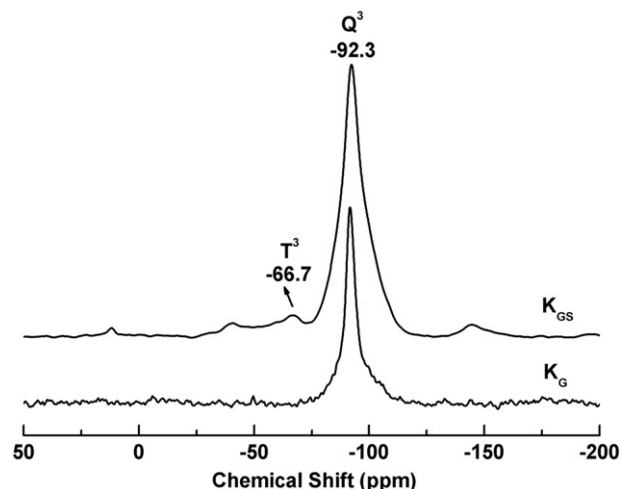
Fig. 2. ^{29}Si NMR spectra of ground kaolinite before and after silylation.

30 to 900 °C under a nitrogen flow of 60 cm^3 min^{-1}. The cross polarization magic angle spinning solid-state nuclear magnetic resonance spectra (^{29}Si CP/MAS NMR) were acquired using a Bruker Advanced 300 NMR spectrometer operating at 59.63 MHz. The contact time was 5 ms, the recycle delay was 3 s, and the spinning rate was 5.5 kHz. Tetramethylsilane (TMS) was used as the external reference.

Curing kinetics of pure epoxy and epoxy/clay system were investigated by nonisothermal dynamic scanning mode in a TA thermal series DSC (TA-Q20). A small quantity of the sample (7–10 mg) before curing was placed in a standard aluminum pan. An identical empty aluminum pan was taken as reference. Dynamic curing scans were conducted from 25 °C to 350 °C at different heating rates of 2.5, 5, 10, and 20 °C min^{-1}, respectively, under nitrogen atmosphere at a constant flow of 50 cm^3 min^{-1}.

3. Results and discussion

Solid-state ^{29}Si MAS NMR spectrum provides evidences for the silane grafted onto K_G surface. T^n notations (n = 0, 1, 2, and 3) are used to describe the different numbers of "O bridge" structures and the different kinds of siloxane bonds formed between APTES and clay or the neighboring APTES (Feng et al., 1997; Tao et al., 2011). Both K_G and K_{GS} displayed resonance at −92.3 ppm, corresponding to the Si in the tetrahedral clay sheets (Fig. 2). After silane grafting, a new resonance was observed at −66.7 ppm in the ^{29}Si NMR spectrum of
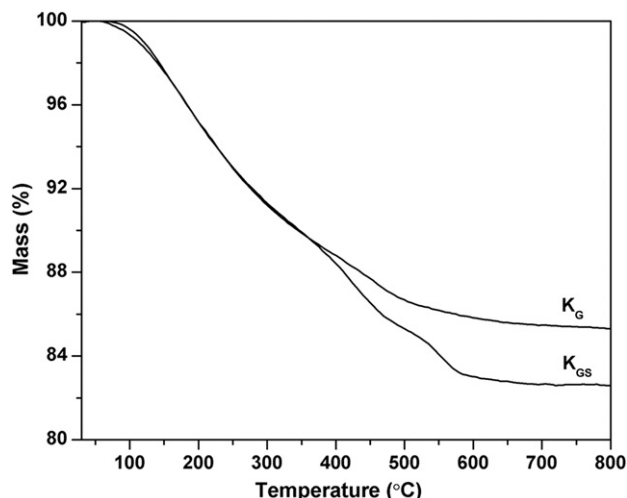
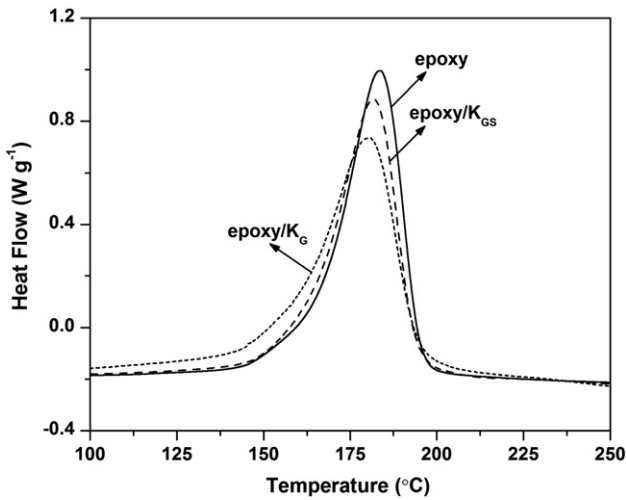Fig. 3. TG curves of ground kaolinite before and after silane grafted.

Fig. 4. Nonisothermal DSC curves of pure epoxy, epoxy/K$_G$ and epoxy/K$_{GS}$ at heating rate of 5 °C min^{-1}.

the K$_{GS}$. This signal was attributed to the hydrolyzed tridentate (T^3) bonding and demonstrated the successful grafting APTES onto clay surface. Compared with K$_G$, the thermal decomposition of K$_{GS}$ displayed a new mass loss over the 400–600 °C temperature range (Fig. 3) with a mass loss of ca. 4.6%. This mass loss was attributed to the decomposition of the grafted silane (He et al., 2005; Piscitelli et al., 2010).

The effects of the silylated clay on the cure kinetics of epoxy resin were evaluated by a nonisothermal DSC dynamic method with a heating rate of 5 °C min^{-1} (Fig. 4). The corresponding initial curing temperature (T$_i$), exothermic peak temperature (T$_p$) and curing enthalpy (ΔH) values were summarized in Table 1. Pure epoxy system showed a single exotherm with T$_i$ and T$_p$ at 163.6 and 183.9 °C, respectively. The addition of K$_G$ and K$_{GS}$ to the epoxy resin leads to a decrease in the T$_i$ and

Table 1
DSC parameters obtained for the different epoxy/clay systems at heating rate of 5 °C min^{-1}.

System	T$_i$ (°C)	T$_p$ (°C)	ΔH (J g^{-1})
Epoxy	163.6	183.9	326.0
Epoxy/K$_G$	155.5	180.7	316.8
Epoxy/K$_{GS}$	160.5	182.2	301.6

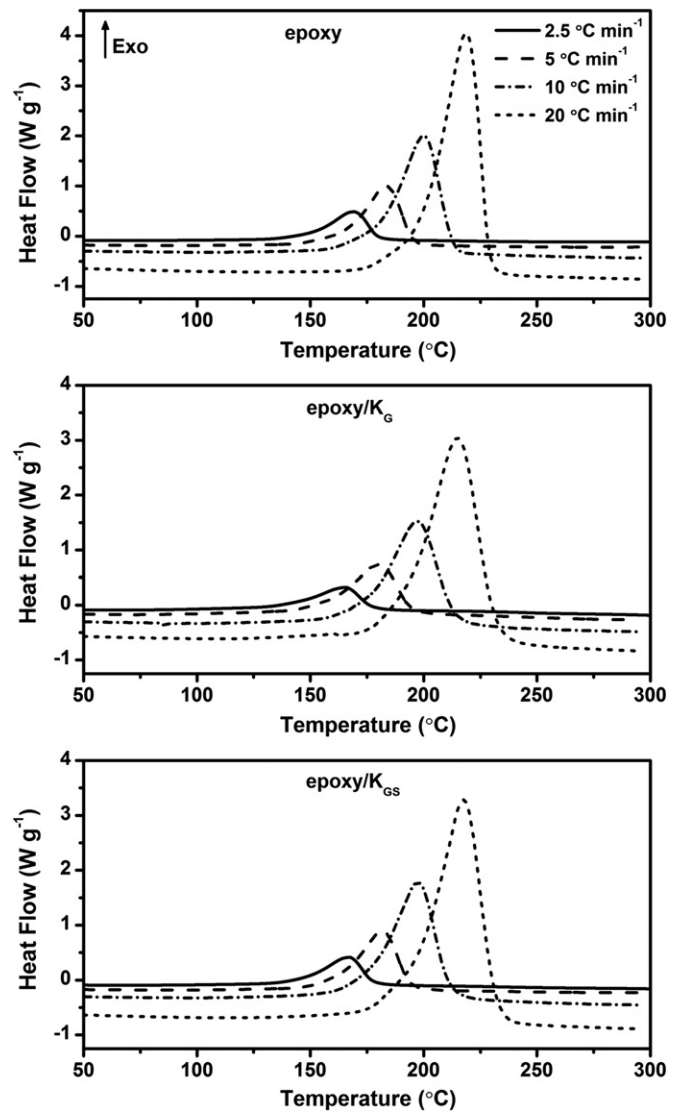Fig. 6. Nonisothermal DSC curves of pure epoxy, epoxy/K$_G$ and epoxy/K$_{GS}$ at heating rates of 2.5, 5, 10 and 20 °C min^{-1}.

Fig. 5. Degree of conversion of pure epoxy, epoxy/K$_G$ and epoxy/K$_{GS}$ at heating rate of 5 °C min^{-1}.
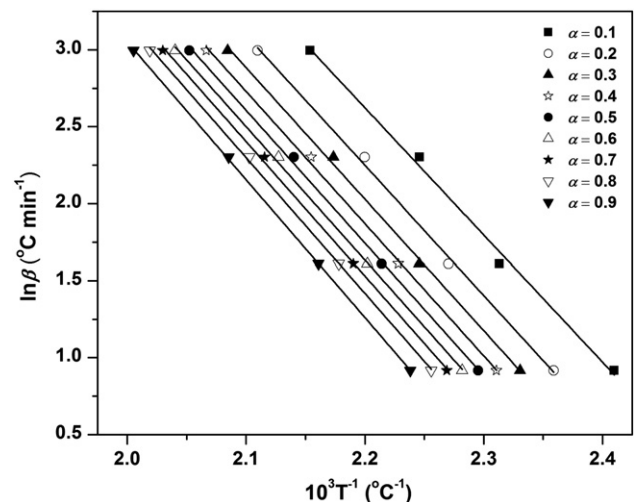

Fig. 7. Isoconversional plots of epoxy/K$_{GS}$ system by Flynn–Wall–Ozawa method.
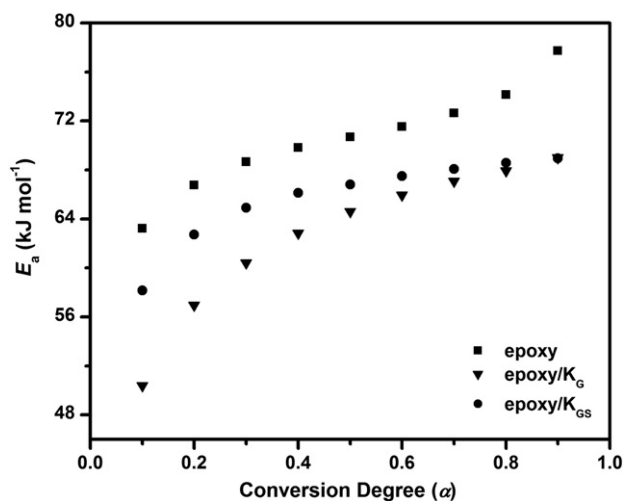
Fig. 8. Dependence of activation energy (E_a) on the degree of conversion (α).

T_p of the products, corresponding to the advance of the onset temperature of epoxy cure reaction.

This advanced cure reaction behavior was further assessed by the degree of conversion at a heating rate of 5 °C min^{-1} for pure epoxy, epoxy/K_G and epoxy/K_{GS} (Fig. 5). Compared with the pure epoxy, epoxy/K_G showed a significant shift to a lower temperature in the curve of percentage conversion, while epoxy/K_{GS} displayed a very small variation. Reports in the literature showed that the degree of conversion of the curing reaction is related to the concentration of hydroxyl groups on the clay surfaces (Erdoğan et al., 2008; Lee et al., 1997). In the case of epoxy/K_{GS}, hydroxyl groups of kaolinite were consumed by reacting with silane. The lower concentration of hydroxyl groups resulted in lowering of the acceleration effect on the curing reaction.

On the other hand, the clay in the epoxy system caused a steric hindrance and disrupts the stoichiometric reaction between epoxide and anhydride at the molecular level. As a result, the networks of the clay/epoxy are not synthesized homogeneously and tightly as those of the pure epoxy resin (Harsch et al., 2007). The presence of the clay causes an increase in viscosity, lowers the mobility of the reactive species, and results in a lower total enthalpy (ΔH) in the epoxy/clay system compared with the pure epoxy resin (Table 1).

To understand better the curing kinetics, the reaction was conducted at heating rates of 2.5, 5, 10, and 20 °C min^{-1} (Fig. 6). The DSC curves indicated that T_i and T_p increased with the ascending of the heating rate. A lower heating rate offered enough time to diffuse the active groups and allowed further reaction. With a higher heating rate, the active groups would have not enough time to diffuse and react completely. As a result, a shift of the DSC curves to a higher temperature would occur in order to compensate for the insufficient time. This is in accordance with the results of the other functionalized mineral modified epoxy resin, such as graphitic (Fu and Zhong, 2011).

The reaction activation energy E_a represents the potential barrier for the curing reaction. The Flynn–Wall–Ozawa method is a convenient approach to calculate the activation energy. The most important advantage of this method is that no kinetic model for the curing reaction is required. It is also less sensitive to instrumental noise due to its integral character (Fu and Zhong, 2011; Opfermann and Kaisersberger, 1992). Generally, the Flynn–Wall–Ozawa method includes the following equation (Fu and Zhong, 2011; Opfermann and Kaisersberger, 1992):

$$\ln\beta = \ln\left(\frac{AEa}{R}\right) - \ln g(\alpha) - 5.3305 - 1.052\left(\frac{Ea}{RT}\right) \tag{1}$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{2}$$

where, β is the heating rate (°C min^{-1}), A is the pre-exponential constant, T is the temperature (K), E_a is the activation energy (kJ mol^{-1}) at the specific conversion, R is the gas constant (8.314 J · mol^{-1} · °C^{-1}), and $g(\alpha)$ is a conversion dependence function.
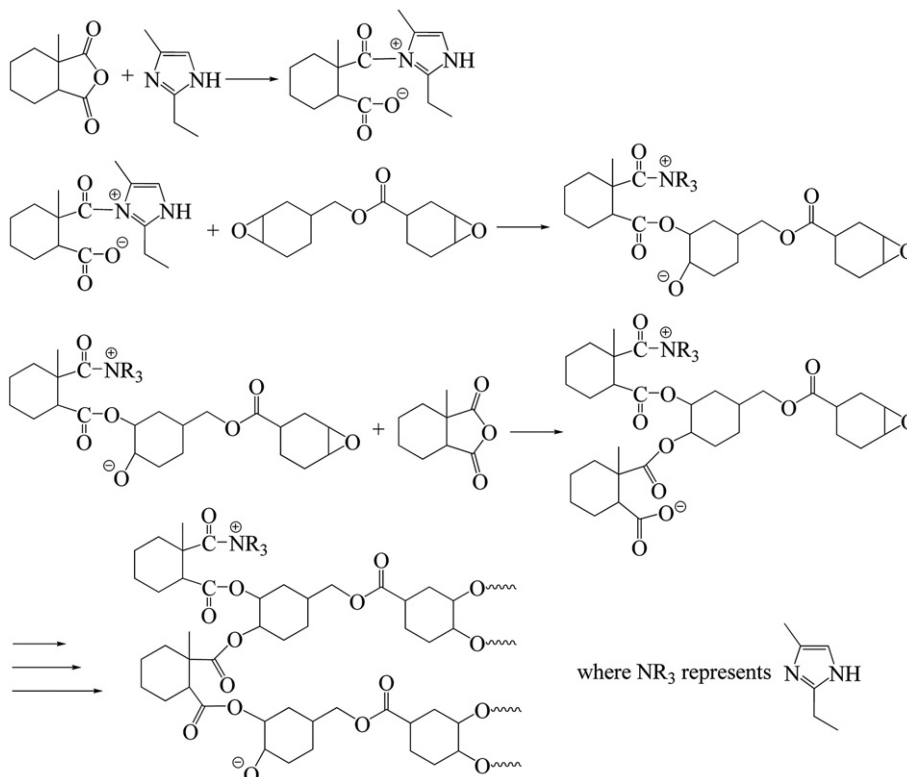

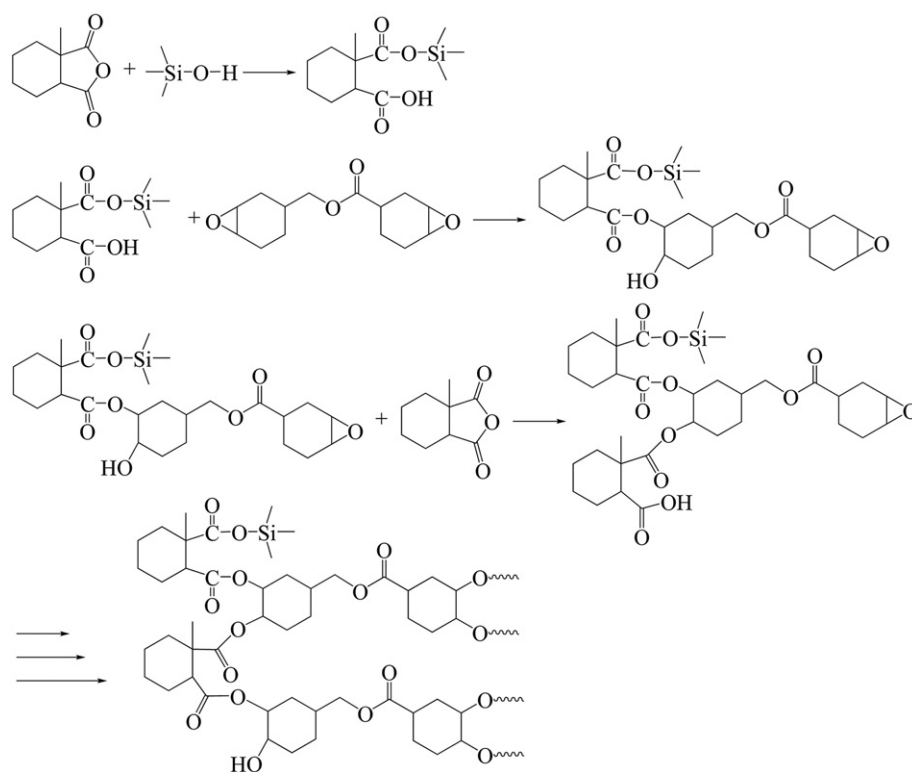Fig. 9. Schematic illustration of epoxy/anhydride system.

Fig. 10. Proposed reaction mechanism of epoxy/clay system.

To obtain the change of E_a values during the curing reaction, a set of α was chosen from the full range of experimental data at the multiple heating rates, i.e. $\alpha = 0.1, 0.2…0.8$, and 0.9. Based on Eq. (1), the plots of ($\ln\beta$) versus (1000/T) were obtained at various heating rates (Fig. 7). Isoconversional plots at different heating rates exhibited a linear curve over the range of α with the linear correlation coefficient (R^2) greater than 0.990. E_a value for all epoxy systems was calculated using the slope of straight lines and Eq. (1) (Fig. 8). These values increased with the increase of α. This resulted from the gradually increased density of cross-linking, which leads to increasing constraints for the reactive species to react with one another (Boey and Qiang, 2000; Saad et al., 2011). E_a value of epoxy/clay systems (epoxy/K_G and epoxy/K_{GS}) is lower than that of pure epoxy system over the range of α. This phenomenon could also be determined from the concentration of hydroxyl groups on the clay surfaces (Erdoğan et al., 2008; Lee et al., 1997; Shen et al., 2005). The abovementioned literatures also revealed that surface hydroxyl groups of the minerals (such as, zeolite and montmorillonite) could accelerate the curing reaction. This was verified by showing a lower increment of E_a at a higher conversion percentage in the epoxy/K_G systems. The present study showed a larger E_a in the epoxy/K_{GS} system, resulting from the consumption of the hydroxyl groups on clay surfaces during silane grafting process.

The curing mechanism of cycloaliphatic epoxy with anhydride in the presence of EMI was shown in Fig. 9 (Fischer, 1960; Kolář and Svítilová, 2007). EMI was selected to accelerate the epoxide–anhydride reaction during the curing process. In the initial stage of curing, EMI opened the anhydride ring by generating a carboxyl anion. This carboxyl anion reacted with an epoxide, forming an ester linkage and generating an alkoxide anion. The alkoxide anion then reacted with another anhydride to produce carboxyl anion for another epoxide ring opening reaction. These reaction processes were repeated until all the anhydride was exhausted.

Hydroxyl groups could be involved in the anhydride ring opening process (Kolář and Svítilová, 2007) (Figs. 9, 10). They helped to open the anhydride rings, and to form an ester bond and a carboxyl group.

Therefore, for epoxy/kaolinite system, the surface hydroxyl groups of kaolinite could catalyze the curing reaction and facilitated the epoxide–anhydride reaction. Since more curing activator is involved in the acceleration process, the curing rate of the epoxy/kaolinite increased and the activation energies decreased compared with that of the pure epoxy system.

4. Conclusions

The effect of kaolinite (K_G) and silylated kaolinite (K_{GS}) was investigated on the curing behavior of the cycloaliphatic epoxy resin. The kinetic analysis indicated that the clay accelerates the curing rate and decreases the reaction activation energy of the epoxy. The surface hydroxyl groups of clay accelerated this curing process by catalyzing the ring opening reaction of the anhydride. Silylation process decreased the concentration of the surface hydroxyl groups, and led to a decrease in the catalysis effect of clay on curing of cycloaliphatic epoxy resin.

Acknowledgments

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