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Effect of MDA-endcapped CTBN on the cure kinetics of epoxy system by autocatalytic cure rate expression

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The cure rate of diglycidyl ether of bisphenol A (DGEBA)/4,4′-methylene dianiline (MDA) system with or without MDA-endcapped carboxyl-terminated butadiene acrylonitrile (CTBN) rubber was studied by autocatalytic cure rate expression. All the cumulative conversion curves for DGEBA/MDA system with or without MDA-endcapped CTBN (20 phr) showed s-shape and this meant that the two systems followed the typical autocatalytic reaction. The cure rate of the system with MDA-endcapped CTBN (20 phr) was faster than that of the system without MDA-endcapped CTBN (20 phr). The activation energies of k_1 and k_2 for DGEBA/MDA system were 54.01 kJ/mol and 44.06 kJ/mol, respectively and those of k_1 and k_2 for the system with MDA-endcapped CTBN (20 phr) were 47.71 kJ/mol and 40.95 kJ/mol. © *2000 Kluwer Academic Publishers*

1. Introduction

A lot of attention has been devoted to characterize the cure reaction of epoxy resin in order to make the optimum applications such as adhesives, coatings, sealants, matrix for components, etc. and to get suitable processes such as pultrusion process, filament winding process, laminate process, encapsulation, etc. [1–6]. Because the physical, mechanical, thermal and electrical properties of an epoxy resin are closely related to the curing history and cure degree, it is very important to monitor the exact cure rate at various cure temperatures.

Many researchers have proposed various cure rate expressions and techniques, and studied the cure kinetics of each epoxy system by these expressions and techniques [1–6]. The cure kinetic expressions are mainly divided into two groups. One is nth order expression and the other is autocatalytic cure rate expression, and in this study, the latter was used to investigate the cure kinetics of diglycidyl ether of bisphenol A (DGEBA)/4,4′-methylene dianiline (MDA) system modified with MDA-endcapped carboxyl-terminated butadiene acrylonitrile rubber (CTBN) to give the toughness and to enhance the compatibility between base epoxy resin and CTBN. The autocatalytic cure rate expression [1, 2] is

$$\dot{\alpha} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(k_1 + k_2\alpha^m\right)(1-\alpha)^n \qquad (1)$$

Where, $\dot{\alpha}$: cure rate, α: cure degree of monomers, k_1, k_2: cure rate constants and m, n: reaction orders.

2. Experiment

Diglycidyl ether of bisphenol A (DGEBA, Epon 828 grade) supplied by Shell Co. was used as a base resin and 4,4′-methylene dianiline (MDA) was used as a curing agent [7, 8]. Carboxyl-terminated butadiene acrylonitrile rubber (CTBN) manufactured by B. F. Goodrich Co. under the trade name of Hycar 1300 × 8 was terminated by MDA at 160°C for 1 hr.

DGEBA and MDA-endcapped CTBN (0 and 20 phr) were well mixed with MDA (30 phr) and the sample was placed at -13°C free from water molecules to prevent the cure reaction and absorbing of water during the store time. To investigate the cure rate, isothermal DSC run was carried out at 80–120°C in the nitrogen flow rate of 40 ml/min.

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3. Results and discussion

The cure mechanism of epoxy resin with diamine curing agent are well established [9–14]. A hydrogen atom of the primary amine group reacts with an epoxide group and forms a secondary amine with a hydroxyl group. Successively, the secondary amine group reacts with another epoxide group and forms a tertiary amine with a new hydroxyl group. It is assumed that the cure rate and the heat generation of these two steps are same and they are consisted with a single activation energy. These reactions are noncatalytic reactions. However, the newly formed hydroxyl groups play a role of catalyst in the reactions between amine and epoxide groups and make the cure rate accelerated by the formation of termolecular transition state, so the cure reaction of epoxy/diamine system is called autocatalytic reaction. In the autocatalytic cure rate expression of Equation 1, k_1 represents the rate constant of noncatalytic reaction and k_2 stands for the rate constant of autocatalytic reaction. k_1 also stands for the catalytic reaction caused by the hydroxyl group which exists in the molecular formulae of reactants.

Fig. 1 shows the isothermal cure curves for DGEBA/MDA system without MDA-endcapped CTBN at various cure temperatures. All curves showed that the cure rate increased until peak value and decreased with the increment of cure time and this meant that the cure reaction of the system followed the typical autocatalytic reaction. When cure temperature was increased, the cure rate increased more steeply and decreased more rapidly, and the maximum peak value was highered. These results said that the cure rate became faster with the increasing cure temperature like the general chemical reaction. $\dot{\alpha}_p$ and t_p were listed on Table I and the relationships between $\ln \dot{\alpha}_p$ or $\ln t_p$ and $1/T$ were shown in Fig. 2. The linear expressions for Fig. 2 were as the follows.

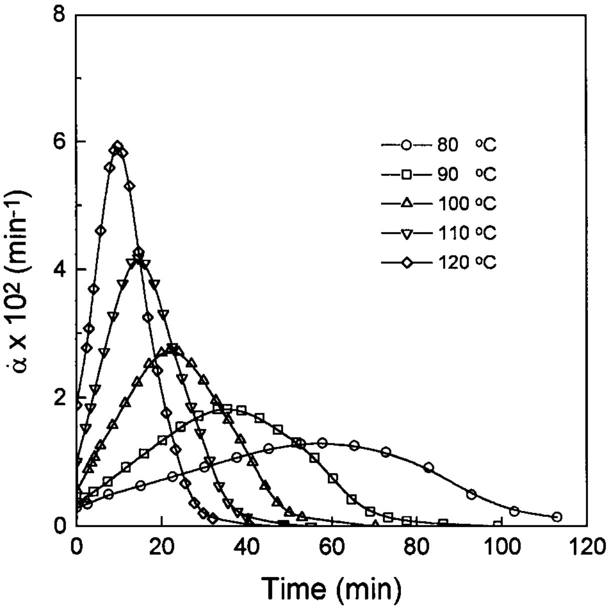

Figure 1 Isothermal cure curves for DGEBA/MDA system without MDA-endcapped CTBN.

TABLE I Temperature dependence of cure kinetic variables for DGEBA/MDA system without MDA-endcapped CTBN

Temperature (K)	$\dot{\alpha}_p \times 10^2$	t_p (min)	α_p	$k_1 \times 10^2$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	m	n
353	1.30	57.8	0.42	0.30	4.32	0.91	1.09
363	1.83	35.5	0.41	0.37	6.20	0.88	1.12
373	2.73	22.2	0.39	0.56	9.31	0.84	1.16
383	4.18	14.5	0.41	1.01	14.52	0.89	1.11
393	5.94	9.76	0.39	1.89	18.91	0.88	1.12

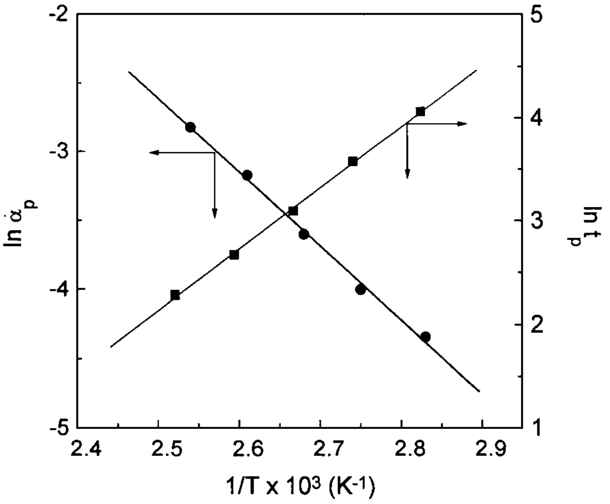

Figure 2 The relationship between $\ln \dot{\alpha}_p$ or $\ln t_p$ and $1/T$ for DGEBA/MDA system without MDA-endcapped CTBN.

$$\ln \dot{\alpha}_p = -5.37 \times 10^3 \frac{1}{T} + 10.81$$

$$\ln t_p = 6.20 \times 10^3 \frac{1}{T} - 13.48$$

The temperature dependence of both $\dot{\alpha}_p$ and t_p could be accurately described by means of an Arrhenius relationship.

The initial cure rate was obtained from Equation 1 by the substitution of $t = 0$ and it became Equation 2. So, k_1 was directly obtained from the y-intersect in Fig. 1 and these were listed on Table I.

$$k_1 = \dot{\alpha}_{t=0} = \left(\frac{d\alpha}{dt}\right)_{t=0} \tag{2}$$

The relationships between monomer conversion and cure time for DGEBA/MDA system without MDA-endcapped CTBN were obtained by the integrating the cure curves in Fig. 1 and they were displayed in Fig. 3. All the curves showed s-shape and this meant that the system followed the autocatalytic cure mechanism. In the initial stage, amine-epoxy reaction took place slowly and formed hydroxyl group which acted as a catalyst in the epoxy-amine reaction. As the cure reaction proceeded, the concentration of hydroxyl group increased, so the cure rate steeply increased. In the late stage, however, the cure reaction was controlled by diffusion of functional groups, so the cure rate decreased.

To get reaction orders, m and n, the following two equations were used.

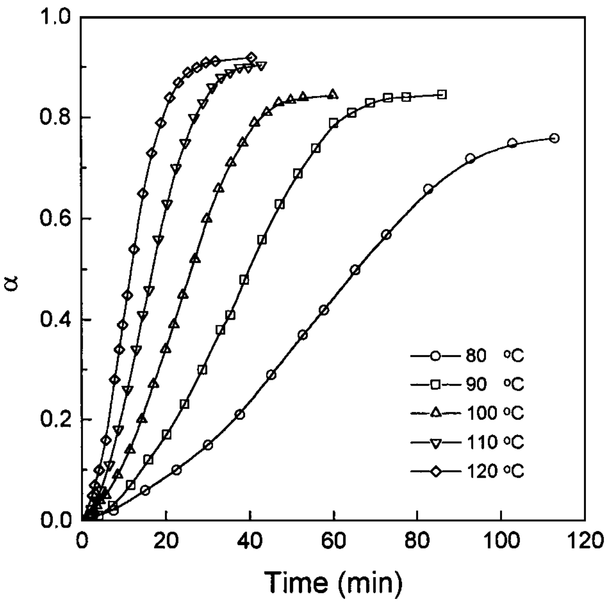

Figure 3 Conversion vs. time for DGEBA/MDA system without MDA-endcapped CTBN.

$$m + n = 2 \tag{3}$$

$$m = \frac{\ln\left(\frac{\dot{\alpha}_p/(1-\alpha_p)^{2-m} - k_1}{(2-m)k_1\alpha_p^{1-m}/(m-2\alpha_p)}\right)}{\ln \alpha_p} \tag{4}$$

where, $\dot{\alpha}_p$: the maximum cure rate at exothermic peak and α_p: the degree of conversion at the maximum exothermic peak. When $\dot{\alpha}_p$ (Fig. 1), α_p (Fig. 3) and k_1 (Equation 1) were introduced to Equation 4, the reaction order, *m* was easily obtained and the other reaction order, *n* was obtained from Equation 3. These were listed on Table I.

$$k_2 = \frac{(2-m)k_1\alpha_p^{1-m}}{m - 2\alpha_p} \tag{5}$$

k_2 at various cure temperatures could be calculated and also listed on Table I. As known in the general chemical reaction, the rate constant increased with the increasing reaction temperature. From Table I, the Arrhenius relationships for k_1 and k_2 were expressed as follows and were shown in Fig. 4.

$$-\ln k_1 = 6.47 \times 10^3 \frac{1}{T} - 12.33$$

$$-\ln k_2 = 5.28 \times 10^3 \frac{1}{T} - 11.78$$

k_2 was far higher than k_1 and this was well agreed that k_2 represents autocatalytic reaction and k_1 stands for non-catalytic reaction. From the slope and *y*-intersection, activation energy and pre-exponential factor were calculated. The activation energy and pre-exponential factor for k_2 were 44.06 kJ/mol and 13.06×10^4 min^{-1}, respectively, and those for k_1 were 54.01 kJ/mol and 22.64×104 min^{-1}, respectively.

Fig. 5 shows the cure rate vs. conversion for DGEBA/MDA system without MDA-endcapped CTBN. The cure rate increased with the increasing monomer conversion at low conversion and decreased after maximum cure rate at about $\alpha = 0.4$ regardless of cure temperature, and the maximum conversion value increased with the increment of cure temperature. As conversion increased, the mobility of functional groups was disturbed due to the gel formation and increasing viscosity, and this state was called as diffusion control. Furthermore, the concentration of the functional groups decreased, so the cure rate decreased at some high conversion.

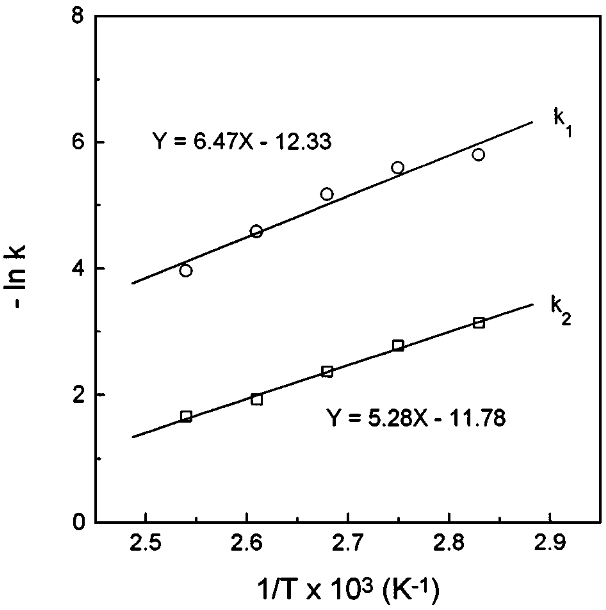

Figure 4 $-\ln k$ vs. $1/T$ for DGEBA/MDA system without MDA-endcapped CTBN.

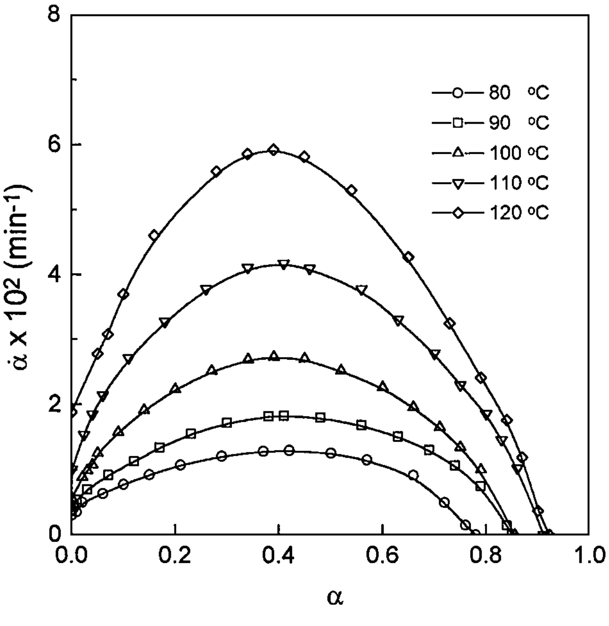

Figure 5 Cure rate vs. conversion for DGEBA/MDA system without MDA-endcapped CTBN.

Isothermal cure curves for DGEBA/MDA system with MDA-end capped CTBN (20 phr) at five temperatures were shown in Fig. 6. This system also showed the typical autocatalytic cure reaction like the curves in Fig. 1, but all curves of the system with MDA-endcapped CTBN (20 phr) were shifted to lower x-axis than those of the system without MDA-endcapped CTBN. $\dot{\alpha}_p$ and t_p were listed on

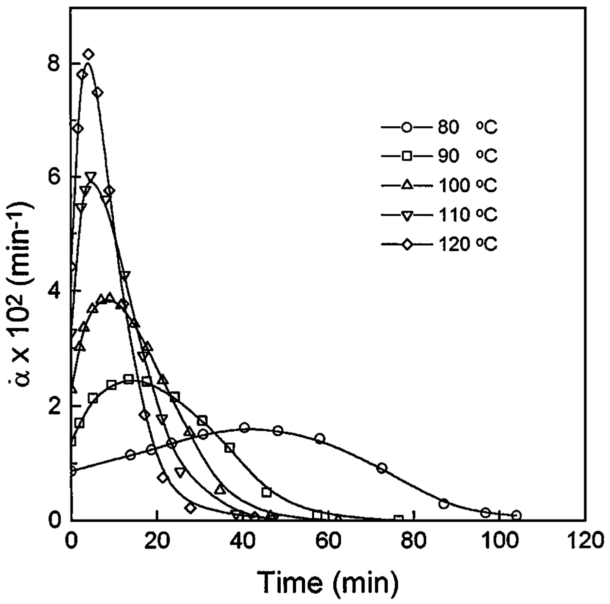

Figure 6 Isothermal cure curves for DGEBA/MDA system with MDA-endcapped CTBN (20 phr).

TABLE II Temperature dependence of cure kinetic variables for DGEBA/MDA system with MDA-endcapped CTBN (20 phr)

Temperature (K)	$\dot{\alpha}_p \times 10^2$	t_p (min)	α_p	$k_1 \times 10^2$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	m	n
353	1.63	32.6	0.45	0.87	4.74	1.08	0.92
363	2.46	13.4	0.31	1.39	6.35	0.83	1.17
373	3.86	9.08	0.31	2.28	9.97	0.84	1.16
383	6.02	4.60	0.21	3.29	13.10	0.61	1.39
393	8.18	4.16	0.24	4.43	19.36	0.67	1.33

Table II. When DGEBA/MDA system was added with MDA-endcapped CTBN (20 phr), $\dot{\alpha}_p$ was highered at lower t_p for each curve at the same temperature. The relationships between $\ln \dot{\alpha}_p$ or $\ln t_p$ and $1/T$ could be expressed as follows.

$$\ln \dot{\alpha}_p = -5.71 \times 10^3 \frac{1}{T} + 12.03$$

$$\ln t_p = 7.24 \times 10^3 \frac{1}{T} - 17.17$$

The temperature dependence of both $\dot{\alpha}_p$ and t_p could be also accurately described by means of an Arrhenius relationship.

k_1 could be obtained from Fig. 6 and Equation 2, and these were listed on Table II. The k_1 for the system with MDA-endcapped CTBN were higher than those without MDA-endcapped CTBN. From the comparing the data of $\dot{\alpha}_p$, t_p and k_1, it was found that MDA-endcapped CTBN made the cure rate of DGEBA/MDA system fast, and it was explained by the increased amine concentration due to the addition of MDA-endcapped CTBN. The amine group of MDA-endcapped CTBN reacted with epoxy group in the initial state as shown in the reaction between amine group of MDA and epoxy group and formed a hydroxyl group which could be acted as a catalyst. Therefore, cure rate of the system with MDA-endcapped CTBN (20 phr) was faster than that of the system without MDA-endcapped CTBN.

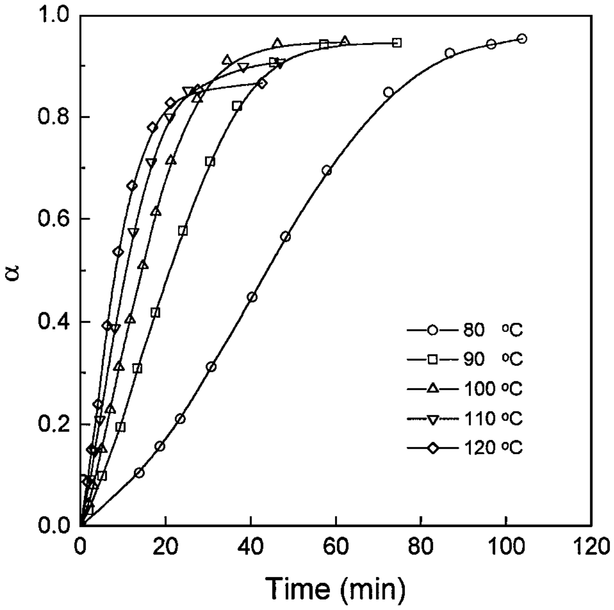

Figure 7 Conversion vs. time for DGEBA/MDA system with MDA-endcapped CTBN (20 phr).

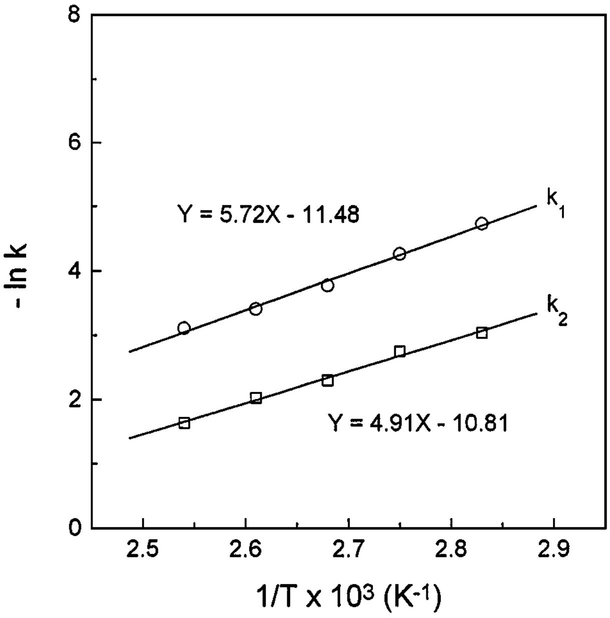

Figure 8 $-\ln k$ vs. $1/T$ for DGEBA/MDA system with MDA-endcapped CTBN (20 phr).

The cumulative conversion for DGEBA/MDA system with MDA-endcapped CTBN (20 phr) were obtained by the integrating Fig. 6 and they were displayed in Fig. 7. All the curves showed s-shape and this meant that the system followed the autocatalytic cure mechanism.

To get other kinetic parameters, $\dot{\alpha}_p$ (Fig. 6), α_p (Fig. 7) and k_1 (Equation 1) were introduced to Equations 3–5 and the values were also listed on Table II. The Arrhenius relationships for k_1 and k_2 were expressed as follows and were shown in Fig. 8.

$$-\ln k_1 = 5.72 \times 10^3 \frac{1}{T} - 11.48$$

$$-\ln k_2 = 4.91 \times 10^3 \frac{1}{T} - 10.81$$

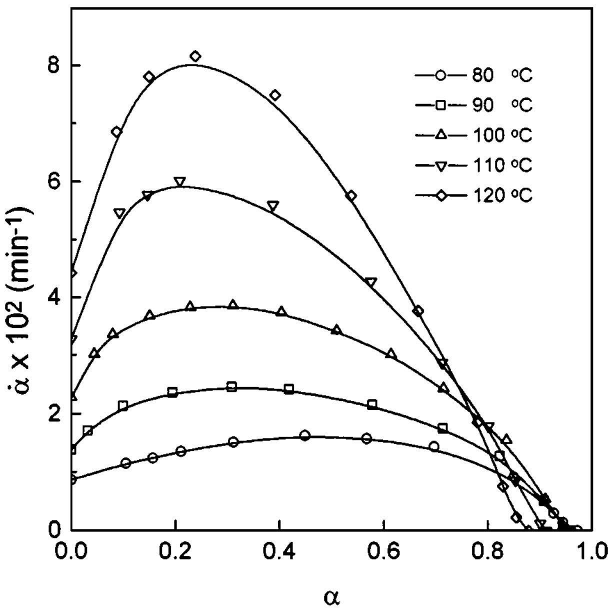

Figure 9 Cure rate vs. conversion for DGEBA/MDA system with MDA-endcapped CTBN (20 phr).

k_2 for autocatalytic cure reaction was far higher than k_1 for noncatalytic reaction. From the slope and y-intersection, activation energy and pre-exponential factor were calculated. The activation energy and pre-exponential factor for k_2 were 40.95 kJ/mol and 4.95×10^4 min^{-1}, respectively, and those for k_1 were 47.71 kJ/mol and 9.68×10^4 min^{-1}, respectively.

The dependence of the cure rate on the conversion for DGEBA/MDA/ MDA-endcapped CTBN (20 phr) system was shown in Fig. 9. The cure rate for this system also increased with the increment of monomer conversion at low conversion and decreased after maximum cure rate. The maximum conversion at the final state decreased with the increment of cure temperature. It may be because there was no sufficient time for the functional groups to diffuse at high temperature.

4. Conclusions

All the cumulative conversion curves for DGEBA/ MDA system with or without MDA-endcapped CTBN (20 phr) showed s-shape and this meant that the two systems followed the typical autocatalytic reaction. The cure rate of the system with MDA-endcapped CTBN (20 phr) was faster than that of the system without MDA-endcapped CTBN (20 phr). This was due to the amine group of MDA-endcapped CTBN which reacted with epoxy group in the initial state and made hydroxyl group which could be acted as a catalyst. k_2 for the autocatalytic mechanism was far higher than k_1 for the noncatalytic mechanism. The activation energies of k_1 and k_2 for DGEBA/MDA system were 54.01 kJ/mol and 44.06 kJ/mol, respectively and those of k_1 and k_2 for the system with MDA-endcapped CTBN (20 phr) were 47.71 kJ/mol and 40.95 kJ/mol.

Acknowledgements

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