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The cure kinetics of CTBN-modified epoxy system

Summary — In an epoxy system modified with a carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) rubber, the cure kinetics was studied in terms of the Kissinger equation (eqn. 1) and of the autocatalytic cure rate expression (eqn. 2). By the former equation, a simple *n*-th order rate equation, DSC measurements allowed to determine the activation energy and the pre-exponential factor; by the latter equation, isothermal DSC analysis allowed to determine the rate constants and reaction orders. The two methods were found suitable to follow the cure kinetics of the epoxy system. In the system modified with CTBN, the cure rate was initially higher than that in the system with CTBN added, on account of the catalytic role of the -COOH groups in CTBN. At a degree of conversion equal to about 0.6, the cure rate was inverted on account of the formation of the CTBN domain.

Key words: cure kinetics, COOH-terminated butadiene-acrylonitrile copolymer (CTBN), CTBN-modified epoxy system, Kissinger equation, autocatalytic cure rate expression.

Many methods have been proposed to enhance the fracture toughness of cured epoxy systems; one of the best known methods is to incorporate various amounts of a reactive liquid rubber [1—6]. When an epoxy resin mixed with a liquid rubber is cured, rubber-rich domains are separated from the epoxy-rich matrix on account of the incompatibility of the epoxy resin with the liquid rubber, and the improvement in toughness is attributed to the rubbery domains dispersed in the continuous epoxy matrix.

When impact is applied to the epoxy system, the impact energy is dissipated by the rubber domains, whereby toughness is improved [1—4]. The improving effects are various according to the distribution, size and shape of the domains.

In this study, carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) rubber was introduced to diglycidyl ether of bisphenol A (DGEBA)/4,4'-methylene dianiline (MDA)/phenyl glycidyl ether (PGE)-acetamide (AcAm) system to modify toughness and the effect of CTBN on the cure kinetics of the system was investigated in terms of the Kissinger method and the autocatalytic expression [5—10]. The Kissinger equation [5—7] which is derived from the simple *n*-th order expression is:

$$-\ln\left(\frac{q}{T_p^2}\right)=\frac{E_a}{R}\cdot\frac{1}{T_p}-\ln\left(\frac{AR}{E_a}\right) \tag{1}$$

where: *q — heating rate, T_p — exothermic peak temperature, E_a — activation energy, A — pre-exponential factor, and R — gas constant.*

From this equation, the activation energy and the pre-exponential factor can be obtained, provided the reaction order is assumed to be known. However, the simple *n*-th order kinetic expression is unable to allow to provide the accurate kinetic parameters. So, we also studied the cure rate of the system by using the autocatalytic expression and compared the kinetic parameters. The autocatalytic expression [8—10] is:

$$\dot{\alpha}=\frac{d\alpha}{dt}=(k_1+k_2\alpha^m)(1-\alpha)^n \tag{2}$$

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

EXPERIMENTAL

The materials included a DGEBA (Epon 828, Shell Co.) type epoxy resins as a base resin, MDA (Fluka Chemie, AG) as a curing agent, PGE-AcAm as a reactive additive and CTBN rubber (B. F. Goodrich Co., 1300x8) as a toughening modifier [11, 12]. DGEMA/MDA (30 phr)/PGE-AcAm (10 phr) and CTBN (0 and 20 phr) were well mixed at 80°C and placed at -13°C to prevent the cure reaction during the storage.

Dynamic DSC analysis was carried out as follows. An aluminum pan containing a sample, 2.5—3.0 mg, was placed in the DSC cell and temperature was incre-

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ased from 30°C to 300°C at rates of 5, 10 and 15°C/min. Isothermal DSC analysis was performed at 80°C, 90°C, 100°C, 110°C, and 120°C. Nitrogen gas was allowed to flow at a rate of 40 ml/min to prevent oxidation of the sample.

RESULTS AND DISCUSSION

The effect of CTBN on the epoxy system examined is shown in terms of dynamic DSC thermograms (Fig. 1). With 20 phr of CTBN added to the epoxy system, the reaction starting temperature and the exothermic peak temperature were found to be lower. The addition of CTBN in thus seen to have reduced the temperature of the cure reaction of the DGEBA/MDA/PGE-AcAm system. The -COOH group is well known to act as a catalyst in the cure reaction of the epoxide group and amine group in the same way as the -OH group acts as a catalyst [13, 14]. Upon addition of CTBN the exothermic heat decreased from 385 kJ/mg to 371 kJ/mg which means that diffusion of functional groups was disturbed in the CTBN domain.

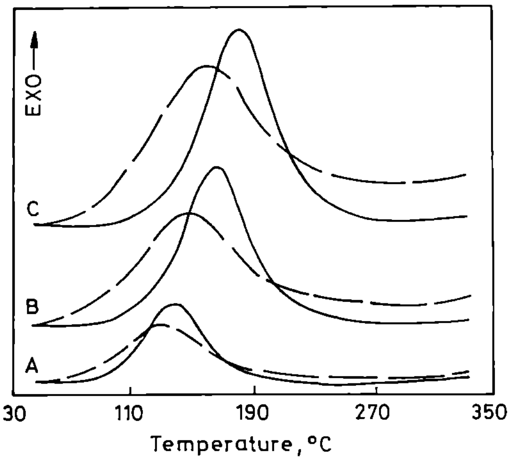

Fig. 1. Dynamic DSC thermograms for the DGEBA /MDA/PGE-AcAm (10 phr) system with (---) and without (—) CTBN (20 phr): (A) 5°C/min, (B) 10°C/min and (C) 15°C/min

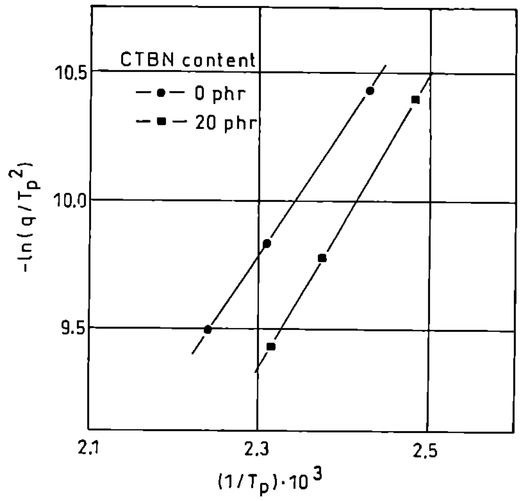

Fig. 2. Plots of $-\ln(q/T_p^2)$ vs. $1/T_p$ for DGEBA /MDA/PGE-AcAm (10 phr) system with and without CTBN (20 phr)

From the exothermic peak temperatures (T_p) at different heating rates (q) (Fig. 1), the relationship $-\ln(q/T_p^2)$ vs. $1/T_p$ was plotted (Fig. 2), based on equation (1). The activation energy was obtained from the slope and the pre-exponential factor was calculated from the intercept. The activation energy of the DGEBA /MDA/PGE-AcAm system was 40.21 kJ/mol (9.61 · 10^3 cal/mol) and the pre-exponential factor was 1.38 · 10^4 min^{-1}; for the system modified with CTBN the respective values were 45.90 kJ/mol (10.97 · 10^3 cal/mol) and 1.56 · 10^5 min^{-1}. So the overall rate constants, k, for the two systems can be expressed as:

k (min^{-1}) = 1.38 · 10^4 exp (-9.61 · 10^3 cal mol^{-1}/RT) (unmodified)

k (min^{-1}) = 1.56 · 10^5 exp (-10.97 · 10^3 cal mol^{-1}/RT) (modified with CTBN)

At 80°C, the rate constants are calculated for the systems with no CTBN and with CTBN added as 1.56 · 10^{-2} min^{-1} and 2.53 · 10^{-2} min^{-1}, respectively. These data confirm the effect of CTBN on the cure rate.

To evaluate the reaction order, the kinetic constant and an assumed reaction order were introduced into the following general rate expression:

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

where: α — *conversion*, t — *time, and* n — *reaction order.*

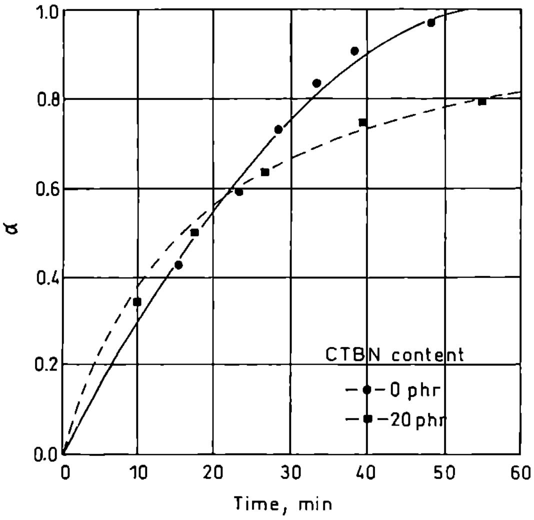

Fig. 3. Comparison of theoretical curves (lines) with experimental points (symbols) at 100°C for DGEBA /MDA/PGE-AcAm (10 phr) with and without CTBN (20 phr)

This equation was used to plot the theoretical isothermal cure curves which were compared with the experimental isothermal curves (Fig. 3); if the two curves coincided, the reaction order was assumed to be correct.

Figure 3 shows the theoretical curves (continuous line) to coincide with the experimental points (symbols) at 100°C with the reaction orders assumed to be 0.43 for the epoxy system with no CTBN and 1.78 for the epoxy system with CTBN added. As explained above, the role of -COOH in CTBN is to fasten the reaction rate of the system with CTBN over that of the system without CTBN up to α = 5.9. However, at α-values higher than that, the cure rate was inversed owing to the formation of CTBN domains during the cure reaction that disturbed diffusion of the functional groups. By the same method, the reaction orders were obtained at other temperatures (Table 1). Generally, the reaction order is only a function of concentration and is not affected by temperature. But in these cases, the values varied with temperature, a fact explicable in terms of a change in the reaction pathway [11, 12].

Table 1. **Reaction orders, *n*, for DGEBA/MDA/PGE-AcAm (10 phr) with and without CTBN (20 phr) at five temperatures**

Temperature, °C / CTBN content, phr	80	90	100	110	120
0	0.83	0.62	0.43	0.47	0.48
20	2.12	1.64	1.78	2.21	1.92

Figure 4 shows the isothermal cure rate for DGEBA/MDA/PGE-AcAm (10 phr) with CTBN added (solid symbols) and with no CTBN added (open symbols) at three different temperatures. In each thermogram the cure rate first abruptly rises to attain a peak, then suddenly decreases. The existence of a peak is suggestive of a catalytic effect due to the hydroxyl group and carboxyl group in the reactants and products, and the higher concentration of the groups affected the cure rate to a greater extent. With CTBN added to the system, the maximum point on the thermogram appeared in a shorter time, which indicates that the cure rate was faster than when no CTBN was added the system. To estimate the kinetic parameters, the autocatalytic cure rate expression (eqn. 2) was used. As $\alpha = 0$ at $t = 0$, the initial rate constant, k_1 became $\dot{\alpha}_{t=0}$. The values were easily obtained from the isothermal thermograms and they are listed in Table 2. The k_1 was associated with the noncatalytic reaction and the catalytic reaction due to the existence of hydroxyl and carboxyl groups in the initial formulation. The effect of the catalytic reaction of the carboxyl group in CTBN on the initial cure rate was confirmed by comparing the initial cure rate constants, k_1. When 20 phr of CTBN was added to the system, the value of k_1 rose and this meant that the carboxyl group of CTBN acted as a catalyst in the initial cure state.

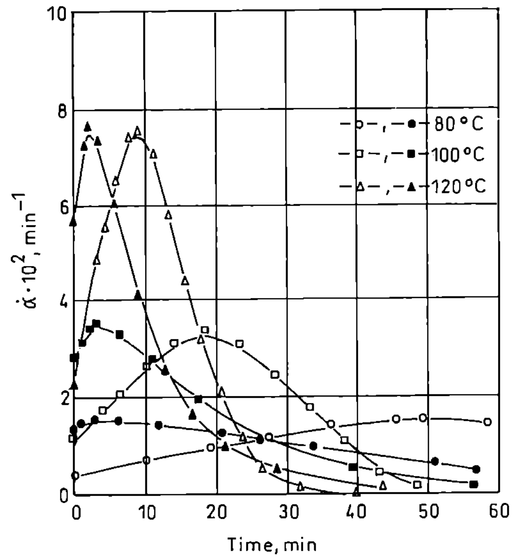

Fig. 4. Cure rate vs. time for DGEBA/MDA/PGE-AcAm (10 phr) with (solid symbols) and without (open symbols) CTBN (20 phr)

From the proportional relationship between the exothermic heat and the conversion, α was plotted against time (Fig. 5). The s-shaped curves indicate that the systems with and without CTBN have followed an autocatalytic cure mechanism, the cure rate of the system with CTBN added being faster than that of the system

Table 2. **Kinetic parameters for DGEBA/MDA/PGE-AcAm (10 phr) with and without CTBN (20 phr) by autocatalytic cure reaction**

CTBN content, phr	Temp., K	$k \cdot 10^2$, min^{-1}		*E*, kcal/mol		$A \cdot 10^{-4}$, min^{-1}		*m*	*n*
		k_1	k_2	E_{a1}	E_{a2}	A_1	A_2		
0	353	0.40	5.40	11.74	10.87	7.63	26.97	1.08	0.92
	363	0.66	7.48					1.01	0.99
	373	1.12	10.82					0.96	1.04
	383	1.48	16.55					0.95	1.05
	393	2.24	26.19					0.92	1.08
20	353	1.34	1.79	9.74	12.20	1.40	66.66	0.61	1.39
	363	1.97	3.14					0.69	1.31
	373	2.75	5.14					0.60	1.40
	383	3.85	7.94					0.43	1.57
	393	5.63	10.17					0.42	1.58

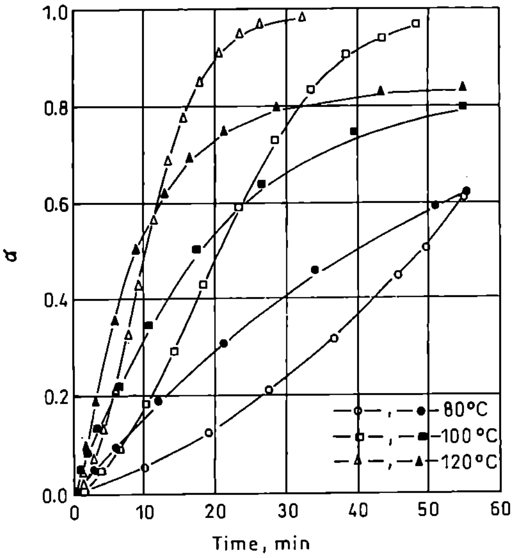

Fig. 5. Conversion vs. time for DGEBA/MDA/PGE-AcAm (10 phr) with (solid symbols) and without (open symbols) CTBN (20 phr)

with no CTBN added. However, at α ≈ 6.0, the conversion was crossed and, above the value, the cure rate was inversed due to the diffusion control exercised by CTBN domains. To get the other parameters, k_2, m and n, in eqn. 2, the following three equations were used (Table 2):

$$m + n = 2 \tag{4}$$

$$m = \frac{\ln\left(\dfrac{\dot{\alpha}_p/(1-\alpha_p)^{2-m} - k_1}{(2-m)k_1\alpha_p^{1-m}/(m-2\alpha_p)}\right)}{\ln\alpha_p} \tag{5}$$

$$k_2 = \frac{(2-m)k_1\alpha_p^{1-m}}{m-2\alpha_p} \tag{6}$$

where: α_p — *degree of cure at exothermic peak and* $\dot{\alpha}_p$ — *cure rate at exothermic peak;* k_2 — *the kinetic rate constant associated with the autocatalytic cure reaction of the -OH groups generated in the reaction between the epoxide groups and the amine groups.*

If k_1 and k_2 for the two systems are compared, k_2 is seen to be higher than k_1, which implies that the autocatalytic cure reaction affected more the cure reaction after the initial state. The inversion of cure rate at α ≈ 0.6 was explained by comparison of the k_2 for the two systems. At the initial cure rate, k_1 of the system with CTBN was higher than that of the system with no CTBN added; however, k_2 of the system with CTBN was lowered due to the formation of CTBN domains.

The rate constants k_1 and k_2 for the two systems followed the Arrhenius-type behavior (Figs. 6 and 7). From the slopes and intercepts, the activation energy E_a and the pre-exponential factor A were evaluated (Table 2) and these values confirmed the catalytic effect of the

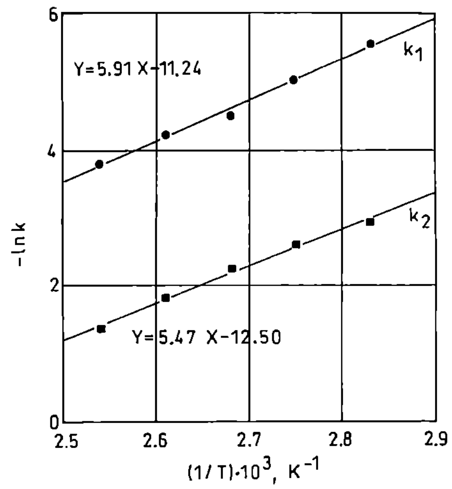

Fig. 6. A plot of -ln k vs. 1/T for DGEBA/MDA/PGE-AcAm (10 phr) system without CTBN

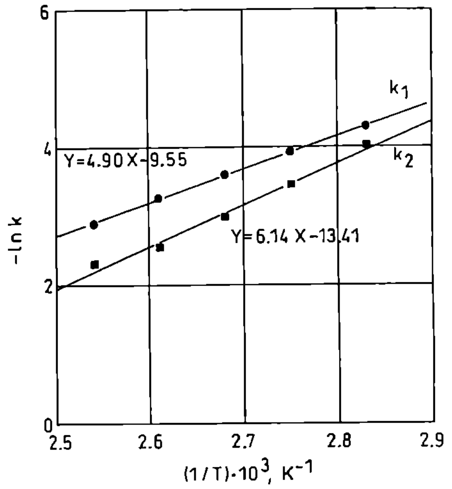

Fig. 7. A plot of -ln k vs. 1/T for DGEBA/MDA/PGE-AcAm (10 phr) system with CTBN (20 phr)

carboxyl group in CTBN and the diffusion control effect of CTBN domains as explained above.

CONCLUSIONS

The cure rate of the system modified with CTBN was faster than that of the system with no CTBN added, on account of the catalytic role of -COOH. However, at α = 0.6, the cure rate was inversed owing to the formation of CTBN domains. In the Kissinger equation, the activation energy and the pre-exponential factor for the system with CTBN were 10.97 · 10^3 cal/mol and 1.56 · 10^5 min^{-1}, and those of the system with no CTBN added were 9.61 · 10^3 cal/mol and 1.38 · 10^4 min^{-1}, respectively. In the autocatalytic cure rate expression, k_1 for the system with CTBN was higher than that of the system with no CTBN added, owing to the role of -COOH; k_2

for the system with CTBN was lower than that of the system with no CTBN added, owing to the formation of a CTBN domain.

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KALENDARZ IMPREZ

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6—9 czerwca 2000 r. Lwów, Ukraina. 5 Międzynarodowa Konferencja "Problems of Corrosion and Anticorrosion Protection of Constructional Materials — CORROSION-2000".

Informacje: Prof. V. Pokhmurskii, Ukrainian Association of Corrosionists, Naukova St., 29 0601 Lviv, Ukraine. Fax: +380 322 63 15 77, e-mail: polimurs @ah.ipm.lviv.ua.

4 września 2000 r. Rozpoczęcie studium podyplomowego: "Korozja i ochrona przed korozją" — Współorganizatorzy: Technische Universität, Bergakademie Freiberg.

20 września 2000 r. Seminarium tematyczne: "Zastosowanie materiałów w urządzeniach przesyłających wodę pitną" — Współorganizator: Gesellschaft für Korrosionsschutz.

3 listopada 2000 r. (Drezno) i **29 listopada 2000 r.** (Duisburg). Szkolenia i pokazy nt. "Pokrycia antykorozyjne".

Współorganizator: Bundesverband Korrosionsschutz.

8—10 listopada 2000 r. Wiedeń, Austria. 2nd International Symposium on Food — Ensuring the Safety and Quality of Food.

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