Effects of DICY Content and Metal Oxide on the Curing Behavior of a Brominated Epoxy Resin

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SYNOPSIS

The curing characteristics of a brominated epoxy resin/dicyandiamide (DICY) system in the presence of different DICY contents and metal oxides are studied using isothermal differential scanning calorimetry (DSC). From the exotherms obtained, it is found that the reaction heats increase with increasing DICY content and curing temperature because of greater amounts of DICY reacted. The amine–epoxy-related reaction dominates the major curing behavior and the T_g especially at the high curing temperature, while the etherification is more significant at low temperature and conversion and plays an important role in determining the rate of liquid-to-solid transition during the cure. The addition of metal oxides, Fe_2O_3, $Al(OH)_3$, and ZnO, results in changes in the initial transition rate, T_g, activation energy, reaction heat, reaction rate, and reaction order. Three fillers respond differently because of a difference in the surface-activated reaction. Regardless of the complex curing mechanisms involved in the specimens, a simple kinetic expression can describe the curing extent at 180°C with good accuracy. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The curing reactions of various epoxy/dicyandiamide (DICY) systems have been investigated by many investigators because of their wide applications in adhesives and molding compounds. It was reported that the equivalent weight of the epoxy resin, the accelerator, the particle size of DICY, the DICY-to-epoxy ratio, and the curing temperature all could affect the curing kinetic and mechanism of the epoxy/DICY system.[1-9] As regards the brominated epoxy resin, Opresnik et al. indicated that the temperature of the maximal reaction rate was found to decrease with increasing amounts of DICY and benzyl-N,N-dimethylamine accelerator, but increase with increasing bromine content in the resin.[10] The bromine content could also affect the heat of reaction and the activation energy of the curing system.[10]

In addition to the complex curing reaction of DICY-cured epoxy systems, interesting results were obtained when such resins were cured on metal sur-

faces. DICY could react with zinc and aluminum oxide during a high-temperature cure.[11-13] Carter et al. found that DICY was reduced when heated with metallic zinc at 170°C for a few minutes, whereas no reaction was observed when heated against steel or zinc oxide.[11,12] Brockmann et al. also indicated that DICY reacted with water to form guanylurea upon heating at 120°C on the surface of an anodic aluminum oxide.[13]

A physical attraction may also happen between the constituents in the epoxy resin and the metal substrates. Boerio and Hong found that DICY was preferentially adsorbed from the epoxy adhesive onto the silver surface to form an interface that was relatively abundant in the DICY curing agent.[14] This behavior caused the extent of the cure and the physical property in the interface to be different from those in the bulk of the adhesive. In the previous study, it was also obtained that the presence of small amounts of CuO and Cu_2O powders significantly increased the amounts of unreacted DICY left in the cured brominated epoxy resin/DICY/2-MI system because of the preferential adsorption of DICY on copper surfaces.[15] The amounts of residual DICY decreased when the 2-MI accelerator or a higher curing temperature was used. The dependence of

Table I The Compositions of Prepared Specimens

Specimen	Epoxy	DICY	2-MI	Fe$_2$O$_3$	Al(OH)$_3$	ZnO (phr)
A	100	3.0	0.05	0	0	0
B	100	4.1	0.05	0	0	0
C	100	5.0	0.05	0	0	0
D	100	6.0	0.05	0	0	0
E	100	4.1	0.05	0.1	0	0
F	100	4.1	0.05	0	0.1	0
G	100	4.1	0.05	0	0	0.1

curing mechanisms on the curing temperature were also proven.[15]

The influence of fillers on the properties of epoxy resins was reported by some investigators. It was found that the mobility and the glass transition temperature of the filled resin were changed because the presence of fillers resulted in different chain movements and residual stresses around fillers and different adsorptions of polymer molecules onto filler surfaces.[16–19] The structural change of the cured epoxy, which resulted from the change in curing characteristics, was also induced by the addition of fillers.[20,21]

In this work, the curing kinetics of a commercial brominated epoxy/DICY system (used for building FR-4 laminates) in the presence of different DICY contents and fillers were studied with differential scanning calorimetry (DSC). Interesting curing behaviors in these filled resins are demonstrated.

EXPERIMENTAL

The brominated epoxy resin (brominated diglycidyl ether of bisphenol-A with an epoxide equivalent weight = 460, bromine content = 20%, and addition of 5 wt % proprietary novolac epoxy resin) were obtained from the Shin-Ya Chemical Co., Taiwan. The curing agent DICY (> 98% pure) and the accelerator 2-MI (> 98% pure) are products of the Tokyo Kasei Kogyo Co. DICY particles have an average diameter near 120 microns. The 2-MI (0.05 phr) was used as received. Three different particulate fillers, Fe$_2$O$_3$ (99.999% pure, with a BET surface area = 24.64 m^2/g), Al(OH)$_3$ (99.0% pure, with a BET surface area = 5.80 m^2/g), and ZnO (99.999% pure, with a BET surface area = 10.11 m^2/g) were purchased from Strem Chemicals.

The brominated epoxy resin was dissolved in acetone at ambient temperature and subsequently mixed with other ingredients in a blade mixer. The compositions of specimens tested are listed in Table

I. Specimen B was formulated in the stoichiometric balance of the amine/epoxy mol ratio = 0.9. The mixed paste was air-dried overnight and then vacuum-dried at room temperature for 4 h before the DSC experiment. The homogeneity of the specimens prepared can be confirmed by the small standard deviations obtained from the DSC curing exotherms.

A DuPont-910 DSC was used to measure the curing exotherm and the glass transition temperature (T_g) of the different specimens. The isothermal curing exotherm was measured at 150, 160, 170, and 180°C under a nitrogen environment (with a nitrogen flow rate of 30 mL/min). The specimen in an unsealed Al pan was inserted into the DSC cell when the interested curing temperature was reached.[3] In general, the profiles of curing exotherms are similar to those shown previously.[15] After the isothermal measurement, the same specimen was rescanned at a scanning rate of 20°C/min from room temperature to 250°C to determine the T_g and the endotherm of the unreacted residual DICY in the cured specimen.

RESULTS AND DISCUSSION

Isothermal Curing Reactions of Specimens with Different DICY Contents

The reaction heats obtained from the exotherms are shown in Table II. For specimen A, the reaction heats are between 57.5 and 72.8 kJ/mol at various curing temperatures. The generated heat values are lower than those obtained previously because of the different brominated epoxy resin used.[15] In addition, the reaction heat increases with increasing curing temperature. This trend is consistent with the result obtained before.[15]

The heat value is closely related to the amount of DICY reacted. It is shown in Table III that the amount of unreacted residual DICY decreases with increasing curing temperature. The amount of residual DICY is an indication of the extent of the

Table II   The Curing Exotherms of Specimens Cured at Different Temperature

		Curing Temp (°C)			
		150	160	170	180
A	Heat (kJ/mol)	57.5 (1.2)	65.0 (0.1)	69.6 (0.2)	72.8 (0.3)
	tp (min)	3.6 (0.2)	2.3 (0.3)	1.3 (0.1)	0.7 (0.1)
B	Heat (kJ/mol)	64.7 (0.7)	76.2 (0.5)	81.7 (0.4)	92.9 (0.3)
	tp (min)	4.6 (0.1)	2.5 (0.1)	1.4 (0.1)	0.8 (0.1)
C	Heat (kJ/mol)	69.5 (0.1)	78.5 (0.3)	88.7 (0.7)	91.4 (0.1)
	tp (min)	4.6 (0.3)	2.5 (0.1)	1.4 (0.1)	0.8 (0.1)
D	Heat (kJ/mol)	79.9 (0.1)	87.7 (0.5)	92.9 (0.8)	96.7 (0.2)
	tp (min)	3.1 (0.1)	1.8 (0.1)	1.0 (0.1)	0.6 (0.1)
E	Heat (kJ/mol)	68.6 (0.5)	80.0 (0.5)	82.9 (0.8)	96.7 (0.2)
	tp (min)	3.5 (0.2)	1.8 (0.2)	1.1 (0.1)	0.7 (0.1)
F	Heat (kJ/mol)	67.6 (0.6)	75.8 (0.5)	80.0 (0.6)	92.6 (0.2)
	tp (min)	3.6 (0.2)	1.9 (0.1)	1.2 (0.1)	0.7 (0.1)
G	Heat (kJ/mol)	55.8 (0.1)	76.4 (0.9)	84.6 (0.3)	86.0 (0.2)
	tp (min)	3.6 (0.2)	1.3 (0.1)	0.9 (0.1)	0.6 (0.1)

Nos. in parentheses = standard deviation.

reaction between the epoxy and DICY. The more residual DICY left in the specimen resulted in less reaction heat evolved. A similar result was reported elsewhere.[15] A higher curing temperature facilitated the dissolution of DICY and, henceforth, facilitated the reaction between DICY and epoxy and speeded

Table III   The Amounts of Residual and Reacted DICY Calculated from the DICY Endotherms of Different Specimens

		Curing Temp (°C)			
		150	160	170	180
A	Residual DICY (wt %)	31 (1)	24 (3)	20 (1)	13 (2)
	Reacted DICY (phr)	2.1	2.3	2.4	2.6
B	Residual DICY (wt %)	31 (1)	28 (1)	21 (3)	13 (1)
	Reacted DICY (phr)	2.8	3.0	3.2	3.6
C	Residual DICY (wt %)	37 (1)	32 (1)	25 (1)	17 (2)
	Reacted DICY (phr)	3.2	3.4	3.8	4.2
D	Residual DICY (wt %)	41 (1)	33 (1)	26 (2)	19 (2)
	Reacted DICY (phr)	3.5	4.0	4.4	4.9
E	Residual DICY (wt %)	32 (1)	28 (1)	19 (1)	13 (1)
	Reacted DICY (phr)	2.8	3.0	3.3	3.6
F	Residual DICY (wt %)	30 (1)	25 (1)	18 (1)	13 (2)
	Reacted DICY (phr)	2.9	3.1	3.4	3.6
G	Residual DICY (wt %)	34 (1)	23 (1)	19 (1)	13 (1)
	Reacted DICY (phr)	2.7	3.2	3.3	3.6

Nos. in parentheses = standard deviation.

the reaction rate.[15] The intermediate compound formed during the reaction also helped the further dissolution and reaction of unreacted DICY.[14] As a result, a greater exotherm is obtained at a higher temperature.

The relation between DICY and reaction heat can also be confirmed by comparing results obtained from specimens with different DICY contents. Table II shows that the heat evolved during cure increases in the order of A < B < C < D regardless of the different curing temperatures tested. This trend is similar to the trend of reacted DICY contents shown in Table III, confirming that the more DICY reacted, the more heat is released. Although the etherification and the cyclization reactions during curing of epoxy/DICY systems also delivered heat, some authors indicated that the main curing exotherm came from the amine-epoxy-related reactions.[6,7]

However, different specimens could have different exotherms even with a similar amount of reacted DICY. From Tables II and III, specimen B cured at 170°C consumes 3.2 phr DICY, which is the same as that from specimen C after being cured at 150°C, yet more heat is evolved from specimen B (81.7 kJ/mol). This result may imply that different products are generated at two curing temperatures even when the same amount of DICY is reacted. A similar observation can be obtained from other specimens. It is also possible that the amounts of DICY reacted shown in Table III are greater than the actual amounts of reacted DICY since the residual DICY is calculated from the endotherms at the melting temperature of DICY, while a partially reacted DICY has no endotherm. This can also be confirmed from the fact that the amount of DICY reacted in specimen D after a 180°C cure is more than the stoichiometric amount (4.5 phr) but the released heats have only a small increase.

The change in curing mechanisms can be obtained by comparing the kinetic constant k and the reaction order n shown in Table IV. The nth order kinetic form $[d\alpha/dt = A \exp(-E/RT)(1 - \alpha)^n$, where A is the frequency factor; E, the activation energy; R, the gas constant; and α, the conversion] is used in the calculation. The kinetic constant k and the reaction order n are obtained from the slope and the intercept of the plot $\ln(dH/dt)$ vs. $\ln(H_r)$, where dH/dt is the heat-evolution rate at time t, and H_r, the total heat evolved from time t to the end of the cure.[22] The reaction order n changes between 1.0 and 1.7 and increases with increasing curing temperature. The significant difference in n indicates that the curing mechanism of the system studied is temperature-dependent. Lin et al. indi-

Table IV   The Curing Characteristics Obtained from Specimens Cured at Different Temperatures

		Curing Temp (°C)			
		150	160	170	180
A	n	1.0	1.2	1.4	1.6
	R.L. (%)	7–70	5–79	5–82	2–86
	k	0.05	0.08	0.14	0.25
B	n	1.0	1.2	1.5	1.6
	R.L. (%)	8–74	5–83	5–86	2–91
	k	0.05	0.09	0.16	0.23
C	n	1.0	1.2	1.5	1.6
	R.L. (%)	7–75	6–86	4–88	3–91
	k	0.05	0.09	0.16	0.28
D	n	1.1	1.4	1.6	1.7
	R.L. (%)	5–82	5–86	3–88	1–92
	k	0.08	0.10	0.20	0.33
E	n	1.1	1.3	1.5	1.6
	R.L. (%)	7–77	4–84	4–86	3–90
	k	0.06	0.10	0.15	0.20
F	n	1.0	1.2	1.4	1.7
	R.L. (%)	8–77	6–85	3–88	3–90
	k	0.05	0.09	0.17	0.26
G	n	1.0	1.2	1.5	1.7
	R.L. (%)	6–80	5–84	2–90	1–91
	k	0.06	0.09	0.24	0.35

R.L., range of linearity.

cated that the DICY-cured epoxy system consisted of two highly temperature-dependent reactions: the etherification and the amine–epoxy reaction.[6] The etherification is favored at a lower curing temperature. Additionally, Grenier-Loustalot et al. found that a third reaction, resulting from the formation of melamine by the rearrangement, occurred in the curing temperature range between 150 and 200°C.[8] The differences in the amount of DICY reacted and the competition between these reactions at different temperatures all can affect the curing mechanism and change the kinetic parameters obtained.

From the glass transition temperature (T_g) shown in Table V, it is clear that the T_g increases with increasing curing temperature and the loading of DICY. The trend is similar to that from the curing heats evolved. The T_g of specimen A is much smaller than that of others and this is attributed to the fact that an amount of DICY less than the stoichiometric ratio is added and reacted. On the other hand, the T_g of specimen D after 150°C cure is much greater than that of others on similar grounds. Considering

Table V   The T_g Obtained from Specimens After Being Cured at Different Temperatures

	Curing Temp (°C)			
	150	160	170	180
A	90 (4)	99 (1)	107 (1)	107 (1)
B	103 (4)	117 (3)	132 (2)	136 (1)
C	109 (8)	128 (1)	130 (1)	132 (1)
D	127 (9)	133 (1)	134 (1)	133 (1)
E	99 (1)	113 (5)	130 (2)	130 (1)
F	99 (1)	108 (1)	130 (2)	132 (3)
G	101 (1)	106 (1)	135 (1)	131 (1)

Nos. in parentheses = standard deviation.

these facts and the significant differences in the amounts of unreacted DICY at different curing temperatures among specimens, it is believed that the T_g is dependent mainly on the amine–epoxy-related reactions. Although the etherification, which is favored at the low curing temperature and DICY content, could enhance the crosslinking of some epoxy resins and increase the T_g of some epoxy resins, its effect on T_g is not great in the epoxy system studied and this result also implies that the type of epoxy resin is important in determining the effect of etherification.[6,15–18]

Regarding the influence of the DICY loading, the values of k and n between specimens A, B, C, and D are basically changed with respect to the curing temperature. The difference in k between specimens is more significant at the high curing temperature. As mentioned before, various competing reactions are present during the cure. These reactions are not only temperature-dependent but also DICY/epoxy-ratio-dependent.[6,7] The difference in initial DICY/epoxy ratios could affect the reaction rates of different competing routes by altering the collision and reaction rates between reactive functional groups.

At 150°C, n and k from specimens A, B, and C have no difference, since the reaction order and the kinetic constant are obtained from the linear region of the plot $\ln(dH/dt)$ vs. $\ln(H_r)$.[15,22] This indicates that a similar curing mechanism dominates over a conversion range of about 63–68% for specimens A, B, and C. The range of linearity increases as the DICY content increases (the correlation coefficient of the linear regression is better than 0.992 in all cases). Regardless of the great differences in the original DICY contents, amounts of DICY reacted, and complex reactions involved, this implies that specimens A, B, and C have similar mechanisms which dominate the cure to near 70% conversions

at 150°C. The changes in n and k appear only in the specimen with the greatest DICY content, i.e., specimen D.

Similar trends in n and k between specimens are obtained at other high curing temperatures. However, the dominated linear conversion range increases from about 65% at 150°C to near 90% at 180°C cure (see the representative diagram shown in Fig. 1). The specimen with a greater DICY content also has a greater range of linearity. Combined with the fact that the amount of reacted DICY increases simultaneously, it is believed that the curing mechanism based on the amine–epoxy reaction dominates at the higher curing temperature and the higher DICY content. The amine–epoxy reaction dominates at the higher curing temperature and the higher DICY content. The amine–epoxy reaction may have a higher order than that of other competitive reactions. In the system studied, a simple kinetic expression gives a good estimation of isothermal curing kinetics at 180°C.

However, the rate constant increases with increasing DICY content at higher temperatures, indicating a change in the activation energy among specimens. From k obtained at different temperatures, the activation energy E is calculated. As shown in Table VI, the activation energies of specimens decrease in the order of C > A > B > D, indicating that the curing mechanisms are sensitive to the initial DICY loadings. This result is consistent with the result obtained previously.[15] The amount of DICY could affect the relative rates of various tem-
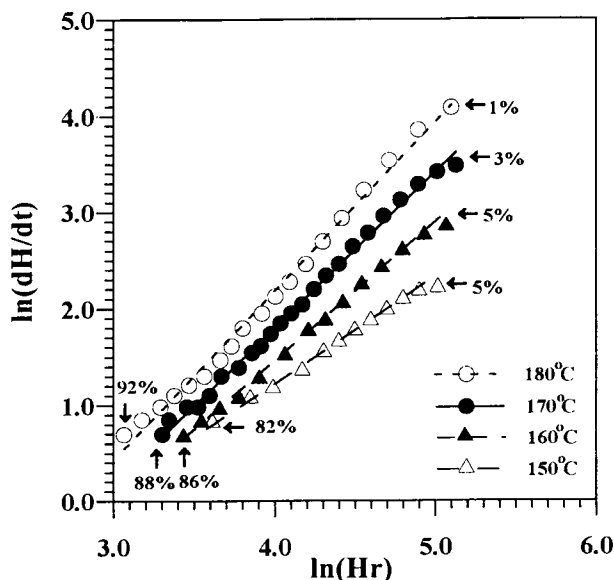

Figure 1 The representative diagram of isothermal curing exotherms calculated from specimen D.

Table VI The Curing Activation Energies of Different Specimens

Specimen	E (kJ/mol)
A	86.1
B	82.5
C	91.8
D	78.9
E	64.4
F	89.3
G	100.3

perature-dependent curing reactions and result in the change of the overall activation energy observed. Interestingly, specimens B and D have lower activation energies than those of specimens A and C, implying that the rates of various curing routes could change differently by varying the amount of DICY used.

The influence of the DICY content can also be obtained from the t_p—the time to reach the maximal curing rate. In general, t_p has been referred to as a gel point by some authors.[2,23] As shown, the values of t_p decrease in the order of B = C > A > D, indicating that the accelerated initial curing rates are different among specimens. The t_p exhibits a maximum at DICY contents near 4.1 and 5 phr (around the stoichiometric amount: 4.5 phr). Table VII also lists the average conversions at t_p for various specimens. It is interesting to note that for specimen A, which has the smallest DICY loading, the conversion at t_p is even less than those from specimens B and C (see Table VII). Considering this fact and that different amounts of DICY are reacted at t_p, the results confirm that the generated chains other than products from the simple amine–epoxy reaction (such as the product from the etherification) may play a significant role in determining this liquid-to-solid transition (when t_p is closely related to a gel point). Any factor which may affect the etherification, the rearrangement, and the amine–epoxy reactions during the cure will also affect the characteristics of t_p in various manners. As a result, various specimens have different values of t_p and different conversions at this point. In addition, t_p decreases when the curing temperature increases because of the better dissolution of the DICY and the faster reaction between amino and epoxide groups at the high temperature.

From the T_g, the range of linearity, the t_p, and the conversion at t_p obtained from specimens A, B, C, and D, it is concluded that the etherification (or any reaction other than the amine–epoxy reaction)

may play a significant role at low conversions in affecting the liquid-to-solid transformation, but not dominate the major extent of the reaction, and contribute little to increase the T_g of the specimen. This conclusion can be further confirmed by the results obtained as follows.

The Effects of Metal Oxides on the Curing Reaction

Different curing characteristics are obtained when metal oxides are added. It is shown in Table II that the reaction heats generated from specimen E are all greater than those of specimen B regardless of the different curing temperatures used. However, the amount of DICY reacted has few differences from that from specimen B. As a result, the addition of Fe_2O_3 to the epoxy/DICY system could result in a change in the curing behavior. The effect of Fe_2O_3 can be better observed by comparing other kinetic parameters.

The kinetic constants n and k obtained from isothermal exotherms of specimen E are shown in Table IV. It is interesting to notice that n and k of specimen E are greater than those of specimen B at 150 and 160°C. While at higher curing temperatures of 170 and 180°C, specimen E has a smaller k and a similar n than does specimen B. This implies that the addition of Fe_2O_3 can affect the curing kinetics of the epoxy/DICY system since the changes in n and k are indications of the difference in competition between various curing mechanisms, as explained previously.

Although no reaction between DICY and Fe_2O_3 was found, the catalytic nature of iron oxides on the epoxy resin was reported by some investigators. Inoue et al. indicated that the terminal epoxide groups in the epoxy resin could react with the surface hydroxyl groups of γ-Fe_2O_3 particles and result in a

Table VII The Conversions at t_p Obtained from Specimens Cured at Different Temperatures

	Curing Temp (°C)			
	150	160	170	180
A	14%	11%	10%	7%
B	15%	13%	13%	7%
C	15%	15%	11%	9%
D	11%	13%	11%	14%
E	15%	10%	11%	9%
F	14%	11%	12%	8%
G	16%	11%	10%	12%

chemisorption of the epoxy resin onto the γ-Fe_2O_3 surface.[24] A similar reaction which was reported as a steel surface-catalyzed homopolymerization of the epoxy resin was also shown by Nigro and Ishida.[25] In this study, the change in reaction heats, n, and k values at lower curing temperatures may result from a similar iron oxide-related etherification. The effect is more significant at 150 and 160°C because the etherification is favored at low temperatures in the epoxy/DICY system. Compared to those of the specimen B, a greater k obtained at the low curing temperature, but a smaller k at the high temperature in specimen E also results in a low activation energy, 64.4 kJ/mol, for the Fe_2O_3-added specimen (see Table VI).

From Tables II and VII, it is also shown that t_p of specimen E is much smaller than that of specimen B and this difference decreases with increasing curing temperature, yet the conversion at t_p varies with the temperature. This result is consistent with the fact that t_p is an indication of the transition from liquid to solid. The added filler increases the viscosity and limits the resin flow and, henceforth, causes t_p to decrease. However, the surface-related reaction also plays an important role in determining t_p. From the ratio of (conversion at t_p)/t_p, it is clear that ratios from specimen E are all greater than those of specimen B regardless of the different curing temperatures used, indicating that the average rate of conversion during the transition period is higher in the Fe_2O_3-added specimen. This is attributed to the probable iron oxide-catalyzed etherification. Such a result is consistent with the comparison obtained from specimens A and B at 150°C.

Furthermore, although the amount of reacted DICY in specimen E is similar to that in specimen B (yet with greater reaction heats), the lower T_g of the iron oxide-added specimen E implies that the probable surface-catalyzed etherification or surface-affected curing reaction may alter the final crosslinking density of the specimen (see Tables III and V).

The surface-related reaction is also obtained in the $Al(OH)_3$-added specimen. From the reaction heat shown in Table II, it can be seen that specimen F has more generated heats than has specimen B at 150°C, but vice versa at other higher curing temperatures. Zukas et al. reported a similar result in studying the effect of aluminum oxide surfaces on the curing of the epoxy/diaminodiphenyl sulfone system.[26] Interestingly, amounts of reacted DICY from specimen F are all greater than those of specimen B except at 180°C (see Table III). This result may confirm that the residual DICY calculated from

the endotherm at the melting temperature of DICY is less than the actual amount of reacted DICY containing unreacted N—H groups.

From Tables II and VII, it is clear that t_p decreases as $Al(OH)_3$ is added to the resin. The average conversion rates (from 0 to t_p min) of specimen F are also all higher than those of specimen B. This result is similar to that found in specimen E. A much faster initial curing rate was also observed for an activated alumina-filled epoxy system, which was attributed to the accelerated homopolymerization of the epoxy resin on the surface of alumina.[26]

However, Fondeur and Koenig credited this change to different amounts of epoxy and the DICY curing agent and a formation of DICY salt near the aluminum surface.[27] Nonetheless, the result obtained here seems to support a homopolymerization happening on the $Al(OH)_3$ surface because specimen F has a higher reaction heat but with a similar amount of reacted DICY and a lower T_g than those of specimen B after 150°C cure (see Tables II, III, and V). A lower T_g of the alumina-filled specimen was also reported by Zukas et al.[2] and Petrovic and Stojakovic[28] who believed the surface of Al_2O_3 affected the curing reaction and resulted in structures with fewer crosslinks.

A change in curing kinetics in the $Al(OH)_3$-added specimen is further confirmed by an increase in the activation energy (see Table VI). Such an increase results mainly from increase in the rate constants for specimen F at 170 and 180°C (see Table IV). Alumina trihydrate is usually used as a flame retardant which can decompose to form aluminum oxide and water near 200°C. The observed change in k may result from both the possible decomposition of $Al(OH)_3$ and the temperature-dependent curing mechanism under the influence of fillers (see Table IV). A similar conclusion was drawn by Zukas et al. In addition, the change in reaction order n is also obtained at 170 and 180°C.

The influence of the metal oxide on the curing reaction is also confirmed by the result obtained from specimen G which contains zinc oxide powders. The difference in reaction heats between specimens B and G changes with respect to the curing temperature (see Table II). At 150°C, specimen G has the lowest heat value but the greatest residual DICY among specimens B, E, F, and G. This result also indicates that the main curing exotherm is from the epoxy–DICY-related reaction. However, such a low value should be closely related to the effect of ZnO since even specimen A has greater heats yet a smaller reacted DICY content than does specimen G. As the curing temperature increases, the reaction heat of

specimen G increases and is similar to that of specimen B at 160°C and then becomes greater than that of specimen B at 170°C. Finally, at 180°C, the reaction heat of specimen G is the smallest again. Despite experimental errors shown in Table II, the difference detected has a high confidence level. The role of ZnO in affecting the cure of such an epoxy system is complex and temperature-dependent.

The reaction between zinc and DICY was reported by some authors. Carter et al. indicated that a complex was formed between DICY and the zinc surface through a surface-activated redox reaction.[11,12] However, they found no reaction between ZnO and DICY. Sanchez et al. detected a lower exotherm in the epoxy resin with an addition of zinc powders by using DSC.[29] To our knowledge, no reaction between ZnO and epoxy/DICY has been reported elsewhere.

The influence of ZnO becomes clear by comparing the results shown in Table IV. The kinetic constant k of specimen G is greater than that of specimen B, especially at high curing temperatures such as 170 and 180°C. The activation energy obtained from specimen G is also the greatest among specimens studied because of the greatest change in k during the temperature range tested (see Table VI). This may also imply that the effect of ZnO on the curing reaction is probably the greatest among three fillers.

The accelerated curing rate is also confirmed by the t_p and average conversion rate obtained. As shown in Table II, specimen G has the smallest t_p at 160, 170, and 180°C. When the conversions shown in Table VII are considered, the average conversion rates of specimen G are the greatest among specimens tested regardless of the curing temperature used. It is believed that ZnO can generate the reaction that speeds the rate of the liquid-to-solid transition and also the overall curing rate. The study of this surface-related behavior is in progress.

Although the nature of this ZnO-activated reaction is unknown at this stage, the variation in T_g indicates that a different structure is produced in the cured specimen G. From the T_g obtained after the 150°C cure, specimen G has a similar T_g as those of specimens E and F, yet with a much lower reaction heat and the greater residual DICY (see Tables III and V). A possible explanation is that a considerable extent of the ZnO-activated reaction, with a lower exotherm than that of the epoxy–DICY reaction, happens and results in a change in structure that could affect the T_g. However, from the T_g, the reaction heat, and the amount of reacted DICY at 160°C cure, it seems that this reaction is temperature-dependent and responds differently

when a high curing temperature is used. This conclusion can be confirmed by comparing the curing characteristics obtained from specimens B and G (see Tables II–V).

It is interesting to indicate that the linear ranges, from which n and k are calculated, obtained from specimens E, F, and G are similar to those of specimen B and also increase with the curing temperature (see Table IV). This indicates that regardless of the complex curing mechanisms involved in the filler-added specimens a simple kinetic equation can describe the curing rate at 180°C with good accuracy. This can be confirmed by a representative conversion profile obtained from specimen F shown in Figure 2. The deviation between calculated and experimental results begins about 90% conversion, which is consistent with the linear range obtained shown in Table IV.

CONCLUSIONS

The effects of DICY contents and metal oxides on the curing of a brominated epoxy resin system were studied using the isotherm DSC technique. The difference in DICY contents results in changes in curing characteristics because of a change in relative reaction rates of various temperature-dependent curing mechanisms. The etherification may play a significant role in determining the rate of liquid-to-solid transition.
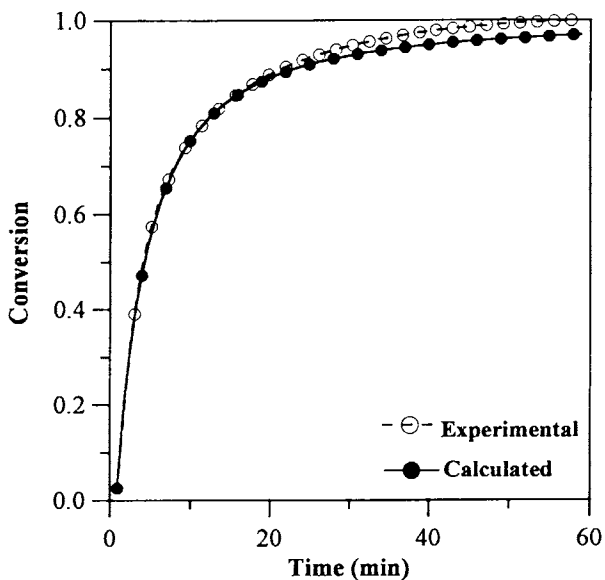

Figure 2 The representative experimental and calculated conversion profiles from specimen F at 180°C cure.

The presence of metal oxides also affects the curing behavior of the system studied. In general, the addition of metal oxides causes a decrease in T_g especially at the low curing temperature due to the surface-activated reaction which is also responsible for differences observed in reaction rates, reaction orders, activation energies, and reaction exotherms. The initial curing rates from filler-added specimens are all greater than that of the unfilled specimen. In addition, a simple kinetic equation can describe the curing extent at 180°C with a good accuracy for all specimens regardless of different complex curing mechanisms involved.

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