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The effect of copper oxides on the curing of brominated epoxy resins

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Abstract

The kinetics of the curing of the brominated epoxy resin/dicyandiamide (DICY) system in the presence of copper oxides was investigated by isothermal differential scanning calorimetry (DSC). In essence, the heat of curing of brominated epoxy resins increases with increasing temperature as a result of the decrease in unreacted residual DICY at high temperature. The addition of small amounts of CuO and Cu_2O to the resins results in an increase in unreacted DICY left in the cured resins. Preferential adsorption of DICY on copper oxides is responsible for this difference. However, the amounts of unreacted DICY can be decreased by adding 2-methylimidazole (2-MI) to the resins. From large differences in enthalpy values and reaction orders but relatively unchanged T_g values among various specimens obtained during curing of brominated epoxy/DICY/2-MI, it can be established that the system during curing could involve complex competing reaction mechanisms which cannot be described with a simple mathematical expression.

INTRODUCTION

The brominated epoxy/dicyandiamide system is widely used for constructing multilayer printed circuit boards (PCB) because of its good thermal stability and flame resistance. Although epoxy resins are generally believed to form strong bonds with many metal surfaces, a partial delamination known as the "pink ring" is frequently observed around drilled holes in PCB. The formation of such a defect is thought to be due to the removal of the bonding copper oxide layer by corrosive (acidic, reductive) hole-cleaning chemicals used in PCB manufacturing practice, and to the related decay in bond strength with time at elevated temperatures.

Regardless of various manufacturing parameters associated with the formation of a "pink ring", the structure and composition of the Cu/epoxy pre-preg interphase play important roles in determining the strength and durability of the adhesive bond and the generation of the undesired pink

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ring. Altering the chemical and physical aspects of the interphase during cure leads to changes in the mechanical strength, corrosion resistance, durability of the bonding system, and the formation of a "pink ring".

The curing of epoxy/DICY systems has been studied by many investigators [1–6]. Sacher found that the particle size of DICY could affect the curing kinetics of a diglycidyl ether of bisphenol-A (DGEBA) epoxy resin (such as Der332), in such a way that the pre-exponential was reduced by $10^6 \mathrm{s}^{-1}$ and the activation energy reduced by half as the particle size of DICY changed from fine ($<125\,\mu$m) to coarse ($250-500\,\mu$m) [1]. The formation of melamine resulting from the decomposition of DICY during cure was confirmed by IR analysis. The melamine was present as in insoluble precipitate in the Der332 [1]. Muroi et al. also showed that the curing rate of a DICY-cured epoxy system varied inversely with the logarithm of the DICY particle sizes and directly with the total surface area of the DICY particles [2]. The final conversion of the epoxide group decreased with increasing particle size of DICY [2].

Regarding the effects of accelerators, the addition of small amounts of 2-MI accelerator did not significantly decrease the activation energy of the unaccelerated system [3]. As a result, Miller and Oebser concluded that imidazoles function as an additional co-reactant because they did not catalyze the reaction of DICY with the epoxy group. From the curing data of the systems tested it was also demonstrated that the cure time depended more on the equivalent weight of the epoxy resin, and/or the DICY/epoxy ratio than on the level of 2-MI [3]. The synergistic effect between DICY and accelerator in the curing of epoxy resin was obtained from the exotherm profiles [4]. Son and Weber found that the addition of 3-(*p*-chlorophenyl-1,1-dimethylurea) accelerator could cure an epoxy/DICY system faster at 120°C than in the case without an accelerator [4].

In a diuron-accelerated DICY/epoxy system, Barton and Greenfield found that diuron had a significant effect in reducing the activation energy and the overall heat of cure [5]. They indicated that the presence of diuron resulted in a change in reaction mechanism. Lin et al. also showed that the curing mechanism of a benzyldimethylamine-catalyzed DICY–DGEBA system varied with temperature, especially at the beginning of the reaction [6]. The curing mechanism of such an epoxy system had a strong dependence on accelerator and reaction temperature, and the reaction rate did not follow the Arrhenius law. A change in reaction mechanism with curing temperature over the range 100–160°C was reported.

The curing of brominated epoxy resins was also studied by Opresnik et al. [7]. The temperatures of the maximal reaction rate were found to decrease with increasing amounts of DICY curing agent and benzyl-*N*,*N*-dimethylamine accelerator, but increase with increasing bromine contents in the resin. The bromine content could also affect the heat of reaction and the activation energy of the curing system [7].

In spite of the complex curing reactions of DICY-cured epoxy systems, interesting phenomena were observed when such resins were cured on metal substrates. Cater et al. reported that DICY was reduced when heated against metallic zinc at 170°C for several minutes [8, 9]. No reaction was observed when DICY was heated against steel or zinc oxide. Brockmann et al. also showed that DICY could react with water to form guanylurea upon heating at 120°C on the surface of anodic aluminum oxides [10]. In addition to chemical reactions, Boerio and Hong found that DICY was preferentially adsorbed from the epoxy adhesive on the silver surface to form an interface that was relatively abundant in DICY curing agent [11]. Such a behavior caused the extent of cure and the physical properties on the interface to be different from those in the bulk of the adhesive.

In order to achieve a better understanding of the industrial adhesion problem, such as the pink ring, curing of the brominated epoxy/DICY/2-MI system in the presence of copper oxides was studied using isothermal DSC to evaluate the effects of copper oxides on the epoxy cure.

EXPERIMENTAL

The brominated epoxy resin (brominated diglycidyl ether of bisphenol-A with an epoxide equivalent weight of 490 and a bromine content of 20%) was obtained from the Asia Chemical Co. DICY (>98% pure) and 2-MI (>98% pure) were products from Tokyo Kasei Kogyo Co., Ltd. The curing agent, DICY (3.8 parts per hundred, phr), was ground to less than 120 μm particle size before use. The 2-MI (0.05 phr) was used as received. The Cu_2O (99.9% pure) and CuO (99.999% pure) fillers were obtained from Strem Chemicals, Inc.

The brominated epoxy resin was dissolved in acetone at ambient temperature and subsequently mixed with the other ingredients in a blade mixer. The mixed paste was air-dried overnight and then vacuum-dried at room temperature for four hours before the DSC experiments. The compositions of the specimens tested are listed in Table 1.

A Du Pont-910 DSC was used to measure the curing exotherms and the glass transition temperatures T_g of different specimens. The curing exotherms were measured isothermally at four different curing temperatures, 150, 160, 170, and 180°C. The specimen, placed in an unsealed Al pan, was inserted into the DSC cell when the curing temperature of interest was reached [3]. After the isothermal measurement, the same specimen was rescanned at a scanning rate of 20°C min^{-1} from room temperature to 250°C to determine the T_g and the endotherm of the unreacted residual DICY in the specimen. All DSC measurements were performed under nitrogen atmosphere.

TABLE 1

The compositions of the prepared specimens

Specimen	Epoxy	DICY	2-MI	CuO/phr	Cu_2O/phr
A	100	3.8	0.05	0	0
B	100	3.8	0.05	0.1	0
C	100	3.8	0.05	0	0.1
D	100	3.8	0	0	0
E	100	3.8	0	0.1	0
F	100	3.8	0	0	0.1
G	100	0	0	0	0
H	100	0	0.05	0	0
I	100	0	0	0.1	0
J	100	0	0	0	0.1

RESULTS AND DISCUSSION

Isothermal curing reactions

The reaction heats calculated per mole of epoxide groups from the exotherms are shown in Table 2. In the case of specimen A, the reaction heats are between 84 and 112 kJ mol^{-1} at various curing temperatures. Opresnik et al. reported a value of 77 kJ mol^{-1} for a similar brominated epoxy system cured with 4 phr DICY and 0.25 phr benzyl-*N*,*N*-dimethylamine using a 5°C min^{-1} dynamic scan [7]. As seen from Table 2, the reaction heats increase with increasing temperature of curing. It was reported by Fava that the magnitudes of the reaction heats of an epoxy resin depend on the curing temperatures and scanning rates used in the DSC measurements [12]. However, the explanations proposed by Fava do not explain the great difference observed here.

TABLE 2

The curing heats of specimens cured at different temperatures

Curing temp. in °C	A		B		C	
	Heat in kJ mol^{-1}	t_p in min	Heat in kJ mol^{-1}	t_p in min	Heat in kJ mol^{-1}	t_p in min
150	84.6	2.5	72.2	2.9	77	2.6
160	91.0	1.6	83.9	1.5	82.6	1.3
170	94.3	1.0	93.4	0.8	90.5	0.7
180	111.6	0.6	102.8	0.6	106.0	0.5

TABLE 3

The amounts of residual DICY found in specimens after curing at different temperatures

Curing temp. in °C	Residual DICY in wt%		
	A	B	C
150	35.1	47.8	54.7
160	24.7	30.1	34.8
170	13.5	16.7	22.9
180	6.8	8.9	11.5

The difference in reaction heats obtained could be related to various amounts of unreacted DICY in the cured specimens. It is shown in Table 3 that the amounts of unreacted residual DICY decrease with increasing the temperature used in curing. The more residual DICY in the specimen, the less conversion occurred between DICY and epoxy resins, with less reaction heat evolved. (Other curing reactions predominated, see below.) The presence of unreacted DICY was also reported by other investigators. Shah et al. detected unreacted DICY in the cured and post-cured laminates using infrared spectroscopy and high-performance liquid chromatography [13]. Sacher also reported that in the coarse DICY system, incomplete reaction of coarse particles led to residual unmelted DICY after curing [1].

It was believed that a higher curing temperature facilitated the reaction between DICY and epoxy, and speeded up the reaction rate. Accordingly, the time to reach the maximal exotherm t_p was shortened as the curing temperature increased (see Table 2). Hagnauer and Dunn found that the intermediate compound formed in the reaction mixture could help the dissolution of unreacted DICY [14]. As a result, the formation of soluble intermediate can serve a dual function, favoring better dissolution of unreacted DICY and increasing the reaction rate through a mutual promoting effect.

From the isothermal exotherms, the reaction order n and the kinetic constant k can be obtained from the slope and the intercept of the plot of $\ln(\mathrm{d}H/\mathrm{d}t)$ versus $\ln(H_r)$, where $\mathrm{d}H/\mathrm{d}t$ is the heat evolution rate at time t and H_r is the total heat evolved from time t to the end of cure [15]. The calculated n and k values are listed in Table 4. As shown, the reaction orders of specimen A are in the range 1.14–1.67, and the kinetic constants are between 0.06 and 0.30 min^{-1}. Both values increase with increasing isothermal curing temperatures. The significant changes in reaction orders indicate that the curing mechanisms of the specimen are temperature dependent. Lin et al. indicated that DICY-cured epoxy has a complex curing mechanism which consists of two highly temperature-dependent reactions, the etherification and the reaction between DICY and epoxy [6].

TABLE 4

The curing kinetic parameters obtained from specimens cured at different temperatures

Curing temp. in °C	A			B			C		
	n	k in min^{-1}	R.L.[a] in %	n	k in min^{-1}	R.L.[a] in %	n	k in min^{-1}	R.L.[a] in %
150	1.14	0.06	12–89	1.13	0.06	12–90	1.16	0.06	12–86
160	1.40	0.11	6–84	1.33	0.11	7–76	1.46	0.10	6–84
170	1.55	0.19	10–82	1.54	0.19	6–78	1.55	0.16	7–90
180	1.67	0.30	6–73	1.73	0.28	6–79	1.68	0.26	7–84

[a] Range of linearity (fraction reacted).

In this case, not only the amounts of residual DICY but also the competition between the etherification and the DICY–epoxide reaction at different temperatures can affect the curing mechanisms. Moreover, the difference in n and k also indicates that a simple kinetic form, from which the kinetic parameters are derived, may be inadequate to describe the curing reaction of such a complex system.

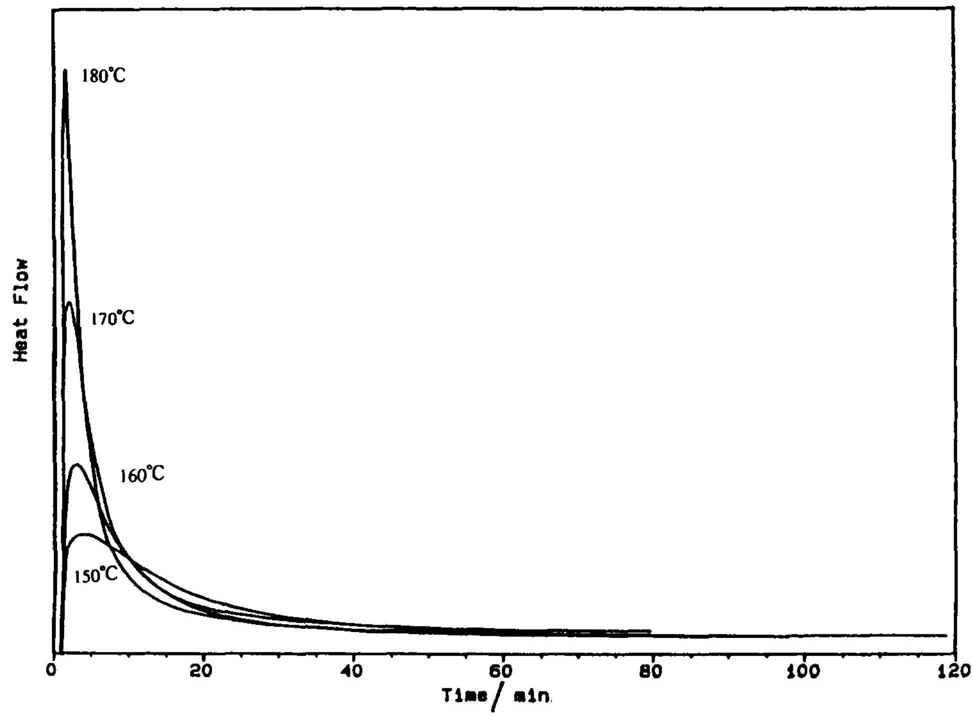

Fig. 1. Representative plot of isothermal DSC data from specimen A.

TABLE 5

The curing characteristics obtained from specimens cured at 180°C

	Heat in kJ mol^{-1} [a]	t_p in min	DICY residue in wt%	T_g in °C
D	109.3	8.3	16.5	120.3
E	117.6	8.6	25.7	121.7
F	114.0	11.7	34.7	120.4
G	7.8	5.1		
H	12.3	1.3		
I	26.5	1.5		
J	9.7	3.5		

[a] 180°C cured.

It is also shown in Table 4 that reaction orders and kinetic constants are obtained from the linear regions of the curves plotted in Fig. 1. The curvatures shown in Fig. 1 indicate that the curing of specimen A is accelerated at the beginning of cure. A higher curing temperature results in a faster initial curing rate. In the absence of 2-MI, no significant curing reaction can be observed at 150°C. The synergistic effect of DICY and 2-MI on the curing rate can be obtained by comparing the t_p values of specimens A, D, and H (180°C cured).

The addition of 2-MI not only accelerates the curing reaction but also decreases the amount of residual DICY in the epoxy resin. The curing exotherm of specimen D, which consisted of only brominated epoxy resins and DICY, was obtained for comparison. Table 5 shows that the reaction heat for specimen D cured at 180°C is 109.3 kJ mol^{-1} which is only slightly different from that obtained from specimen A (111.6 kJ mol^{-1}). However, t_p and the amount of residual DICY increase (from 6.8% to 16.5%) in the absence of 2-MI (see Tables 2 and 5). It is believed that the presence of 2-MI increases the reaction rate of DICY with the epoxy which may lead to better dissolution of DICY during cure. Hagnauer and Dunn also indicated that the addition of Monuron could enhance the solubility of DICY in phenylglycidylether (PGE) and thus might further accelerate the curing reaction [14]. In addition, specimens A and D were found to have different amounts of unreacted DICY but similar values of reaction heats, which indicates that different curing reactions are taking place in these two specimens.

It is well known that the glass transition temperature T_g of a thermosetting resin is related to the crosslinking density after cure. From a comparison of the T_g values listed in Table 6, it is clear that the T_g values of specimen A remain unchanged regardless of the different curing temperatures used. Considering the significant difference in the amounts of unreacted DICY at different curing temperatures, it is believed that etherification

TABLE 6

The T_g obtained from specimens after curing at different temperatures

Curing temp. in °C	T_g in °C		
	A	B	C
150	120.2	120.7	119.9
160	120.3	119.7	120.4
170	120.5	120.4	122.6
180	120.3	121.2	121.2

and various DICY/epoxy reaction paths also contribute to the crosslinking of the epoxy resin. Schneider et al. have suggested that the formation polyether results from a reaction between epoxide and hydroxyl groups; this also takes part in the crosslinking process because of insufficient DICY present to lead to complete reaction of epoxide groups [16]. Similar conclusions have also been drawn by other investigators [17, 18]. However, 2-MI may also react with the epoxy resins and act as a co-curing agent. Farkas and Strohm found that 2-ethyl-4-methylimidazole (EMI) could react with phenyl glycidyl ether and permanently attach to the polymer chain [19].

It is also apparent that the brominated epoxy/DICY (no 2-MI) system has similar T_g values, irrespective of the significant amounts of unreacted DICY curing agent left in the resins (see Tables 5 and 6). It can be concluded that complex competing reactions other than the simple DICY/epoxy reaction must play significant parts in the curing process of the system.

The effects of copper oxides on the curing reaction

Different reaction heats were also obtained from specimen B. It is shown in Table 2 that the exotherms of specimen B are similar to those of specimen A, increasing in parallel with increasing isothermal curing temperatures. As explained previously, a higher curing temperature facilitates the reaction and the dissolution of DICY, and leads to higher exotherms. No great difference in t_p values between specimens A and B is observed. However, the values of the exotherms of specimen B are smaller than those of specimen A at lower curing temperatures.

The difference in exothermic values can also be explained from the different amounts of unreacted DICY left in two specimens after cure. It is shown in Table 3 that the amounts of unreacted residual DICY in specimen B vary from 47.8 to 8.9 wt% when isothermal curing temperatures change from 150 to 180°C. More unreacted DICY was left in specimen B than in specimen A when cured at the same temperature. As shown previously, the more residual DICY in the specmen, the less the extent of reaction, evolving less reaction heat.

The variation in the amounts of residual DICY between specimens A and B is attributed to the preferential adsorption of DICY molecules on the CuO particle surfaces. The abundance of amino groups near the copper surface has been confirmed by X-ray photoelectron spectroscopy analysis [20]. Racich and Koutsky observed that amine curing agents were preferentially adsorbed on a copper substrate in contact with mixed epoxy [21].

The reaction orders and kinetic constants obtained from the isothermal exotherms of specimen B are shown in Table 4. It is interesting to note that the values of n and k from specimens A and B are very similar. Moreover, the T_g values obtained from specimen B also remain unchanged. Considering the great difference in the amounts of unreacted DICY left in the specimens, the results are surprising. As stated previously, some possible reactions can explain the phenomena observed. Firstly, the etherification may contribute significantly to the crosslinking at lower curing temperatures. Secondly, different extents and mechanisms of the DICY/epoxy reactions occur at different curing temperatures. Lin et al. pointed out that the curing temperature could affect the competition between various reaction paths in the curing process, leading to variations in the network formation and in the properties of the cured products [6]. In addition, the 2-MI functions as a co-crosslinking agent and affects the curing reactions differently at different curing temperatures. Finally, the CuO fillers can also increase the T_g of the resin and initiate the curing reaction (see Table 5, specimens G and I). Although the effects of 2-MI and CuO can explain some of the phenomena observed, their contributions are rather small.

The reaction of CuO with epoxy resins was confirmed by isothermal DSC measurement. The reaction heat of blank epoxy resin with 0.1 wt% CuO (specimen I), reacted isothermally at 180°C, is 26.5 kJ mol^{-1} which is greater than that obtained from blank epoxy resin (16.1 kJ mol^{-1}, see Table 5, specimen G). The t_p also decreases when CuO is added. These results indicate that CuO can behave as an initiator to affect the curing reaction. Regarding the effect of metal surface on the epoxy curing reaction, Zukas et al. also indicated that activated alumina surfaces catalyzed epoxy/amine reactions and shifted the DSC exotherm peak to a lower temperature [22].

In the absence of 2-MI, the amounts of unreacted residual DICY in the resin also increased (specimen E). From a comparison of specimens E and B (Tables 5 and 3), the residual DICY increases from 8.9 to 25.7 wt% after isothermal curing at 180°C without the addition of 2-MI. This result is consistent with that from specimens A and D and shows the effect of 2-MI in reducing the amount of residual DICY.

The preferential adsorption of DICY on CuO can also be observed from the results of specimens D and E (in Table 5). The unreacted DICY in the cured resins increases from 16.5 to 25.7 wt% in the presence of 0.1 wt% CuO

TABLE 7

The curing activation energies and frequency factors of different specimens

	E in kJ mol^{-1}	ln(A/s^{-1})
A	83.0	16.7
B	80.0	15.9
C	76.5	14.9

but the T_g values of these two specimens show no difference. Such results are consistent with those obtained previously.

The effects of Cu_2O on the curing behavior of the epoxy system studied are similar to those of CuO, increasing the amounts of unreacted DICY but with little change in T_g, n, and k. However, the amount of residual DICY in specimen C was highest among the specimens A, B, and C. Thus, Cu_2O can also preferentially adsorb DICY curing agents. Considering the differences in surface areas and particle sizes between CuO (0.6 m^2 g^{-1}, 60 μm, porous) and Cu_2O (1.9 m^2 g^{-1}, 15 μm, solid), further work is in progress to differentiate the effects of CuO and Cu_2O.

The presence of high concentrations of DICY in the cured resins could lead to a deterioration in the properites of the resins. The undissolved DICY particles could act as stress concentration sites in the resin matrix and, being hydrophilic, become spots for water absorption [23]. When the resin absorbs water the glass transition temperature is lowered [13].

In addition, when preferential adsorption occurs on the copper surface, the durability of the bonding system decreases because of the hydrophilic nature of the amino groups. The physical properties of the epoxy resin near the interphase could also be changed because of the stoichiometric imbalance of the functional groups resulting from the preferential adsorption [24, 25].

The reaction of epoxide groups is also affected by Cu_2O (Table 5, specimens J and G), but the effect is not as significant as that observed from CuO (specimens I and G). Nevertheless, the curing rate and the curing mechanism are affected when large amounts of DICY are adsorbed on the Cu_2O. It is shown in Table 5 that specimen F has more residual DICY but cures more slowly than specimen D. As expected, the T_g of specimen F remains unchanged.

The activation energies and frequency factors calculated from specimens A, B, and C show little difference regardless of the considerable differences between these specimens (see Table 7). This result indicates that complex reaction mechanisms other than the simple dissolution of DICY (the initial reaction of DICY and epoxy) dominate over a considerable range during the curing process.

Relatively similar t_p values obtained from specimens A, B, and C may imply that the influences of CuO and Cu_2O on 2-MI are insignificant.

CONCLUSIONS

The effects of copper oxides on the curing of a brominated epoxy resin/DICY/2-MI system were studied using isothermal DSC. The presence of small amounts of CuO and Cu_2O powders significantly increased the amounts of unreacted DICY left in the cured resins due to the preferential adsorption of DICY on the copper surfaces. However, the amounts of residual DICY decreased with the addition of 2-MI to the resin, accompanied by an increase in the isothermal curing temperature.

In addition, the exotherms during cure increased with increasing curing temperature due to the better dissolution of DICY at higher temperatures and also to the influence of the temperature on the curing mechanisms. The large differences in reaction heats and reaction orders but the relatively unchanged T_g between specimens indicate that the curing of the brominated epoxy/DICY/2-MI proceeds through complex competing reaction paths which cannot be described with a simple mathematical expression. Further work is in progress to clarify the curing mechanism of this system.

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