

## **DSC AND FTIR ANALYSES OF THE CURING BEHAVIOR OF EPOXY/DICY/SOLVENT SYSTEMS ON HERMETIC SPECIMENS**

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### **Abstract**

The curing characteristics of a dicyandiamide-cured epoxy system under the influence of solvents in a closed environment were studied by means of isothermal differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). The DSC analyses revealed that the presence of solvent results in decreases in the curing exotherm, the initial curing rate, the glass transition temperature, the reaction rate and the reaction order of the epoxy resin. The greatest decreases were caused by the solvent with the highest boiling temperature. A change in temperature-dependent curing route due to the heat absorbed during solvent evaporation is responsible for the difference. The FTIR analyses confirmed that the composition of the cured resin is affected by the solvent, the curing temperature and the specimen configuration. As compared with those obtained from open systems, specimens produced in a closed environment have an enhanced curing exotherm, initial curing rate, glass transition temperature, reaction rate and reaction order because of the retention of volatile catalytic by-products.

**Keywords:** cure, dicyandiamide, DSC, epoxy, hermetic, solvent

### **Introduction**

The curing reactions that occur in the epoxy/dicyandiamide (DICY) system have been widely studied because of the popular applications of the epoxy/DICY system in composites, adhesives and molding compounds. In general, the curing kinetics and mechanism of the epoxy/DICY system can be affected by the equivalent mass of the epoxy resin, the accelerator, the DICY particle size, the DICY-to-epoxy ratio, the bromine content and the curing temperature [1–10]. In coating applications, the substrates in contact with the resin system could adsorb or react with DICY, and then affect the curing reaction and the resultant structure of the cured resin at the substrate/resin interface [11–16].

The solvent used during prepreg and coating production processes may also affect the curing reactions in the epoxy system. The differences in the solubilities of the various constituents in solvents can affect the preferential adsorption of species onto the surfaces of fillers or substrates, and result in changes in the curing reaction and

structure of the epoxy-DICY system [17, 18]. Additionally, the solvent released during the cure can form porosities and affect the integrity of the cured resin. The imbalance resulting in the stoichiometry of the constituents in consequence of solvent evaporation may also affect the curing reaction, change the cured structure, and lead to residual stress in the final product [19–21].

It is well known that the solvent in the internal regions of the prepreg is more difficult to evaporate than that in the more outlying regions during the prepreg manufacturing process. As a result, a difference in curing behavior is expected to occur at these two locations in resins. Although there is wide acceptance of the epoxy/DICY system in industry, few studies of the effects of solvents on the curing characteristics of this important resin system have been reported. In previous work, it was shown that the solvent released during curing in an open system caused decreases in  $T_g$ , the curing exotherm, the reaction rate and the reaction order because of the resultant absorption of heat [22]. For purposes of comparison the curing behavior of epoxy/DICY/solvent systems in a closed environment was studied in the present work. The curing behavior is demonstrated to differ from that in the open system.

## Experimental

The epoxy resin (Epon-828, diglycidyl ether of bisphenol-A with epoxide equivalent mass=190, from the Shell Chemical Co.), the dicyandiamide curing agent (DICY>98% pure, particle size <1 micron, from Tokyo Kasei Kogyo Co., Ltd.), and the accelerator 2-methylimidazole (2-MI, >98% pure, also from Tokyo Kasei Kogyo Co., Ltd.) were used as received. Three different solvents, acetone, tetrahydrofuran (THF) and toluene (>99% pure, all from Tokyo Kasei Ltd.), were used. The specimens with the compositions shown in Table 1 were prepared with a blade mixer at ambient temperature.

**Table 1** Compositions of tested specimens

Sample	Epon 828	DICY	2-MI	Acetone	THF	Toluene
A1	100	11	0.05	0	0	0
A2	100	11	0.05	5	0	0
A3	100	11	0.05	0	5	0
A4	100	11	0.05	0	0	5

(Units used: parts per hundred for Epon 828, DICY and 2-MI; wt% for acetone, THF and toluene)

At least three specimens prepared in hermetic aluminum pans were tested for each isothermal measurement. The exotherm was measured at 150, 160 and 170°C under a nitrogen flow rate of 30 ml min<sup>-1</sup> with a Perkin Elmer DSC-7. The specified curing temperature was reached at a rate of 500°C min<sup>-1</sup>. The exotherm baseline was corrected via data on the empty aluminum pan. The uniformity of the prepared specimens was confirmed by the small standard deviations obtained. After the isothermal measurement, the specimen was scanned at a rate of 20°C min<sup>-1</sup> from room temperature up to 250°C in order to find the glass transition temperature ( $T_g$ ) and the endotherm of the unreacted DICY. The

resins taken from the isothermally cured DSC specimens were ground and pressed into KBr pellets for transmission IR analyses. IR spectra were acquired at a resolution of  $4\text{ cm}^{-1}$  on a Perkin Elmer 1725 Fourier transform IR (FTIR) spectrophotometer.

## Results and discussion

The reaction heats obtained on specimen A1 at various curing temperatures were between  $76.2$  and  $94.1\text{ kJ mol}^{-1}$ ; they increased with increasing curing temperature (Table 2). A higher curing temperature facilitated the dissolution of DICY, and hence improved the reaction between DICY and epoxy [11, 12]. In the complex DICY-cured system, the change of curing temperature also resulted in changes in the relative rates among the competing curing mechanisms and the formation of intermediate compounds and partially reacted DICY, and caused differences in the reaction exotherm [23, 24].

**Table 2** Curing characteristics obtained from DSC exotherms

Sample		Curing temp./°C		
		150	160	170
A1	$\Delta H/\text{kJ mol}^{-1}$	76.2 (0.2)	87.7 (0.3)	94.1 (0.5)
	$t_p/\text{min}$	3.03 (0.02)	1.58 (0.05)	1.05 (0.05)
	$T_g/^\circ\text{C}$	103	119	125
A2	$\Delta H/\text{kJ mol}^{-1}$	67.2 (0.2)	78.0 (0.3)	85.6 (0.5)
	$t_p/\text{min}$	4.35 (0.07)	2.43 (0.03)	1.51 (0.04)
	$T_g/^\circ\text{C}$	102	107	116
A3	$\Delta H/\text{kJ mol}^{-1}$	65.8 (0.4)	77.0 (0.4)	82.8 (0.1)
	$t_p/\text{min}$	4.65 (0.08)	2.50 (0.09)	1.64 (0.06)
	$T_g/^\circ\text{C}$	101	103	107
A4	$\Delta H/\text{kJ mol}^{-1}$	60.7 (0.5)	72.6 (0.7)	78.2 (0.4)
	$t_p/\text{min}$	4.73 (0.05)	2.61 (0.03)	1.72 (0.05)
	$T_g/^\circ\text{C}$	98	101	104

( ): standard deviation

In a previous study, the curing exotherms for A1 after a 150, 160 or 170°C cure in open aluminum pans were  $67.3$ ,  $81.7$  and  $88.0\text{ kJ mol}^{-1}$ , respectively [22]. The higher exotherm obtained for the closed system than for the open system is an indication of the effect of the specimen configuration on the curing reactions. A similar result was obtained for specimens A2-A4. Despite the effect of the pressure difference resulting from these two kinds of specimens, it was shown that the main factors causing the change were possibly the evaporation of adventitious catalyst, the evaporation of reactants, and the evaporation of volatile by-products during the cure [25]. In the DICY-cured system, ammonia and volatile side-products (e.g. aminotriazines) were

usually produced [25, 26]. As stated previously, some of the intermediates are capable of promoting the dissolution and reaction of DICY [24]. The loss of these as-formed volatile amino by-products is believed to result in smaller exotherms being observed for specimens with the open configuration. The smaller  $T_g$  obtained for the open specimens than the  $T_g$  listed in Table 2 confirms that the extent of curing is greater in the closed specimens [22].

The solvent in the resin has a significant effect on the curing characteristics. It is obvious from Table 2 that the reaction exotherms follow the sequence  $A4 < A3 < A2 < A1$ , regardless of the different curing temperatures applied (the masses of all specimens remained unchanged during the test). This is similar to the finding obtained for the open specimens [22]. The decrease in the exotherm is attributed to the change in curing reaction resulting from the heat absorbed by the solvent during the cure. The sequence of the exotherms suggests that the ease of evaporation of the solvent is more important than the amount of heat absorbed in affecting the curing behaviour. The boiling point sequence is acetone ( $56^\circ\text{C}$ ) < THF ( $66^\circ\text{C}$ ) < toluene ( $110^\circ\text{C}$ ), while the evaporation heat sequence is acetone ( $543.3 \text{ J g}^{-1}$ ) > THF ( $444.3 \text{ J g}^{-1}$ ) > toluene ( $413.2 \text{ J g}^{-1}$ ).

It is proposed that the heat absorbed during the solvent evaporation causes a change in local temperature, which subsequently generates a difference in relative reaction rates and a change in reaction order among the various temperature-dependent mechanisms [22]. These changes result in the lower exotherms observed for A2-A4.

In this study, the  $n$ -th order kinetic form was used for a qualitative comparison of the differences between specimens [27]. The reaction order  $n$  varies between 0.08 and 1.34 for A1, and increases with increase of the curing temperature (Table 3). The significant difference in  $n$  indicates that the curing mechanism of the system studied is temperature-dependent. It was confirmed that temperature-dependent etherification, amine-epoxy reaction and melamine formation took place in the DICY-cured epoxy system [6, 8].

For specimens with solvents, the  $n$  values obtained for A2-A4 were lower than those for A1, especially at  $150^\circ\text{C}$  (Table 3). Specimen A4 has the lowest  $n$  value confirming that the largest change in curing characteristics is for the specimen containing the solvent with the highest boiling temperature.

The  $n$  values obtained for A2-A4 in this study are greater than those for the open specimens (e.g. specimens A1, A2, A3 and A4 have  $n$  values near 1.35, 1.26, 1.25 and 1.25, respectively, for the open specimens after a  $170^\circ\text{C}$  cure) [22]. In addition, the specimens containing solvents display greater differences in  $n$  between the open and closed specimens than the specimen without solvent. A similar result can also be obtained by comparing  $k$ . Without the presence of solvent, specimen A1 underwent the greatest conversion, and left small space to improve by changing the specimen configuration, especially at high curing temperature. It is also possible that a greater pressure increase and the plasticizing effect due to the solvent can contribute to the larger differences observed in  $n$  and  $k$  between open and closed specimens of A2-A4.

**Table 3** Curing characteristics calculated from DSC exotherms

Sample		Curing temp./°C		
		150	160	170
A1	<i>n</i>	0.80	1.07	1.34
	<i>k</i>	0.13	0.27	0.55
	R.L./%	24.6~98.7	23.5~98.5	14.5~97.7
A2	<i>n</i>	0.73	1.03	1.33
	<i>k</i>	0.12	0.25	0.54
	R.L./%	25.0~98.7	24.9~98.4	20.5~97.7
A3	<i>n</i>	0.71	1.03	1.32
	<i>k</i>	0.12	0.26	0.51
	R.L./%	23.9~98.6	23.0~98.4	21.9~98.1
A4	<i>n</i>	0.68	1.01	1.28
	<i>k</i>	0.11	0.26	0.50
	R.L./%	25.5~98.8	23.3~98.2	25.2~97.8

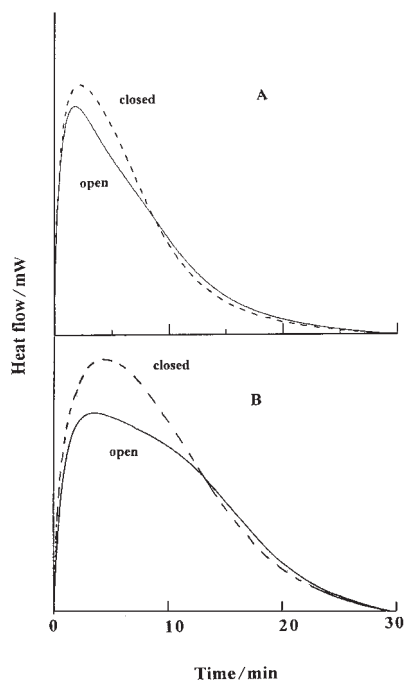
R. L. – range of linearity

**Table 4** Reaction conversions (%) at  $t_p$ 

Sample	Curing temp./°C		
	150	160	170
A1	30	33	37
A2	25	31	34
A3	22	30	33
A4	18	28	30

As shown in Table 3, the range of linearity (used to calculate  $n$  and  $k$ ) obtained for A1 increases from about 74 to 83% as the temperature is increased from 150 to 170°C (the correlation coefficient of the linear regression is better than 0.99 in all cases) [11, 22, 27]. The linear ranges obtained for A2-A4 are similar to those for A1 except at 170°C (Table 3). The  $n$ -th order kinetic model does not correlate well with the experiments in the early stage of the curing reaction, especially for a low-temperature cure and in the solvent-containing systems. Nevertheless, a better R.L. is obtained at the low curing temperature for the specimens prepared with open aluminum pans [22]. This indicates that the specimen configuration and the presence of solvent appreciably affect the curing characteristics.

The difference in curing rates can be obtained by comparing the averaged initial reaction rates (expressed as conversion at  $t_p$  (%) /  $t_p$  (min), where  $t_p$  is the time to reach the maximal curing rate). From Table 2,  $t_p$  decreases at a higher curing temperature because of the resulting higher reaction rate between the amino and epoxide groups [3]. Consequently, the initial reaction rate increases with the curing temperature (Tables 2 and 4).

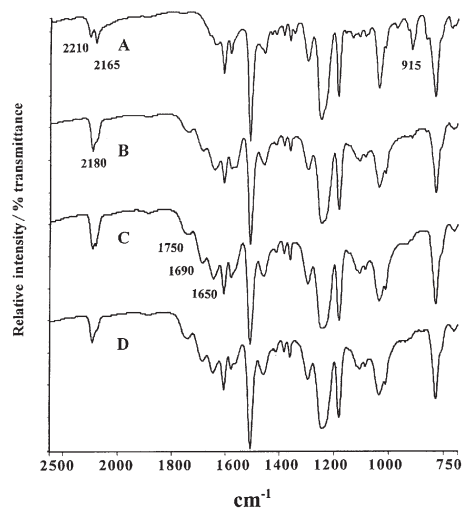


**Fig. 1** Representative DSC isothermal curves of specimens A – A1 and B – A4 cured at 150°C in open and closed aluminum pans

It is interesting that, although the  $t_p$ 's for the closed specimens are all greater than those for the open specimens, the initial reaction rates are generally higher for the closed specimens because of the larger conversion at  $t_p$  [22]. This can clearly be seen from the representative DSC curves shown in Fig. 1A. The difference in curing rates is mainly related to the above-mentioned evaporation loss of adventitious catalyst and catalytic by-product in the open system [25, 26]. Moreover, the difference in conversion at  $t_p$  between the closed and open specimens implies that the curing mechanisms are affected by the specimen configuration.

As regards the influence of solvents, it is to be observed in Tables 2 and 4 that the  $t_p$ 's follow the sequence  $A1 < A2 < A3 < A4$ , while the conversions (%) at  $t_p$  are in the reverse sequence, regardless of the different curing temperatures applied. As a result, the initial reaction rates are in the sequence  $A1 > A2 > A3 > A4$ . The conversion at  $t_p$  decreases significantly when a high boiling temperature solvent is present (Fig. 1B). The lower rate of solvent evaporation leads to a much lower curing rate of the specimen. This result also indicates that the curing mechanism is greatly affected in specimen A4.

The changes in the curing reactions are confirmed by the representative IR spectra of specimen A1 in Fig. 2. In Figs 2A and 2B, the decreases in the bands near  $2210\text{ cm}^{-1}$  (cyano groups of DICY),  $2165\text{ cm}^{-1}$  ( $\text{N}=\text{C}=\text{C}$  of DICY) and  $915\text{ cm}^{-1}$  (epoxide groups), accompanied by the presence of new bands near 1750, 1690 and

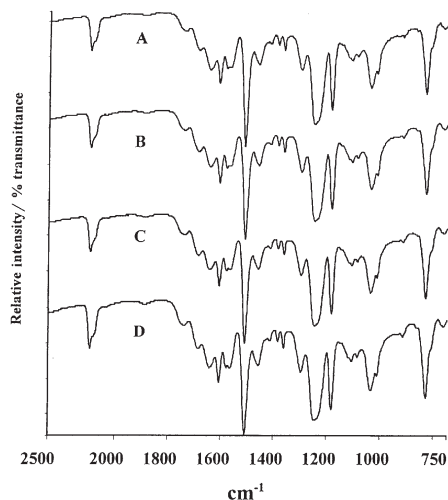


**Fig. 2** Representative IR spectra obtained from specimen A – A1 before cure, and after B – 150, C – 160 and D – 170°C cure

1650  $\text{cm}^{-1}$  (characteristic of 2-oxazolidones, guanyl ureas and imino groups, respectively) after the cure can be clearly identified [28–33]. The curing reaction also shifts the band from 2210 to 2180  $\text{cm}^{-1}$ , due to the formation of alkylated DICY.

Similarly as for the open specimens, the intensities of the bands near 2180  $\text{cm}^{-1}$  decrease in the sequence Fig. 2B>Fig. 2C>Fig. 2D (with the band near 835  $\text{cm}^{-1}$  as an internal standard) [22]. A clear epoxide band near 915  $\text{cm}^{-1}$  is also observed in Fig. 2B. A resin cured at a higher temperature has a higher conversion of reactive groups. This is consistent with the trend of the DSC curing exotherms and the  $T_g$  of the cured resin with respect to the curing temperature. Further, the bands near 1750 and 1690  $\text{cm}^{-1}$  have higher intensities for the specimen cured at higher temperature, indicating the temperature dependence of the structure in the cured resin (Figs 2C, 2D) [23, 26, 29].

As concerns the specimens with solvents, the FTIR spectra support the results obtained from the DSC analyses. It is shown in Fig. 3 that the absorption intensities of the bands near 2180 and 915  $\text{cm}^{-1}$  increase in the sequence A1<A2~A3<A4. The specimen containing the solvent has more residual DICY and epoxy functional groups (the band near 835  $\text{cm}^{-1}$  is used as an internal standard). The changes in the intensities of these bands indicate that the extent of reaction follows the sequence A1>A2~A3>A4. Similar results are obtained at other curing temperatures. This result is consistent with the DSC reaction exotherms and the  $T_g$  obtained. It is shown in Table 2 that  $T_g$  decreases in the sequence A1>A2>A3>A4. Differences in the absorption intensities of the bands near 1750, 1690 and 1650  $\text{cm}^{-1}$  (Figs 3A, 3B, 3C and 3D) can likewise be observed. It is obvious that the solvent type plays an important role in affecting the structures of the cured specimens.



**Fig. 3** Representative IR spectra obtained from specimens A – A1, B – A2, C – A3 and D – A4 after 150°C cure

As compared with those obtained previously on the open specimens, the changes in the intensities of the bands near 2180, 1750, 1690 and 915  $\text{cm}^{-1}$  are all greater for the closed specimens [22]. This result is consistent with those derived previously by comparing the differences in the DSC exotherms and the  $T_g$ 's obtained between open and closed specimens.

## Conclusions

The effects of solvents on the curing of an epoxy resin system in hermetic aluminum pans were studied by using isothermal DSC and FTIR. Similarly as obtained for the open specimens, the presence of solvent decreases the curing exotherm, the initial curing rate, the glass transition temperature, the reaction rate and the reaction order of the epoxy resin because of the change in temperature-dependent curing route resulting from the heat absorbed during solvent evaporation. The extent of the decrease follows the sequence toluene>tetrahydrofuran>acetone. The greatest decrease is for the solvent with the highest boiling temperature. The results of FTIR analyses confirm that the curing extent and the composition of the cured resin are affected by the solvent, the curing temperature and the specimen configuration applied. In general, the specimens in a closed environment display a greater curing exotherm, initial curing rate, glass transition temperature, reaction rate and reaction order than those in the open system because of the retention of volatile catalytic by-products.



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