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DSC and FTIR analysis of the curing behaviors of epoxy/DICY/solvent open systems

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Abstract

The effects of solvents on the curing behaviors of an epoxy (diglycidyl ether of bisphenol-A) and dicyandiamide/2-methyl imidazole system have been studied with differential thermal calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). From DSC analyses of the specimens prepared with unsealed aluminum pans, the reaction exotherm, the time to maximal curing rate, the glass-transition temperature, the rate constant, and the reaction order of the epoxy system decrease in the presence of solvents were obtained. The changes were in the order of toluene>tetra-hydrofuran>acetone and which are consistent with the order of their boiling points. The heat absorbed during the solvent evaporation consumed the curing exotherm and resulted in a change in temperature dependent curing mechanisms. The results from FTIR spectra confirmed that the composition of the cured resin was influenced by the curing temperature and the type of the solvent used. © 1998 Elsevier Science B.V.

Keywords: Curing kinetics; DSC; Dicyandiamide (DICY); Epoxy; FTIR; Solvent

1. Introduction

The popular applications of epoxy/dicyandiamide (DICY) systems in composites, adhesives, and molding compounds generate a great interest in characterizing the curing reaction of various epoxy/DICY systems. It was reported that the equivalent weight of the epoxy resin, the accelerator, the particle size of DICY, the DICY-to-epoxy ratio, the bromine content, and the curing temperature all could affect the curing kinetics and mechanism of the epoxy/DICY system [1–10]. In a previous study, it was demonstrated that the amounts of residual DICY decreased when 2-MI accelerator or a higher curing temperature was used [11,12]. The dependence of curing mechanisms on the curing temperature was also shown.

In spite of these factors, the substrates in contact or solvent used in preparing prepregs and coatings can also affect the curing reaction of the epoxy system. It was shown that the metal substrates could adsorb or react with DICY, thereby, affecting the curing reaction and the cured structure of epoxy/DICY system in the interfacial region [11–16]. As regards the solvent used in the fabrications of composite prepregs or coatings, the differences in solubilities of constituents in various solvents can affect the adsorption of favorable species onto the surfaces of fillers or substrates and change the reaction of DICY with the epoxy resin. Moreover, the solvent evaporation during the high temperature cure will also generate porosity in the cured resin and then affect the performance of the finished parts. The

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uneven distribution of constituents accompanying the solvent release during the cure could affect the curing reaction, change the cured structure, and produce residual stress in the final product [17–19].

Although there is a wide acceptance of the epoxy/DICY system in the industry, few studies on the solvent effect on the curing characteristics of this important resin system have been reported. In this work, the curing behaviors of the epoxy/DICY system in the presence of different solvents are studied using differential scanning calorimetry (DSC) and infrared spectroscopy. Interesting curing behaviors in the prepared specimens are demonstrated.

2. Experimental

The epoxy resin (Epon-828, diglycidyl ether of bisphenol-A with epoxide equivalent weight=190) was obtained from the Shell. The curing agent dicyandiamide (DICY, >98% pure) and the accelerator 2-methylimidazole (2-MI, >98% pure) were obtained from Neuto Products and Tokyo Kasei Kogyo, respectively. DICY particles have an average diameter <1 μm. DICY and 2-MI were used as received.

The epoxy resin was mixed with 1 and 5% w/w solvents at ambient temperature and subsequently mixed with other constituents in a blade mixer (see Table 1). Three different solvents, acetone, tetrahydrofuran (THF), and toluene (from Tokyo Kasei, >99% pure), were used. DICY was added as 11 parts per hundred parts epoxy resins (phr). 2-MI is used as 0.05 phr. The homogeneity of the specimens prepared can be confirmed by the small standard deviations obtained from the DSC curing exotherms.

Table 1
The compositions of tested specimens

Sample	Epon828	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
A5	100	11	0.05	1	0	0
A6	100	11	0.05	0	1	0
A7	100	11	0.05	0	0	1

Unit used: parts per hundred for Epon-828, DICY, and 2-MI; wt.% for Acetone, THF, and Toluene.

A Perkin–Elmer DSC-7 was used to measure the curing exotherm and the glass-transition temperature (T_g) of specimens. The isothermal curing exotherm was measured at 150, 160 and 170°C under nitrogen environment (with a nitrogen flow rate of 30 ml/min). The specimen was inserted into the DSC cell and then the intended temperature was reached at a scanning rate of 500°C/min. Three specimens prepared from open (unsealed) aluminium pans were tested for each isothermal measurement. The exotherm was corrected by the baseline obtained from the empty aluminium pans. 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 possible endotherm of the unreacted residual DICY in the cured resin. In addition, infrared transmission spectra were taken from the isothermally cured DSC specimens which were ground and pressed into KBr pellet. Fifty scans were acquired at a resolution of 4 cm^{-1} from 4000 to 600 cm^{-1} on a Perkin–Elmer 1725 Fourier transform infrared spectrophotometer for each specimen.

3. Results and discussion

3.1. Isothermal curing reactions of specimens in the absence of solvent

The representative isothermal curing scans obtained from the A1 specimen are shown in Fig. 1. The reaction heats calculated are listed in Table 2. The reaction heats were between 67.3 and 88.0 kJ/mol at various curing temperatures. The curing heat increased with increasing the curing temperature. A higher curing temperature facilitated the dissolution of DICY, henceforth, facilitated the reaction between DICY and epoxy and speeded the reaction rate [11,12]. Fava [20] also indicated that in a curing reaction which was dominated by several different parallel reaction routes, the change in curing temperature resulted in a change in relative rates among curing mechanisms, henceforth, caused a difference in reaction exotherm. In the well-known complex curing reactions involved in the DICY cured system, the temperature dependent curing characteristics are expected.

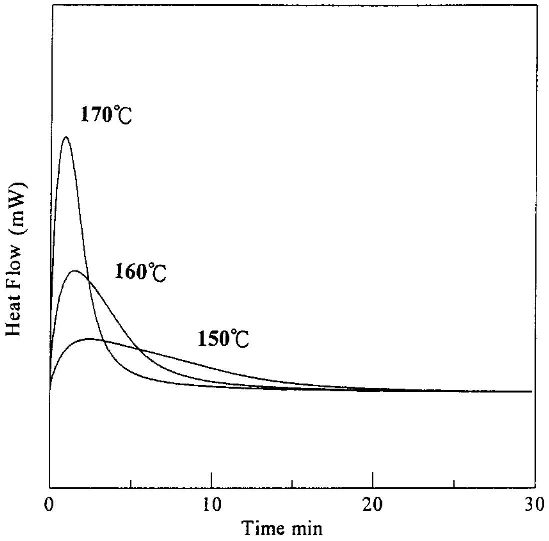

Fig. 1. The representative isothermal curing thermograms of the specimen A1.

In addition, the intermediate compounds formed during the reaction also helped the further dissolution and reaction of DICY and affected the exotherm [21]. The formation of intermediate compounds and partially reacted DICY are both affected by the curing temperature. In this study, no unreacted DICY was found in the isothermally cured specimens due to the fact that the partially reacted DICY exhibited no endotherms in the second DSC scan [11,12]. Yet it was shown later in the FTIR analyses that the amount of partially reacted DICY present varied with the curing temperature. These factors also resulted in the observed difference in curing exotherms.

For qualitative comparison purposes, the *n*th order kinetic form ($d\alpha/dt=k(1-\alpha)^n$), where α is the conversion and k the rate constant.) was used in the calculation of the kinetic parameters. The method of calculation was described elsewhere [22]. The reaction order n changed between 0.71 and 1.35

Table 2
The curing characteristics obtained from DSC exotherms

Sample		Curing temp.		
		150°C	160°C	170°C
A1	ΔH (kJ/mol)	67.3 (0.1)	81.7 (0.4)	88.0 (0.4)
	t_p (min)	2.17 (0.09)	1.55 (0.03)	1.00 (0.09)
	T_g (°C)	88	103	121
A2	ΔH (kJ/mol)	58.5 (0.2)	71.2 (0.3)	78.9 (0.6)
	t_p (min)	3.22 (0.06)	1.77 (0.09)	1.28 (0.09)
	T_g (°C)	85	99	113
A3	ΔH (kJ/mol)	57.3 (0.5)	70.5 (0.4)	74.9 (0.5)
	t_p (min)	3.35 (0.03)	1.94 (0.02)	1.38 (0.09)
	T_g (°C)	84	98	107
A4	ΔH (kJ/mol)	55.6 (0.5)	68.4 (0.4)	72.5 (0.2)
	t_p (min)	3.38 (0.05)	2.37 (0.06)	1.52 (0.08)
	T_g (°C)	78	95	104
A5	ΔH (kJ/mol)	67.0 (0.1)	77.9 (0.4)	86.4 (0.2)
	t_p (min)	2.60 (0.03)	1.70 (0.02)	1.11 (0.01)
	T_g (°C)	88	101	117
A6	ΔH (kJ/mol)	59.0 (0.3)	75.6 (0.9)	84.4 (0.1)
	t_p (min)	2.96 (0.08)	1.86 (0.09)	1.33 (0.05)
	T_g (°C)	87	100	113
A7	ΔH (kJ/mol)	56.8 (0.3)	72.8 (0.8)	80.0 (0.2)
	t_p (min)	3.25 (0.07)	2.13 (0.08)	1.48 (0.07)
	T_g (°C)	86	99	112

( ): Standard deviation.

Table 3
The curing characteristics calculated from DSC exotherms

		Curing temp.		
Sample		150°C	160°C	170°C
A1	*n*	0.71	1.09	1.35
	k	0.11	0.28	0.54
	R.L. (%)	14.3–98.5	18.8–97.8	23.5–97.9
A2	*n*	0.63	1.00	1.26
	k	0.09	0.21	0.43
	R.L. (%) [a]	14.3–98.6	19.1–97.7	20.0–97.8
A3	*n*	0.64	1.00	1.25
	k	0.09	0.20	0.43
	R.L. (%) [a]	13.3–98.6	17.7–96.6	22.9–97.0
A4	*n*	0.60	0.94	1.25
	k	0.10	0.19	0.41
	R.L. (%) [a]	17.2–98.7	20.2–98.1	23.3–97.8
A5	*n*	0.71	1.05	1.30
	k	0.11	0.25	0.47
A6	*n*	0.65	1.02	1.30
	k	0.10	0.22	0.46
A7	*n*	0.59	0.94	1.28
	k	0.09	0.20	0.44

[a] Range of linearity.

and increased with increasing the curing temperature (see Table 3). The significant difference in *n* indicates that the curing mechanism of the system studied is temperature dependent. Lin et al. [6] believed that the two highly temperature dependent reactions were the etherification and the amine-epoxy reaction. A third reaction resulting from the formation of melamine by the rearrangement was also found in the curing temperature range between 150 and 200°C [8]. The differences in the actual 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.

In the calculation, the reaction order and the kinetic constant were obtained from the linear region of the plot ln(d*H*/d*t*) vs. ln(H_r) where d*H*/d*t* is the heat evolution rate at time *t* and H_r the total heat evolved from time *t* to the end of cure (see Fig. 2) [11,22]. Table 3 lists the linear ranges calculated from the DSC exotherms. The range of linearity decreased from ca. 84 to 74% as the temperature increased from 150 to 170°C (the correlation coefficient of the linear regression was better than 0.99 in all cases). Although the *n*th order kinetic model does not correlate well with the early stage of curing reaction, it describes the curing reaction as high as 74–84% conversions (see Fig. 3).

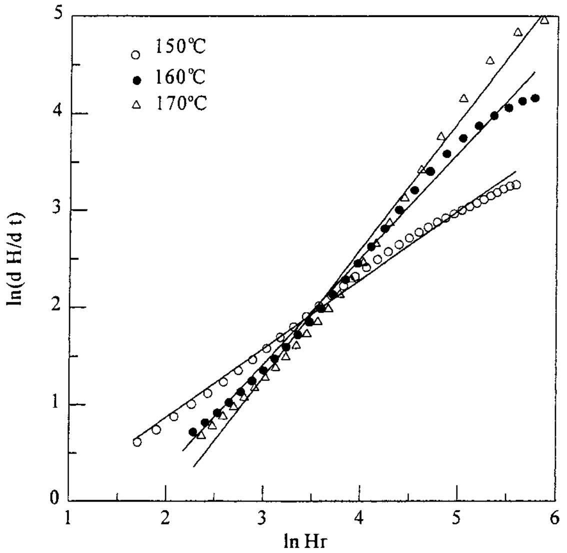

Fig. 2. The representative diagram of isothermal curing exotherms calculated from the specimen A1.

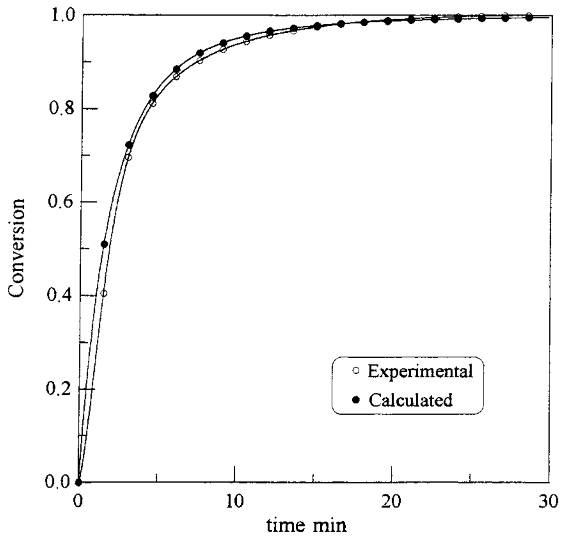

Fig. 3. The representative experimental and calculated conversion profiles from the specimen A1 at 150°C cure.

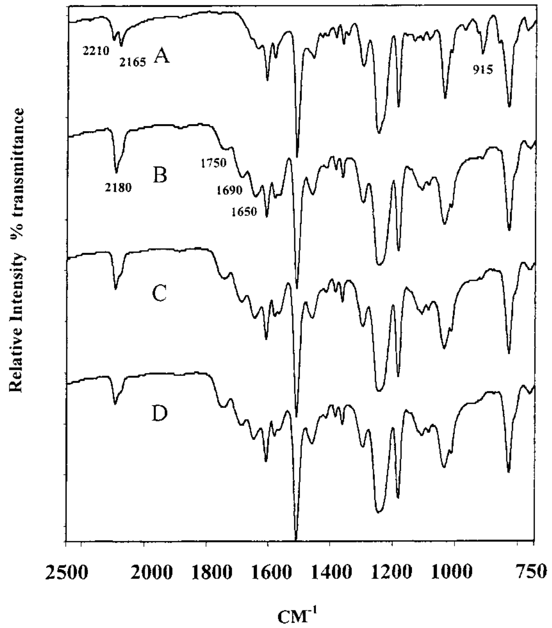

Fig. 4. The representative FTIR spectra obtained from the specimen A1: (A) before cure, and after; (B) 150°C; (C) 160°C; and (D) 170°C cure.

The variation in the extents of curing reactions can be identified in FTIR spectra. The representative IR spectra of the specimen A1 before and after cure are shown in Fig. 4. The changes of absorption bands during cure can be easily observed. The consumptions of cyano (the band near 2210 cm^{-1}) and N=C=N (2165 cm^{-1}) of DICY, and epoxide (915 cm^{-1}) groups from the epoxy resin, accompanied by the formations of new absorbance bands near 1750, 1690, and 1650 cm^{-1} can be clearly identified in Fig. 4(A) and (B). The 1650 cm^{-1} band was assigned to an imino group formed by the intermolecular addition of hydroxyl to the DICY cyano functionality, and/or by the intramolecular nucleophilic substitution of hydroxyl at the imide functionality [23,24]. The absorption bands near 1750 and 1690 cm^{-1} are characteristics of carbonyls formed by the structural rearrangement of the imino esters into 2-oxazolidones and guanyl ureas, respectively [25,26]. The curing reaction also resulted in the shift of the band from 2210 to 2180 cm^{-1} (due to the formation of alkylated DICY). The tentative IR assignments of the DICY and the epoxy resin are listed elsewhere [24,27,28].

The differences in curing structures at different curing temperatures can be obtained in Fig. 4. The absorption intensities of 915 and 2180 cm^{-1} bands decreased in the order of Fig. 4(B)>(C)>(D) indicating that the resin cured at a higher temperature has a higher conversion of reactive groups (using the band near 835 cm^{-1} as an internal standard). This is consistent with the trend of DSC reaction exotherms. In addition, the bands near 1750 cm^{-1} also have the greater intensities than specimens cured at the higher temperature (Fig. 4(C) and (D)). Small changes of bands near 1690 and 1650 cm^{-1} among Fig. 4(B)–(D) were also obtained. It is evident that there are functional and curing differences among specimens cured at different temperatures. A similar result was also reported by other investigators [23,24,29]. These differences would be related to the variation of T_g observed.

As shown in Table 2, it is clear that T_g increased with increasing the curing temperature. The trend was similar to that from the curing heats evolved. As indicated previously and confirmed from FTIR spectra, a higher curing temperature facilitated the dissolution of DICY and promotes the reaction between DICY and epoxy, henceforth, facilitating the cross-linking reaction and increases T_g.

The change in curing rates can also be obtained from t_p – the time to reach the maximal curing rate. The t_p decreases when the curing temperature increases because of the better dissolution of the DICY and the resulting faster reaction rate between amino and epoxide groups at the high temperature [3]. Henceforth, it is clear from Tables 2 and 4 that the initial reaction rate (conversion at t_p(%)/t_p(min)) increased with the curing temperature. In addition,

Table 4
The reaction conversions (%) at t_p

	Curing temp.		
Sample	150°C	160°C	170°C
A1	18	24	31
A2	18	23	28
A3	16	21	27
A4	13	18	25
A5	18	24	31
A6	17	22	29
A7	15	20	26

Table 5
The weight loss (%) of specimens after DSC measurement

Sample	150°C	160°C	170°C
A1	0	0	0
A2	4.23 (3)	4.54 (3)	4.64 (2)
A3	4.12 (2)	4.22 (4)	4.24 (3)
A4	3.82 (2)	4.13 (3)	4.23 (2)
A5	0.98 (2)	0.98 (1)	0.99 (1)
A6	0.97 (2)	0.98 (2)	0.98 (2)
A7	0.96 (1)	0.96 (2)	0.98 (2)

( ): Standard deviation, $\times 10^2$%.

the difference in conversions at t_p(%) among various temperatures confirms that the curing mechanisms are temperature dependent.

3.2. The effects of solvents on the curing reaction

Different curing characteristics were obtained when solvents were present during cure. It is shown in Table 2 that the reaction heats generated from the specimen containing 5% w/w acetone were, as expected, all smaller than those of the A1 system regardless of the different curing temperatures used. The decrease of exotherms becomes smaller as the solvent content was lowered to 1% w/w. As listed in Table 5, the sample A2 loses solvent after isothermal cure. The heat absorbed by the solvent during evaporation is responsible for the decrease in exotherm. In a separate test, it was confirmed that the sealed specimens all have greater exothermic energies than the unsealed specimens [30]. However, the decrease in curing heat may also come from other effects accompanying the simple solvent evaporation since the difference in exotherm is not directly proportional to the solvent content (see Table 2). This can be better observed by comparing other kinetic parameters.

The kinetic constants n and k obtained from isothermal exotherms of A2 are shown in Table 3. The n and k of the specimen having acetone are all smaller than those of the system with no solvent. This implies that the presence of acetone can alter the reaction mechanism and curing speed of the epoxy/DICY system. The change in n is mainly attributed to the temperature variation resulting from the heat absorbed during the solvent evaporation. It was shown previously that the complex reaction mechanisms of DICY cured resin are sensitive to the curing temperature encountered. Henceforth, a change in local temperature can generate a great difference in relative reaction rates among various mechanisms and cause a change in reaction order. The decrease in local temperature resulting from the solvent evaporation also results in a decrease in k. This was similar to the effect obtained by lowering the curing temperature (Table 3).

By comparing the reaction heats obtained from A2–A4 with those of A1, the effect from solvent evaporation may be similar to that obtained by decreasing the curing temperature more than 10°C if the reaction heat is the only considered parameter. Of course, a more subtle experimental set up is needed to find the actual response inside the specimen.

The decrease of curing speed can also be confirmed from the increase in t_p. As shown in Table 2, t_p values of the specimen A2 are greater than those of the specimen A1 regardless of the curing temperature used. The initial reaction rates from A2 are also all slower than those from A1 (see Tables 2 and 4). It is clear that the presence of acetone slowed the curing reaction. Moreover, the differences in conversions (%) at t_p between A2 and A1 at the higher curing temperature imply that the curing mechanisms were changed (see Table 4).

In addition to the effect from evaporation, the changes observed in A2 could also result from a difference in solubilities among epoxy constituents. The evaporation of acetone could bring soluble DICY to the surface region and then result in different cured structures. Yet this effect should be minor because of the limited solubility of DICY in acetone and the relatively large amounts of DICY used. However, the smaller T_g obtained from A2 implies that the presence of acetone during cure can alter the final structure or the crosslinking density of the specimen (see Table 2). In addition to the aforementioned changes in curing mechanisms, the small amounts of residual acetone left after isothermal cure could contribute to the decrease in T_g (see Table 5).

The difference observed in FTIR spectra could explain the results obtained from the DSC analyses. Fig. 5(A) and (B) are IR spectra taken from specimens A1 and A2 after 150°C cure, respectively. In Fig. 5(B), the decreases in intensities of the bands near 2210 and 915 cm^{-1}, while the appearances of the new bands near 1750, 1690 and 1650 cm^{-1} after cure

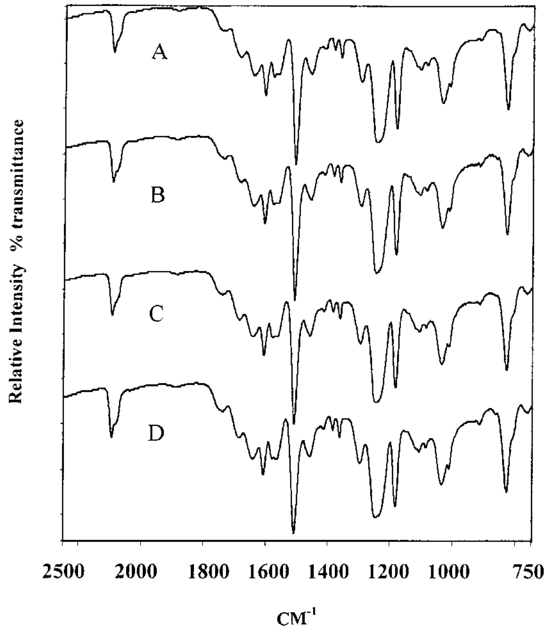

Fig. 5. The representative FTIR spectra obtained from the specimens (A) A1; (B) A2; (C) A3; and (D) A4 after 150°C cure.

are also observed. The assignments of these bands were described previously. Greater relative intensities of bands near 2180 (due to DICY) and 915 cm^{-1} (due to epoxide groups) in spectrum of A2 than those of A1 are observed (the characteristic band of benzene ring deformation near 835 cm^{-1} was chosen as an internal standard for comparison). The changes in intensities of these bands indicate that A2 has a lower extent of curing reaction than A1. This leads to a smaller reaction heat obtained from A2. In addition, a smaller 1690 cm^{-1} band but greater 1750 and 1650 cm^{-1} bands are also obtained from the spectrum of A2 than of A1. Although the differences are small because of the sensitivity of FTIR, the changes imply that different amounts of functional groups are formed which result from the solvent-affected curing mechanisms. Similar results are obtained at other curing temperatures.

The effect of solvent can also be obtained from the THF and toluene added specimens. As shown in Table 2, the reaction heats follow the order of A4<A3<A2<A1. The boiling points of acetone, THF, and toluene are 56, 66 and 110°C, respectively; while the evaporation heats are 543.3, 444.3 and 413.2 J/g, respectively. It is clear that the magnitude of the boiling point but not the evaporation heat play the dominant role in determining the effect of the solvent on the curing behavior. The result is reasonable since the more easily the solvent can evaporate, then the less solvent will affect the curing reaction during the isothermal cure. This can be confirmed from the weight loss percentages listed in Table 5. The specimen prepared with the highest boiling temperature solvent has the greatest residual solvent content.

The slow solvent evaporation of specimens A3 and A4 leads to a slower curing rate. As shown in Table 2, the t_p follows in the order of A4>A3>A2>A1. The relative initial curing rates are in the reverse order since the conversions at t_p decrease significantly when a high boiling temperature solvent is present (see Tables 2 and 4). This result also implies that the curing mechanism is greatly affected in the specimen A4. The variations observed among specimens confirm that the type of the solvent is important in affecting the curing reaction of the studied epoxy system.

As from A2, the changes in curing rate and reaction order of A3 and A4 can also be obtained. In general, the specimen containing the solvent with a higher boiling temperature has both a lower k and n. Since n and k are calculated from the linear curve fits, the variations in R.L. among specimens may actually affect the n and k obtained and generate some discrepancies. However, it is certain that the greatest changes in n and k are obtained from the specimen prepared with the highest boiling solvent-toluene.

As indicated previously, the presence of the solvent affects not only the curing kinetics but also the structure of the cured resin. The implication of structural changes can be obtained from T_g shown in Table 2. T_g decreases in the order of A1>A2>A3>A4 regardless of the curing temperature used. In addition to the decrease in T_g because of the residual solvent in the cured resin, the change in curing mechanisms as confirmed from the differences obtained in exotherms, t_p, n, and k results in a substantial change of the cured structure.

From FTIR spectra shown in Fig. 5, the difference in functional groups, reacting among specimens, can be identified. The absorption intensity of the bands near 915 and 2180 cm^{-1} bands increases in the order of A1<A2–A3<A4 indicating that the specimen containing toluene had the greatest unreacted epoxide and

DICY functional groups. It is evident that A4 has a lower conversion than other specimens. This may explain the lowest T_g and reaction heat obtained from A4.

In addition, it is also shown in Fig. 5 that specimens A3 and A4 have greater absorption intensities near 1750 and 1650 cm^{-1} (characteristic of 2-oxazolidones and imino groups, respectively) but smaller intensities near 1690 cm^{-1} (characteristic of guanyl ureas) than specimen A1. Although the intensity change is not great, the difference in A4 is more obvious than in others. As mentioned previously, the difference in relative intensities of these bands is an indication that the specimens may have different solvent-affected curing reactions. A further study is needed to explain the detailed function of the solvent in affecting the curing reactions.

For comparison purposes, the results obtained from specimens containing 1% w/w solvent are also shown in Tables 2–5. The trend of changes in ΔH, t_p, T_g, n, k, R.L., E_a, and conversion at t_p are similar to those from specimens A2–A4. The only difference is in the magnitude of these changes. The specimens with 1% w/w solvents have smaller differences with A1 than the specimens with 5% w/w solvents. However, it can be seen from Table 2 that the magnitude of change in curing characteristics is not directly proportional to the amount of the solvent used. It is obvious that the effect of the solvent is not just as simple as deducting the evaporation heat from the curing exotherm but is from the resulting temperature changes during the evaporation which affect the temperature dependent mechanisms.

Regardless of the presence of solvent during the cure, the linear ranges obtained from specimens containing solvents are similar to those of the specimen without solvent, and also decrease with increasing the curing temperature (see Table 3). Although curing mechanisms are different among specimens, the nth order kinetic model seems to be applied at similar conversion ranges.

4. Conclusions

The effects of solvents on the curing behavior of epoxy/DICY/2-MI resin system were studied using isothermal DSC and FTIR from specimens prepared with unsealed DSC aluminum pans. The presence of solvents results in changes in curing characteristics. In general, the solvent causes a decrease in T_g, curing exotherm, reaction rate, and reaction order because of the temperature dependent curing mechanisms affected by the absorption of heat during the solvent evaporation. The effects of solvents are in the order of toluene>tetra-hydrofuran>acetone. The solvent with a higher boiling temperature results in greater changes in curing behaviors. The compositional differences of the cured resins are confirmed by the FTIR analyses in which the absorption intensities of characteristic functional groups are found to change with the curing temperature and the solvent used.

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