

The curing behaviors of the epoxy/dicyanamide system modified with epoxidized natural rubber

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Abstract

The effects of epoxidized natural rubber (ENR) on the curing behaviors and adhesive strengths of an epoxy (diglycidyl ether of bisphenol-A) and dicyandiamide/2-methyl imidazole system are studied with differential thermal calorimetry (DSC), scanning electron microscopy (SEM), and Instron tensile testing instrument. From DSC analyses of specimens prepared with unsealed aluminum pans, it is obtained that the reaction exotherm, the time to maximal curing rate, the glass transition temperature, the rate constant, and the reaction order of the epoxy system change with respect to the content of ENR added because of the reaction of ENR with the epoxy system. The results obtained from SEM micrographs indicate that the particle size of the rubber phase increases with increasing the curing temperature and the ENR content. The volume fraction of the separated rubber phase also follows the similar trend except at the high curing temperature which implying that the dissolution of epoxy resin in the ENR phase also depends on the curing temperature and the amount of ENR present. The lap shear strengths of specimens prepared with etched aluminum substrates increase with increasing the curing temperature because of a better cure at a higher temperature, but decrease with increasing the ENR content resulting from an adverse effect of ENR on the mechanical properties of the cured resins. © 2004 Elsevier B.V. All rights reserved.

Keywords: Epoxidized natural rubber; Epoxy; Dicyandiamide; Curing kinetics; Phase separation

1. Introduction

The epoxy systems are widely applied in composites, adhesives, and molding compounds due to their outstanding versatility and mechanical properties. However, the general epoxy systems usually suffer the shortage of toughness because of their highly crosslinked but brittle structure. A lot of studies have been done on toughening the crosslinked epoxy resin by using various rubbery, thermoplastic, or even fiber materials and considerable achievements have been obtained [1–7]. Among these, the most popular material used to increase the toughness and impact resistance of the epoxy system is the reactive rubber, e.g. the acrylic rubber, the hydroxy-terminated acrylonitrile butadiene, the epoxy-terminated acrylonitrile butadiene, the hydroxy-terminated butadiene, the epoxy-terminated butadiene, the carboxyl-terminated acrylonitrile butadiene

(CTBN), and the amine-terminated acrylonitrile butadiene (ATBN) rubber [1–5,8–10].

The toughening mechanisms of the rubber in the epoxy resin, especially CTBN and ATBN, have been well studied in the past [1–3,5,11–17]. It is recognized that the dispersed rubber particulate phase emerging from the initially homogeneous epoxy mixture during cure is a decisive factor on determining the toughness enhancement. Many researchers have investigated the effects of the average particle size, the particle size distribution, the volume fraction, and the adhesion strength of the formed rubber phase on the resulted properties of the modified resin [1–3,5,11–17]. It is concluded that the curing condition/procedure, the type of epoxy resin/curing agent, the concentration of the rubber, and the compatibility (and reaction) of the rubber with the epoxy determine the morphology development in the cured rubber/epoxy system, henceforth, affect the mechanical properties of the modified epoxy resin.

In general, a well-dispersed and good chemically bonded rubbery phase that with a suitable volume fraction and particle size/distribution can offer the best toughness increase to a specific epoxy system but without the significant loss

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of the elastic modulus and yield strength. The optimal formulation and curing condition are dependent on the types of epoxy, curing agent, and rubber used.

In spite of the popular reactive rubber mentioned previously, the epoxidized natural rubber (ENR) is also qualified for the reinforcement of the epoxy resin because of its good reactivity and acceptable compatibility with the epoxy matrix. ENR is usually prepared by epoxidation of natural rubber with peracetic, perbenzoic, and perphthallic acids in solutions [18–20]. The introduction of the epoxy group lets ENR have a higher glass transition temperature, a better oil resistance, and a higher polarity than the natural rubber [18–20]. By varying the degree of epoxidation, ENR with different physical properties, such as T_g , resilience, damping, polarity, oil swelling, and compatibility, can be prepared [18,20].

The polar ENR usually have the promising compatibility with lots of polar polymers like polyvinylchloride, nylon, polyethylene oxide, polyethylene-co-acrylic acid, novolac, resol, carboxylated nitrile rubber, and phenoxy resin [21–27]. In addition, with the reactive epoxides and vinyls groups in its backbone, ENR can be utilized in polymer modification and blending by reacting with common epoxy curing agents and chemicals containing OH, NH, COOH, and C=C groups, etc. [18,28]. A number of new applications of ENR could be derived from this great reaction versatility. For example, the novel damping material can be prepared by using the good damping property of ENR.

Interestingly, few studies regarding the use of ENR in modifying the epoxy resin have been published. Kallitisis and Kalfoglou have shown that the compatibility of the ENR with the aromatic polymers follows the order of ENR/Novolac > ENR/Resole \sim ENR/phenoxy > ENR/bisphenol-A epoxy because of the difference in the acid character of the hydroxyl groups in the resins [24]. In this study, the effects of ENR on the curing behaviors and physical properties of an epoxy (diglycidyl ether of bisphenol-A) and dicyandiamide/2-methyl imidazole system are studied with differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and Instron. The morphology change of the cured resin and the resulting adhesion strength are also shown by varying the amount of ENR added and the isothermal curing temperature applied.

2. Experimental

The epoxy resin (Epon-828, diglycidyl ether of bisphenol-A with epoxide equivalent weight = 190) is obtained from the Shell Chemical Co. ENR (Epoxyrene 50, $T_g = -20^\circ\text{C}$, 50 mol% epoxidized) is purchased from Kumpulan Guthrie Berhad Co. Ltd. The curing agent dicyandiamide (DICY, >98% pure) and the accelerator 2-methylimidazole (2-MI, >98% pure) are obtained from Neuto Products Co. and Tokyo Kasei Kogyo Co. Ltd., respectively. DICY particles have an average diameter less than 1 μm . DICY and 2-MI

Table 1
The compositions of formulated specimens

Specimen	Epoxy	DICY	2-MI	ENR50
A	100	9 ^a	0.05	0
B	100	9	0.05	5
C	100	9	0.05	10
D	100	9	0.05	15

^a Parts per hundred parts epoxy resin.

are used as received. Aluminum substrates (2024-A1) are obtained from the local supplier.

The compositions of the epoxy systems tested are listed in Table 1. ENR is premasticated in a two-roll mill starting from room temperature with cooling water on before use. Then epoxy resin is premixed with the required amount of ENR in a ball mill (Retstch 51) starting at 100 $^\circ\text{C}$ for 30 min twice and cooled to room temperature. The epoxy and ENR mixture is subsequently mixed with DICY and 2-MI in the ball mill at room temperature for another 30 min and then degassed under vacuum. DICY is added as nine parts per hundred parts epoxy resins (phr). 2-MI is used as 0.05 phr. The homogeneity of specimens prepared can be confirmed by the small standard deviations obtained from the DSC curing exotherms.

A TA-910 DSC is used to measure the curing exotherm and the glass transition temperature (T_g) of specimens. The isothermal curing exotherm is measured at 150, 160, and 170 $^\circ\text{C}$ under nitrogen environment (with a nitrogen flow rate of 30 ml/min). The specimen is inserted into the DSC cell and then the interested temperature is reached at the maximal scanning rate (200 $^\circ\text{C}/\text{min}$). Three specimens prepared from open (unsealed) Al pans are tested for each isothermal DSC measurement. The exotherm is corrected by the baseline obtained from the empty Al pans. After the isothermal measurement, the same specimen is rescanned at a scanning rate of 20 $^\circ\text{C}/\text{min}$ from -70 to 250 $^\circ\text{C}$ to determine the T_g of the cured resin. The morphology of the epoxy system cured at different temperatures is also examined with scanning electron microscopy (SEM, Hitachi ABT-60) on the bulk fracture surface. The particle size/distribution and volume fraction of the rubber particles are calculated from the SEM image.

Lap shear strength (LSS) measurements are performed according to ASTM D-1002. Aluminum coupons (2024-A1) are cut into strips (10.2 cm \times 2.5 cm), ultrasonically cleaned in an acetone solution at RT for 5 min, rinsed with deionized water, and then blown dry with nitrogen gas before etching. The clean 2024-A1 coupons are subsequently etched in an aqueous acid solution (30 wt.% H_2SO_4 and 8.5 wt.% $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) at 60 $^\circ\text{C}$ for 30 min, rinsed with deionized water, and finally blown dry with nitrogen gas. Different adhesive formulations are used to bond the adherends with a 1.3 cm overlap to form single lap shear joints. A 0.2 mm spacer is applied to keep the bond-line thickness constant. The residual epoxy adhesive along the bondline is trimmed after cure using a razor blade. The specimens are tested to

failure on an Instron using a strain rate of 1.3 mm/min. Five specimens are tested for each measurement.

3. Results and discussion

3.1. DSC

The reaction heats obtained from the DSC exotherms of different specimens are shown in Table 2. For specimen A, the reaction heats are between 77.6 and 85.2 kJ/mol at three curing temperatures, and increase with increasing the curing temperature. This trend is consistent with the result obtained elsewhere [29]. It was shown that a higher curing temperature helped the dissolution of DICY, henceforth, facilitated the reaction of DICY with epoxy and speeded the reaction rate [29]. Additionally, the intermediate compound formed during the reaction also helped the further dissolution and reaction of unreacted DICY [30]. As a result, a greater exotherm is obtained at a higher temperature.

With the addition of ENR, the exotherms are changed. From Table 2, the reaction heats of specimen B are all greater than those from specimen A regardless of the different curing temperature used. This is attributed to the reaction of epoxide groups in the ENR during cure. It is reported that ENR could react with curing agents that usually applied in the epoxy system and release heat [28]. Consequently, the increase of epoxide concentration in specimen from ENR could result in more epoxide/DICY reaction and deliver more reaction heats. In addition, it is interesting to note that the difference in reaction heats between specimens A and B becomes smaller at a higher curing temperature and which may imply that the presence of ENR facilitates the reaction with DICY more effectively at the lower curing temperature.

However, as the content of ENR increases, the reaction heats do not increase with the similar percentages. It is obtained in Table 2 that the reaction heats of the ENR added specimens follow the order of B > C > D, which indicates that the reaction heat decreases with increasing the ENR content. Since the added DICY content in specimens remains unchanged (9 phr), the large increase in ENR content may actually cause a dilution of the curing agent in the resins and decrease the exotherm. Moreover, the change in stoichiometric ratio of epoxide/DICY resulting from abundant ENR can also result in the change in reaction mecha-

Table 3
The time (min) to reach the maximal exotherm (t_p) obtained from DSC curing exotherms

Specimen	Curing temperature		
	150 °C	160 °C	170 °C
A	2.10 (0.10)	1.40 (0.31)	0.64 (0.09)
B	2.71 (0.08)	1.30 (0.08)	0.66 (0.09)
C	3.80 (0.20)	1.74 (0.09)	0.78 (0.08)
D	4.40 (0.09)	2.00 (0.11)	0.95 (0.09)

The numbers inside the parentheses show S.D.

nisms because the reaction of DICY cured epoxy system is sensitive to the relative loading of DICY and epoxy [31,32]. Thus the change in reaction heats among specimens B–D is observed. The influence of ENR on the curing reaction can be confirmed by comparing the following DSC curing characteristics.

As shown in Table 3, the values of t_p (the time to reach the maximal exotherm) decrease with the curing temperature for specimen A but with similar conversions at t_p (see Table 4). This indicates that the initial curing rates (conversions at t_p (%) / t_p (min)) are faster at the higher curing temperature because of the better dissolution of the DICY and the faster reaction between amino and epoxide groups at the higher temperature [29]. This is also consistent with that obtained in curing heats.

With the addition of ENR, the t_p also decreases with the curing temperature but increases with increasing the ENR content and follows the order of B < C < D. Considering the conversion at t_p for specimens B–D, the initial curing rates are in the order of B > C > D and slower in specimen with more ENR. As described previously, the dilution of the curing agent content because of the abundant ENR would cause the observed decrease of the initial curing rate.

It is interesting to note that for specimen A without any ENR, the conversion at t_p is nearly unchanged and much less than those from specimens B–D regardless of the different curing temperatures used. It was described that the t_p could be related to a gel point [33,34]. The result here may indicate that the reaction extent at liquid to glass transition is changed because of the addition of ENR. This would be attributed to that the flexible ENR have a lower glass transition temperature and the addition of ENR affects the stoichiometric balance and the reaction mechanisms (shown below), henceforth, the structure of the crosslinked resin and so the

Table 2
The reaction heats obtained from different specimens

Specimen	Curing temperature		
	150 °C	160 °C	170 °C
A	77.6 (1.8)	82.4 (0.6)	85.2 (1.4)
B	86.4 (0.2)	87.2 (0.1)	89.2 (0.2)
C	81.5 (1.1)	83.2 (0.2)	86.9 (1.7)
D	80.7 (0.8)	82.9 (0.2)	84.2 (0.4)

The numbers inside the parentheses show S.D.

Table 4
The conversion (%) at t_p obtained from different specimens

Specimen	Curing temperature		
	150 °C	160 °C	170 °C
A	17	18	17
B	26	25	25
C	28	28	27
D	29	31	30

Table 5
The kinetic characteristics calculated by Kamal equation from DSC exotherms of different specimens

Specimen	Curing temperature (°C)	k ($\times 10^3$ s $^{-1}$)	m	n
A	150	0.28 ± 0.01	0.33 ± 0.05	1.67 ± 0.05
	160	0.51 ± 0.02	0.35 ± 0.03	1.65 ± 0.03
	170	0.87 ± 0.06	0.27 ± 0.07	1.73 ± 0.07
B	150	0.44 ± 0.04	0.46 ± 0.05	1.54 ± 0.06
	160	0.81 ± 0.01	0.44 ± 0.01	1.56 ± 0.01
	170	1.49 ± 0.18	0.51 ± 0.03	1.49 ± 0.03
C	150	0.50 ± 0.01	0.60 ± 0.05	1.40 ± 0.05
	160	0.95 ± 0.01	0.59 ± 0.03	1.41 ± 0.03
	170	1.83 ± 0.08	0.43 ± 0.01	1.57 ± 0.01
D	150	0.51 ± 0.00	0.67 ± 0.05	1.33 ± 0.05
	160	1.31 ± 0.37	0.66 ± 0.05	1.34 ± 0.05
	170	2.04 ± 0.19	0.40 ± 0.07	1.60 ± 0.13

The goodness-of-fit is better than 99%.

conversion near to gel are changed. This effect of ENR also leads to that the conversion at t_p slightly increases with the ENR content (see Table 4).

The curing kinetic parameters obtained from four specimens are shown in Table 5. The autocatalytic model proposed by Kamal ($d\alpha/dt = k\alpha^m(1-\alpha)^n$, $k = A \exp(-E_a/RT)$, and $m + n = 2$, where k is the overall rate constant, A the frequency factor, E_a the activation energy, R the gas constant, and α is the conversion) is used in the calculation. The kinetic constant ($\ln k$) and the reaction order (n) are obtained from the intercept and the slope of the plot $\ln[(d\alpha/dt)/\alpha^2]$ versus $\ln[(1-\alpha)/\alpha]$ [35]. From simulated curing curves shown in representative Figs. 1 and 2, it is indicated that a good fit is obtained with Kamal model in the studied epoxy systems. As shown in Table 5, a greater n is usually obtained at a higher curing temperature while a lower n is obtained in the presence of ENR. The reaction order n changes with respect to the curing temperature and the content of the ENR. The temperature dependent curing reaction of the DICY cured epoxy system has

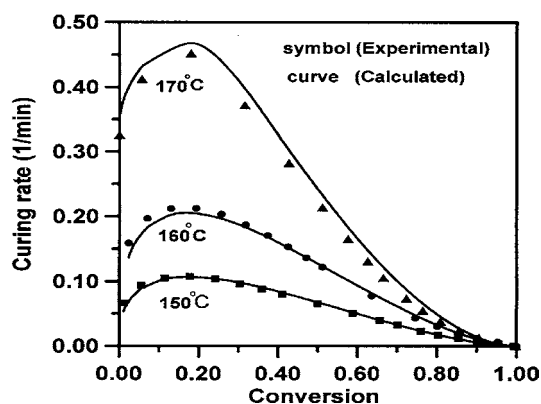


Fig. 1. The simulated and experimental curing curves obtained from specimen A.

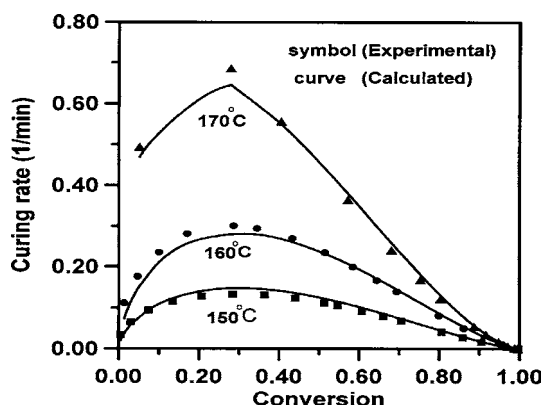


Fig. 2. The simulated and experimental curing curves obtained from specimen C.

been confirmed previously [31,36]. Lin et al. indicated that the DICY cured epoxy system consisted of mainly a low temperature favored etherification and a high temperature favored amine/epoxy reaction [31]. A third reaction, resulting from the formation of melamine by the rearrangement, was also occurred 150 and 200 °C [36]. The competition among these reaction routes is temperature dependent and contributes to the changes observed.

Regarding the effect of ENR, the addition of ENR would change the relative concentration of reactive epoxide and DICY, and the viscosity (and the flexibility or T_g) of the mixed resins, and introduce more epoxide groups but with a different reactivity than the host epoxy resin. The change in initial DICY/epoxy contents could alter the reaction rates of various competing routes by affecting the collision rates between different reactive functional groups. It is confirmed that the DICY/epoxy curing reaction is not only temperature dependent but also DICY/epoxy content dependent [31,32]. Henceforth, the multiple competing reaction routes of the DICY/epoxy are affected and complicated by the presence of ENR. The fact that the reaction order n follows the order of $B > C > D$ at the curing temperatures of 150 and 160 °C but vice versa at 170 °C indicates that there is an interaction effect between the curing temperature and the ENR content on the curing mechanisms. This also confirms the complex influence of ENR on the curing kinetics.

The change in curing characteristics can also be obtained from the rate constant k listed in Table 5. As shown, the system with a higher ENR content and cured at a higher temperature has a greater k . The difference in k among four specimens is more significant at the higher curing temperature. The change in k is expected since k is linked with the activation energy and the frequency factor of the reaction and it is shown above that multiple reaction routes are affected by the curing temperature and the ENR content.

From k obtained at different temperatures, the activation energy (E_a) and the frequency factor (A) are calculated and listed in Table 6. It is obvious that the activation energies and the frequency factors of specimens increase in the order of $A < B < C < D$ indicating that the curing mechanisms

Table 6
The activation energy E_a (kJ/mol) and frequency factor A (s^{-1}) obtained from different specimens

Specimen	E_a (kJ/mol)	$\ln A$
A	85.3	22.9
B	91.8	25.5
C	97.7	27.0
D	104.3	28.9

are sensitive to the ENR content, and the system with a more ENR content has a greater change in the rate constant with increasing the curing temperature, and a greater collision rates during cure. The increase in E_a is usually referred to that the controlling mechanism is changed to a parallel or an alternate reaction route and this result also indicates that the presence of ENR would affect the curing mechanisms.

3.2. Phase separation

The phase separation behavior of the studied ENR/epoxy system can be obtained by analyzing the SEM images of the fracture surface. As shown in Fig. 3, the representative SEM image of one ENR/epoxy system cured at different temperatures, the rubber phase appears as a spherical particle. The spherical rubber domain is usually observed in the polymerization induced spinodal decomposition of the rubber modified epoxy systems [2,37–39]. The formation of the rubber phase is generally attributed to the spinodal decomposition caused by the increase of the molecular weight of the epoxy matrix [2,37,39]. The phase separation starting from an initial rubber/epoxy co-continuous structure and the influence of surface tension in the separated phase usually results in a spherical rubber particle during cure.

The rubber particle size of specimen B increases with increasing the curing temperature (see Table 7). The average diameters are 1.02, 1.13, and 1.38 μm from specimen B cured at 150, 160, and 170 $^\circ\text{C}$, respectively. A similar trend can also be obtained from specimens C and D. The increase of particle size with the curing temperature has been shown

Table 7
The average particle size and the volume fraction of the rubber phase obtained from different specimens

Specimen	Curing temperature ($^\circ\text{C}$)	Average particle size (μm)	Volume fraction (V_f) of rubber phase (%)
B (5.33) ^a	150	1.02 (0.05)	5.93
	160	1.13 (0.05)	6.59
	170	1.38 (0.09)	6.61
C (10.12) ^a	150	1.52 (0.09)	11.79
	160	1.72 (0.07)	14.55
	170	1.83 (0.05)	13.61
D (14.45) ^a	150	1.78 (0.11)	17.23
	160	1.99 (0.10)	20.42
	170	2.24 (0.14)	18.52

The numbers inside the parentheses show S.D.

^a Original volume fraction (%) of ENR-50 in specimen.

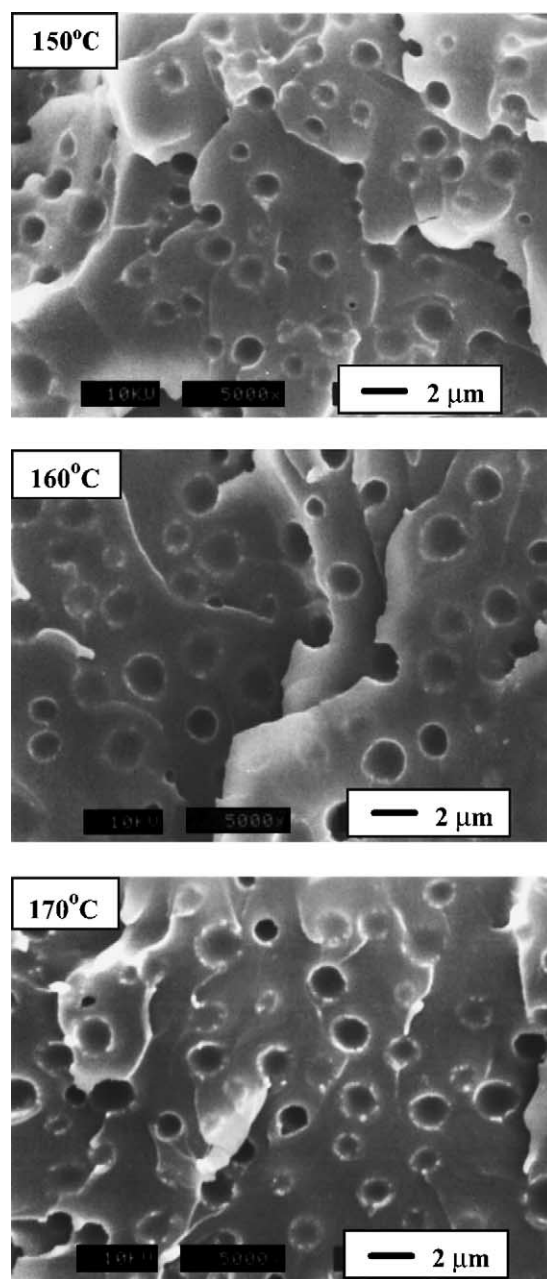


Fig. 3. The representative SEM micrographs obtained from specimen C cured at different temperatures.

in other systems [40]. It is believed that the curing temperature affects the phase separation rate and the polymerization rate differently and which result in the fixation of the separated phase at different time and generate the difference in particle size. A higher curing temperature speeds the cure and gelation and could trap more epoxy resin in the rubber phase before the rubber could be fully phase separated, and then results in a larger particle [40].

The increase in ENR content can also lead to an increase of the particle size of the rubber phase. As shown in Table 7, the average diameters are 1.02, 1.52, and 1.78 μm from specimens B–D cured at 150 $^\circ\text{C}$, respectively. A greater differ-

ence in diameters is present among three specimens as cured at a higher temperature. The increase of particle size with the rubber content is also obtained in other rubber modified epoxy systems [3,40].

The miscibility between ENR and the epoxy resin can be obtained from the volume fraction of ENR in the epoxy matrix after cure. Table 7 lists the volume fractions of the rubber particles in specimens B–D that cured at different temperatures. The volume fraction (V_f) is calculated by using the equation $V_f = (\pi/4)(\sum_i n_i D_i^2 / A_{\text{ref}})$, where n_i is the number of particle i , D_i the diameter of particle i , and A_{ref} is the reference area of the SEM photograph [40]. The original volume fractions of the added ENR before cure are also listed. It is obvious that the volume fractions of the rubber phase increases after cure. Regardless of the error in the calculation of V_f , the increase in V_f is attributed to the epoxy resin dissolved in ENR during cure, which will be shown later.

It is clear in Table 7 that the increase in V_f is varied by changing the curing temperature and the ENR content. For all three specimens, the V_f of specimens cured at 160 and 170 °C are greater than those cured at 150 °C indicating that a higher curing temperature facilitates the dissolution of epoxy resin in ENR. A low curing temperature raises the viscosity slowly; lets rubber have enough time to phase separate, and then could leave less dissolved epoxy in the rubber particle [40]. It is also interesting to note that a maximal V_f is obtained at 160 °C for specimens C and D while for specimen B V_f at 160 °C is similar to that at 170 °C. Comparing to original V_f in specimen, specimens B–D have the percentage increase in V_f about 23.6, 43.7, and 41.3% after 160 °C cure, respectively. The results here indicate that the amount of epoxy resin dissolved in ENR particles have the maximum at an optimal ENR content and the specific curing temperature. This is attributed to the difference in interactive effects of polymerization rate and phase separation rate on the phase separation behaviors in various specimens.

Not only the dissolution of the epoxy resin in ENR but also the dissolution of ENR in the epoxy matrix can be obtained by comparing the change of T_g . It is shown in Table 8 that the epoxy matrix in specimens A–D have T_g near 134, 130, 128, and 121 °C, respectively. It is obvious that the presence of ENR decreases the T_g of the epoxy phase and the T_g decreases with increasing the ENR content. The decrease in T_g of the epoxy matrix because of the addition of modified rubber has been obtained in other studies [38,40,41]. Various

equations have been proposed to calculate the T_g of miscible polymer blends and from which all indicate the increase in miscible content of the low T_g constituent could shift the T_g of miscible blend to a lower temperature. The result obtained here implies that the amount of ENR dissolved in the epoxy matrix follows the order of specimen $D > C > B$. This can also be confirmed from the broadness of the T_g transition region obtained that following the same trend as $D > C > B > A$ (see Table 8).

The change in T_g can also be related to the difference in cured structures since the chemical composition of DICY cured epoxy system depends on the curing temperature, the ratio of epoxy/DICY content, and the type of accelerator. The presence of ENR could affect the relative epoxy/DICY ratio and then cause the curing mechanism and chemical composition to change, consequently, result in the change of T_g . However, the curing temperature dependent effect on T_g for the ENR added specimen is small in this study because T_g obtained from the same formulation that cured at different isothermal temperatures and subsequently postcured at a higher temperature remains almost unchanged.

The T_g of the main rubbery phase in specimens B–D cured at 170 °C are 40, 38, and 39 °C, respectively. All of them are much greater than the T_g (–20 °C) of ENR, which is also observed as a very small signal in DSC thermograms. Interestingly, T_g 's of these three specimens do not change with respect to the increase in V_f which are 24.0, 34.4, and 28.1% increases for specimens B–D at 170 °C, respectively, henceforth, are not proportional to the amount of epoxy resin dissolved in ENR (see Table 7). This implies that considerable amounts of ENR also react with the DICY/epoxy or self-crosslink in the rubbery phase and the reacted (or cured) structure in ENR plays a major role in determining the T_g of this reacted rubbery phase. The increase in T_g of reacted ENR in the cured resin is also shown by Bhowmick and coworkers [42].

The distribution of particle sizes of rubbery phase from ENR/epoxy systems can be obtained in Fig. 4. It is clear that all distributions are broad and asymmetry. But the distribution becomes more symmetric with an increase in ENR content. In spite of this, the distribution is also affected by the curing temperature (see Fig. 5). The particle size distribution during the polymerization induced phase separation process is simulated by Chan and Rey [37]. It is indicated that the separated phase first evolves from a wide distribution of particle sizes and shapes and then gradually becomes one with narrow size and shape range [37]. Many factors such as miscibility, diffusion rate, viscosity, polymerization rate, and the phase separation rate all can affect the formation of the separated domain and result in the different distributions observed.

3.3. Lap shear strength

To obtain the adhesion strength of the formulated ENR/epoxy systems, the LSS of bonded specimens prepared

Table 8
 T_g (°C) obtained from specimens cured at 170 °C

Specimen	T_g of rubber constituent	T_g of epoxy constituent	
		$T_{g\text{broadness}}$	$T_{g\text{epoxy}}$
A		14 (1)	134 (1)
B	40 (3)	18 (1)	130 (2)
C	38 (2)	20 (1)	128 (1)
D	39 (6)	22 (2)	121 (1)

The numbers inside the parentheses show S.D.

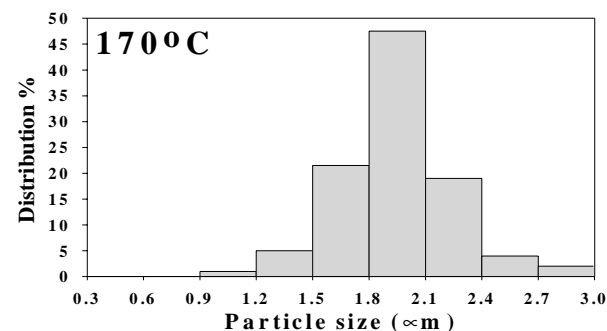
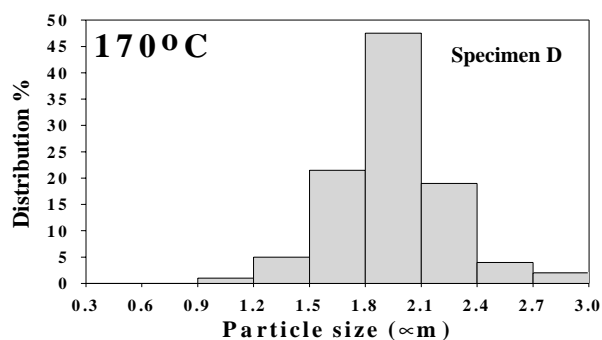
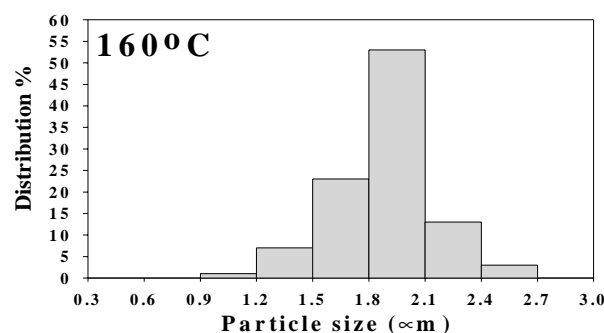
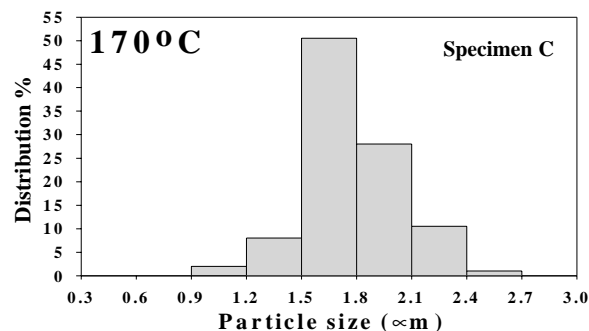
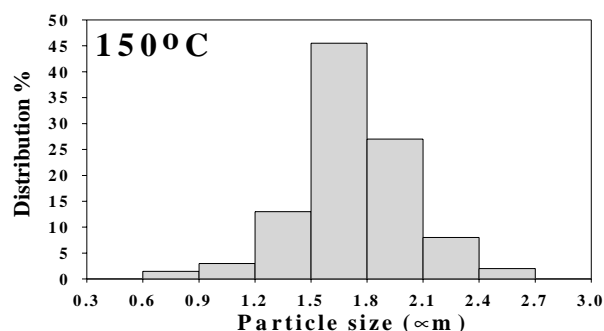
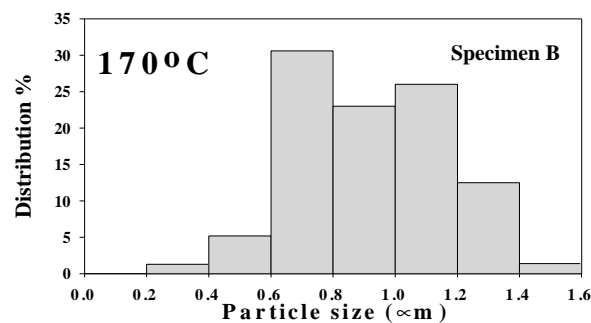


Fig. 4. The particle size distributions obtained from different specimens cured at 170 °C.

Fig. 5. The particle size distributions obtained from specimen D cured at different temperatures.

from four formulations are tested and listed in Table 9. The LSS from specimen A are 4013, 4338, and 4542 psi when cured at 150, 160, and 170 °C, respectively, and increase with the curing temperature. This is consistent with the DSC result in which a better cure is obtained at a higher temperature.

Surprisingly, the addition of ENR decreases the LSS. It is obvious in Table 9 that the LSS from formulation B are all lower than those from formulation A for all curing temperatures used. The presence of ENR could not enhance the adhesion strength. This surprising result is attributed to the effect of ENR on the cure of the epoxy system. The fact that the failure strains from specimen B are all lower than those of specimen A may imply an inferior cured structure. This seems to be contradictory to the previous results obtained from the V_f and T_g in which a soft and flexible cured ENR/epoxy system should be reached because of the dissolution of ENR in the epoxy matrix. It is believed that ENR

Table 9
The lap shear strength obtained from different specimens

Specimen	Curing temperature (°C)	Maximum strength (psi)	Strain (%)
A	150	4013 (361)	7.9 (0.3)
	160	4338 (288)	8.1 (0.4)
	170	4542 (128)	8.8 (0.2)
B	150	3753 (361)	7.73 (0.3)
	160	3984 (161)	7.9 (0.5)
	170	4361 (528)	8.1 (0.5)
C	150	3300 (336)	6.7 (0.5)
	160	3565 (272)	7.0 (0.8)
	170	3578 (407)	7.2 (0.8)
D	150	2415 (427)	5.4 (0.8)
	160	2696 (287)	5.5 (0.5)
	170	2886 (265)	5.8 (0.4)

The numbers inside the parentheses show S.D.

affects the stoichiometric ratio of the epoxy/DICY because of its presence and participation in the curing reaction (confirmed by DSC) and then cause a structural change in the cured epoxy matrix. This may lead to that an inferior cured system is formed in specimen B.

Regarding the LSS from formulations C and D, a similar result can be obtained. It is shown in Table 9 that the LSS follow the order of $A > B > C > D$. The more the ENR is added, the lesser is the LSS. The failure strains also follow the same trend. As previously stated, this decrease in LSS could be attributed to the adverse affect of ENR on the cured structure of the epoxy matrix.

4. Conclusions

The effects of ENR on the curing behaviors and physical properties of an epoxy/dicyandiamide/2-methyl imidazole system are shown. It is obtained from the DSC analyses that the reaction exotherm, the time to maximal curing rate, the glass transition temperature, the rate constant, and the reaction order of the epoxy system can be changed by the presence of ENR because of the participation of ENR in the curing reaction system. The effect of ENR on the curing characteristics becomes more significant in the system with more ENR. The result of SEM indicates that the particle size of the rubber phase increases with increase in the curing temperature and ENR content. The volume fraction of the separated rubber phase also follows the similar trend except at the high curing temperature indicating that the dissolution of epoxy resin in the ENR rubber phase also change with respect to the curing temperature and ENR content. The lap shear strengths obtained from different specimens increase with increase in the curing temperature due to a better cure at the higher temperature, but decrease with increasing the ENR content resulting from an inferior structure formed in the presence of ENR.

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