Effects of Composition of Hardener on the Curing and Aging for an Epoxy Resin System

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ABSTRACT: Different mixture ratios of Shell Epon 828 (based on diglycidyl ether of bisphenol A, DGEBA) and Shell EPI-CURE 3046 (based on triethylenetetramine, TETA) were evaluated under different environments of isothermal curing at 80°C in DSC, room temperature curing in air, and aging in water at 45°C. The curing reactions were monitored using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and infrared spectroscopy (IR). It was shown that the initial curing rate increased with the amount of hardener. However, the epoxy groups in samples with excess hardener were prone to reaction with primary amines located at the ends of TETA molecules, resulting in a less dense epoxy network. During aging in water at 45°C, significant effects of water on the postcure and the increased water absorption with an increase of hardener amount were observed. The DMA results show that the samples with hardener around stoichiometric composition have the greatest storage modulus while curing in air environment. However, the samples with hardener much less than stoichiometric composition have greater storage modulus under aging in water at 45°C. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 580–588, 2006

Key words: aging; curing of polymers; epoxy; hardener; kinetics

INTRODUCTION

Epoxy resins are thermosetting plastics with a wide range of applications where there are great mechanical stresses involved. Epoxy typically consists of two parts: the resin and a hardener, or catalyst, which is always mixed with the resin to cause it to cure, or set. The ratio of hardener to resin varies among brands of epoxy, however, this is usually set to the stoichiometric ratio calculated by supposition of full reaction for both epoxy groups and amine groups. Over the past few years, there has been an increasing interest in problems due to moisture absorption by epoxies and epoxy composites,[1–4] such as degradation of mechanical properties, lowering of the glass transition temperature, and so forth. Hardener plays an important role in water absorption of epoxy,[5,6] and therefore should correlate to these aging problems of epoxy under moisture environment. Correspondingly, the optimizing ratio of hardener to epoxy resin used for moisture environment might not be the same as that used for dry environment.

Even curing under dry condition, the kinetics of cure varies with the ratio of hardener to epoxy resin.

The typical reactions between epoxy and amine hardener are shown in Scheme 1.[7]

Grillet and coworkers[8] found that the reaction rate constant for secondary amines [Scheme 1(b)] is about $0.8 \sim 0.9$ of the reaction rate constant for primary amines [Scheme 1(a)] in a DGEBA/DDS diamine system. Ellis[9] found that the relative rates of reaction of secondary to primary amines increased with cure temperature, 0.25 at 22°C and 0.75 at 50°C. The etherification reaction [Scheme 1(c)] is usually much slower than the amine-epoxy reactions.[9,10] Therefore, for a hardener-rich system, the reactions between the epoxy group and the primary amine dominate the curing reaction, and the etherification reaction can be ignored. For epoxy-rich systems, the etherification reaction might dominate the curing reaction after most of the primary amines and secondary amines are consumed during the initial curing stage.

The different kinetics of cure for different compositions of hardener can lead to different structures and crosslink densities of the epoxy network. Under moisture environment, the kinetics of cure becomes more complicated. It was reported that water could accelerate the curing reaction.[11,12] From the chemical point of view, when epoxy cures or postcures in the presence of water, additional ring-opening polymerization can happen,[2,12] which greatly increases the total reaction rate. From the physical point of view, water can influ-
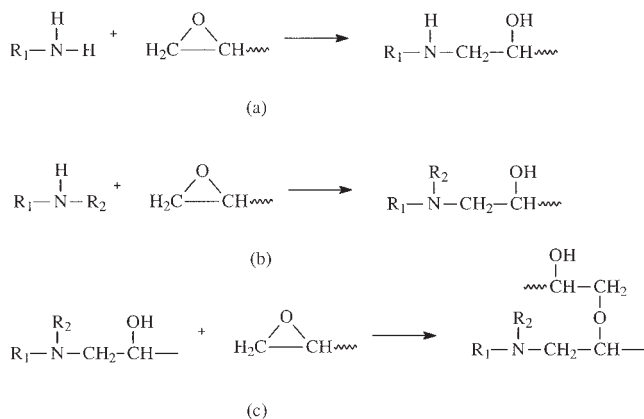
Scheme 1 Chemical reactions for a diepoxy-diamine system: (a) epoxide ring-opening reaction with primary amine, (b) epoxide ring-opening reaction with secondary amine, and (c) etherification reaction between reacted and unreacted epoxy groups.

ence the molecular mobility in the epoxy network; therefore, it might influence both reaction rate and degree of cure. The effects of water on cure and postcure of epoxy can change the epoxy network formation. The change of network formation turns over to influence the water absorption as well. Although effects of water on the curing and properties of epoxy resin exist in various compositions of epoxy resin, the different epoxy/hardener mixture ratios respond in different ways to water. The application of epoxy becomes more and more popular for field applications in construction, either repair or coating. Since humidity and epoxy/hardener mixture ratio cannot always be well controlled in field applications, the information on these effects becomes very important. However, such kinds of studies have not been fully considered so far.

In this work, the effect of the epoxy/hardener mix ratio on the curing reaction was evaluated under both air environment and wet environment. The influences of mix ratio on formation of epoxy network, water absorption, glass transition temperature, and dynamic modulus are discussed.

EXPERIMENTAL

Materials

The epoxy resin used was Shell Epon 828, a diglycidyl ether of bisphenol A with molecular weight about 377, which has the following chemical structure:
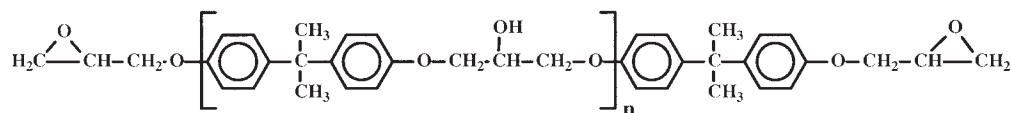
The curing agent used was Shell EPI-CURE 3046, an aliphatic diamine with equivalent weight about 90, which mainly consists of linear triethylenetetramine (TETA) and has the following chemical structure:
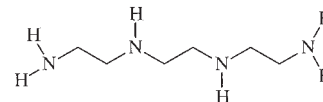
Structure 2

As recommended by the supplier, the curing agent concentration for the stoichiometric ratio is 47 parts by weight per hundred parts of the resin (phr) for this system. In this study, the samples were prepared containing 35, 42, 52, and 60 parts of EPI-CURE 3046 curing agent per hundred parts of Epon 828 resin using the following procedure: The curing agent and epoxy resin were well mixed. Then the mixture was poured into a mold and cured at room temperature (20°C ~ 25°C) for 7 days. The thickness of the epoxy plates was nearly the same (2.6 mm) by controlling the weights of the mixture for curing, which were calculated by area of mold × thickness of epoxy plate × density of resin. The densities of resin used were measured from tentative samples with the same amount of hardener, cured at the same conditions. The cured epoxy plate was cut to 25.4 mm × 25.4 mm squares for moisture absorption tests and a 12.7 mm × 50.8 mm rectangle for DMA tests.

Differential scanning calorimetry (DSC)

The DSC 2010 (TA Instruments) was operated in an isothermal mode to determine the kinetic parameters. The instrument was preheated to the study temperature, 80°C, and kept stable before mixing epoxy and hardener. Then, 10–15 mg samples were sealed in aluminum pans before introducing them into the calorimeter. The isothermal curing tests were conducted at 80°C for 5 h.

Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis was conducted using TA Instruments DMA 983 in fixed frequency mode. The loading frequency was 1 Hz, and the heating rate was 2°C/min. The storage modulus, loss

Structure 1

modulus, and phase angle were recorded from 30 to 160°C.

Water uptake test

The specimens were immersed in water at 45°C to measure the water uptake. Specimens were weighed with an accuracy of 0.01 mg.

Density measurements

Samples for density measurements were 25.4 mm × 25.4 mm squares. For each sample, both the weight in air and the weight in water were measured. From the density of water, the density of samples was calculated.

Infrared (IR) spectroscopy

Reflect infrared spectra of the epoxy systems were recorded using a Thermo Nicolet 670 Fourier transform IR spectrometer with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Isothermal curing at 80°C in DSC

DSC can be used to measure the exothermic heat directly during the curing reaction. Therefore, it can be employed to continuously monitor the process of the curing reaction. The studied epoxy system is normally used at room temperature. However, the exothermic heat of the studied epoxy system, curing at room temperature, is too low to be measured accurately by DSC. Nevertheless, the curing kinetics of epoxy resin at one temperature can give useful information for the study of the curing reaction of the same epoxy resin system at another temperature. The following equation relates curing kinetics at different temperatures[13]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT_c}\right)f(\alpha) \qquad (1)$$

where A is a constant, E is the apparent activation energy for the overall reaction, T_c is the isothermal cure temperature, and $f(\alpha)$ is assumed to depend on α and to be independent of the cure temperature.

Even though DSC cannot be used to monitor the reaction heat accurately for studying epoxy system curing at room temperature, the high curing temperature can result in more unmeasured exothermic heat before the instrument reaches equilibrium temperature. In this study, the mixture of epoxy and curing agent was cured at 80°C in DSC for 5 h. Since the curing reaction of this particular system can happen at room temperature and becomes significant after heating, the reduction of equilibrium time is crucial to
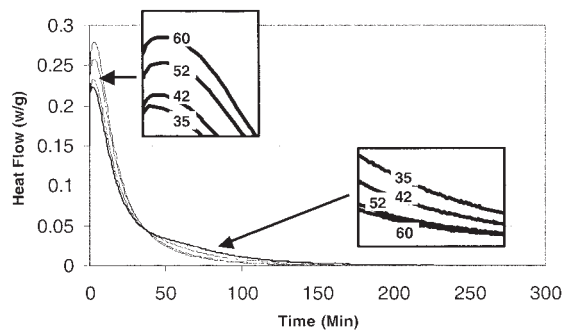
Figure 1 Plot of heat flow versus time of an Epon 828/EPI 3046 system with different ratios of hardener to epoxy resin curing in DSC at isothermal temperature of 80°C.

obtain more precise results. Two experimental techniques exist for reaching stable isothermal temperature.[10] In the first one, the calorimeter is preheated to the desired reaction temperature before the unreacted sample is placed in the calorimeter cell. In the other technique, the sample is placed in the calorimeter cell at a fairly low temperature at which no significant reaction could take place over a short time period, and the temperature is then raised as rapidly as possible to the predetermined reaction temperature. The time from placing the sample to establish equilibrium by the preheating calorimeter method was about 1 min, while the other method took about 5 min to establish equilibrium. Even though neither way can prevent misreading information for the very early stage of curing, the first one seems to be more appropriate and was used in this study.

The DSC curves are shown in Figure 1. It can be seen that during the initial reaction stage, the heat flow, which is in proportion to the reaction rate, increases with the increasing of the ratio of hardener to epoxy resin. Based on the kinetic model of epoxy-amine reactions, catalyzed by the hydroxyl generated by the reaction or by initial hydroxyl or impurities, the reaction rate, in terms of basic concentrations, can be described by the following equation[13]:

$$\frac{d\alpha}{dt} = (K_1' + K_1\alpha^m)(1 - \alpha)^a(B - \alpha)^b \qquad (2)$$

where K_1' and K_1 are constants proportional to rate constants, and B is the initial ratio of diamine equivalents to epoxide equivalents (B equals 1.0 when stoichiometric quantities of the reactants are mixed). a and b are semiempirical coefficients.

During the initial stage, $\alpha \approx 0$, eq. (2) can be simplified to:

$$\frac{d\alpha}{dt} = K_1'B^b \qquad (3)$$

Ratio of hardener to epoxy		Exothermic heat		
Weight : Weight	Equivalent : Equivalent	J/g mixture	kJ mol^{-1} of epoxide	kJ per equivalent of amine
35 : 100	0.733 : 1	383.7	97.6	133.2
42 : 100	0.879 : 1	372.5	99.7	113.3
52 : 100	1.089 : 1	380.2	108.9	100.0
60 : 100	1.257 : 1	389.8	117.6	93.6

b is a positive parameter. Therefore, the rate of reaction $d\alpha/dt$ increases with the hardener content.

During the later reaction stage, the reaction rate for a hardener-rich system becomes lower than that for an epoxy-rich system, as shown in Figure 1, which is due to faster consumption of reactants. This results in very few epoxy groups left for the reaction with amine.

The exothermic heat was calculated by integrating the area below the curves in Figure 1 and is listed in Table I. The plot of exothermic heat per mol epoxide versus time is shown in Figure 2. It can be seen that the exothermic heat per mol epoxide increases with the increase of hardener amount in isothermal curing at 80°C, which is consistent with the DSC results by temperature scanning mode.[14] Higher content of hardener leads to more completed reaction of epoxy groups, resulting in higher exothermic heat per mol epoxide. It was reported[10] that the exothermic heat per mol epoxide is nearly a constant, 107 ± 4 kJ mol^{-1} of epoxide, for various epoxy/diamine systems. Nevertheless, the exothermic heat per mol epoxide for the sample with 60 phr hardener is 117.6 kJ mol^{-1} of epoxide, much higher than the reported value.

de Bakker et al.[15] reported that the exothermic heats for primary amine and secondary amine are 83 ± 2 and 131 ± 9 kJ mol^{-1} of epoxide, respectively. While the amount of epoxide reacting with the primary amines is equal to the amount of epoxide reacting with the secondary amines, the average exothermic heats equal 107 kJ mol^{-1} of epoxide. However, the TETA hardener is a hexafunctional compound with two primary and two secondary amine groups per molecule. A TETA hardener molecule can provide a maximum of two primary amines and four secondary amines to react with epoxide. Two secondary amines located at each end of a TETA molecule are products of primary amine-epoxide reaction, while the other two secondary amines located at the middle of a TETA molecule are pre-existing. The pre-existing secondary amine groups increase the concentration of secondary amine groups and, therefore, increase the chance of secondary amine-epoxide reaction. In hot environments, the

difference between the reaction rate for primary amine-epoxide reaction and secondary amine-epoxide reaction is small,[8,9] so the total secondary amine-epoxide reactions can be more than the total primary amine-epoxide reactions due to higher concentration of secondary amine groups compared to primary amine groups. Since the amount of heat generated by per mol secondary amine reactions is more than the amount of heat generated by per mol primary amine reactions, the exothermic heat per mol epoxide in the studied system can be more than the reported 107 kJ obtained from the conventional epoxy-diamine system, in which the amount of reactable primary is equal to the amount of reactable secondary amines.

Curing at room temperature

DSC can also be used to measure exothermic heat for the residual curing reaction. Thus, the degree of conversion α, can be calculated with:

$$\alpha = \frac{\Delta H_0 - \Delta H_{r,t}}{\Delta H_0} \tag{4}$$

where ΔH_0 is the total exothermic heat for a fully curing reaction, and $\Delta H_{r,t}$ is the residual reaction heat for the curing reaction evolved up to a certain time t. By using dynamic temperature scanning mode, $\Delta H_{r,t}$, which equals the area between the curve of heat flow versus time and the baseline, as shown in Figure 3, can be measured from DSC results. With the same heating rate of 10°C/min, four different compositions of Epon 828/EPI-CURE 3046 samples after 7 days curing at room temperature were tested. The exothermic heats for the residual curing reaction are 52.9, 46.6, 43.2, and 35.5 J/g for samples with 35 phr, 42 phr, 52 phr, and 60 phr of hardener, respectively. Using the ΔH_0 obtained from isothermal curing at 80°C (listed in Table I), the degree of conversion α can be calculated as 86.2%, 87.5%, 88.6%, and 90.9% for samples with 35 phr, 42
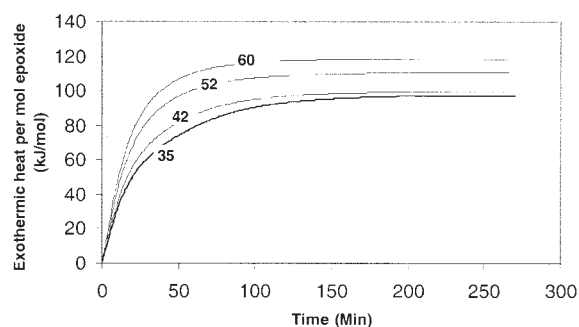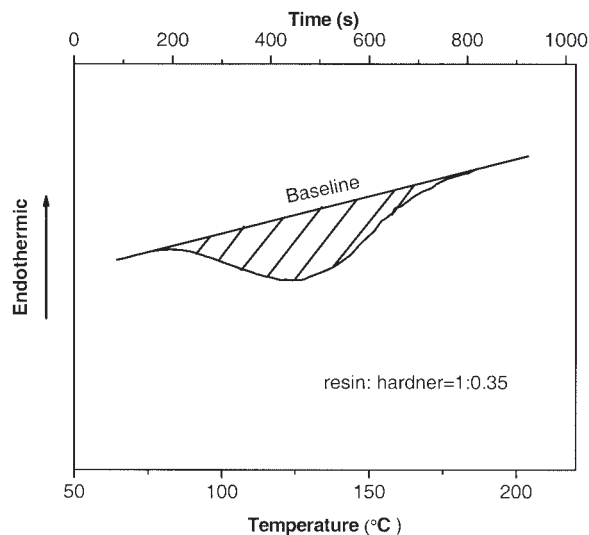

Figure 2 Plot of exothermic heat per mol epoxide versus time of an Epon 828/EPI 3046 system with different ratios of hardener to epoxy resin curing in DSC at isothermal temperature of 80°C.

Figure 3 DSC curve measured by using dynamic temperature scanning mode for an Epon 828/EPI 3046 system after curing at room temperature for 7 days.

phr, 52 phr, and 60 phr of hardener, respectively. The degree of conversion increases with the increase of hardener amount, which is consistent with the results of isothermal curing at 80°C.

After an additional 500 day curing at room temperature, it is hard to see the residual curing reaction peak by DSC. The calorimetric method is not precise enough to measure the differences of degree of cure in the high degree of cure range. However, the remain-

ing epoxy groups can still be observed by FT-IR. Through the ratio of the area or height of the characteristic to the reference absorbance peak, the conversion rate of the epoxy group can be calculated.[16,17]

The characteristic epoxide absorption band is at about 914 cm^{-1}, which can be used to monitor the consumption of epoxide during the curing reaction. The method described by Dyakonov et al.[17] was used in this study. The integrated absorbance of the epoxide band at 914 cm^{-1} was normalized with the integrated absorbance of the phenyl band at 1034 cm^{-1}, which is the band associated with the phenyl group and is taken to be chemically unmodified (as sketched in Fig. 4). The conversion rate of epoxy rings, α_e, was calculated by the following equation:

$$\alpha_e = \frac{R - R_0}{R_0} \tag{5}$$

where $R = Area_{914}/Area_{1033}$ at the specified ratio of hardener to epoxy, and R_0 is R of the resin without hardener.

The results obtained are shown in Table II. The α_e increases with the increasing of hardener amount. It should be noted that the α_e, the conversion rate of epoxy rings, is not always equal to the α in eq. (4), which means the degree of curing reaction. For an epoxy-rich system, the epoxide cannot be fully reacted. Therefore, the α_e does not approach to 1, while α, the degree of curing reaction, approaches 1. For a hardener-rich system, the epoxy groups can be almost
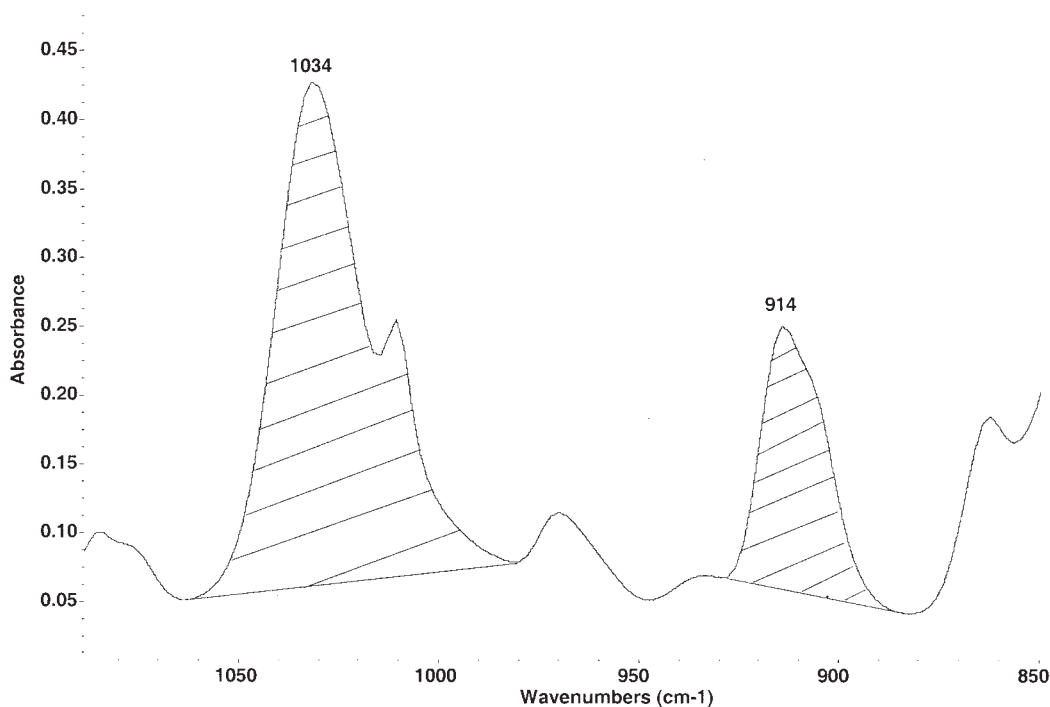
Figure 4 Absorbances in the infrared (IR) spectrum used to determine cure state.
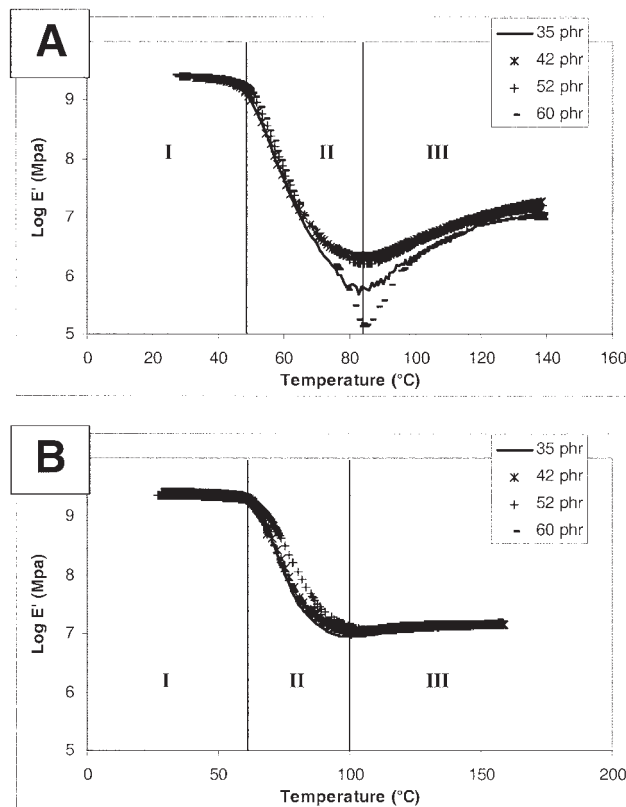
TABLE II
Normalized Integrated Absorbance of Epoxy Band and Conversion Rate of Epoxy Groups as a Function of the Hardener/Resin Ratio after 507 Days Curing at Room Temperature

Ratio of hardener to epoxy	Normalized integrated absorbance of epoxy band	Conversion rate of epoxy groups
Weight : Weight	$R = \dfrac{Area_{914}}{Area_{1033}}$	$\alpha_e = \dfrac{R - R_0}{R_0}$
0 : 100	0.338	0
35 : 100	0.0475	0.759
42 : 100	0.0232	0.931
52 : 100	0.0097	0.973
60 : 100	0.0050	0.985

Figure 5 The storage modulus curves of an Epon 828/EPI 3046 system with different ratios of hardener to epoxy resin after curing at room temperature for 7 days (A) and 507 days (B).

completely reacted; therefore, the α_e is nearly equal to α. The equivalent ratio of hardener to epoxy for the samples with 35 phr of hardener is 0.733 : 1. The full reaction of epoxide and amines will result in 0.733 of the conversion of epoxy rings; therefore, the conversion rate of epoxy rings due to reaction with amines should be less than 0.733. However, the α_e for samples with 35 phr of hardener is 0.759. The high conversion rate of epoxy rings might be due to the etherification reaction between reacted and unreacted epoxy groups [Scheme 1(c)], which is quite slow at room temperature, but might show effects after long-term (507 days) cure.

It was also reported that DMA is more sensitive than DSC in monitoring T_g. In the past decade, equations and models relating T_g to conversion have received widespread acceptance, establishing T_g as a primary measurement of degree of cure.[10] Unlike the residual heat of reaction, T_g displays increasing sensitivity to cure with increasing conversion, thus allowing the final cure state to be more easily and accurately assessed. Thus, DMA is often employed to monitor the changes in cure degree, especially during durability tests.

DMA specimens were tested after curing for 7days and 507 days at room temperature. The glass transition temperatures were obtained using the tempera-

ture at peaks of both phase angle curves and loss modulus curves. The T_gs are listed in Table III.

Comparing the 7 day curing results to the 507 day curing results, the T_gs increase by 15.9 ~ 22.1°C, indicating that the postcure at room temperature is quite slow but does exist. There is no obvious difference between T_gs for four kinds of compositions after 7 days curing at room temperature. The difference between T_gs after 507 days curing is also quite small while the ratios of hardener to epoxy vary from 35 phr to 60 phr. Figure 5(a) shows the storage modulus curves of samples cured at room temperature for 7

TABLE III
T_gs Measured by DMA for the Various Hardener Compositions After 7 Days and 507 Days Curing

Ratio of hardener to epoxy	After curing at room temperature for 7 days		After curing at room temperature for 507 days	
Weight : Weight	T_g by peak of phase angle	T_g by peak of loss modulus	T_g by peak of phase angle	T_g by peak of loss modulus
35 : 100	59.5	48.9	76.8	67.1
42 : 100	60.1	50.7	77.9	66.6
52 : 100	60.6	52.7	82.7	70.6
60 : 100	60.1	52.7	76.0	65.9

TABLE IV
T_g Measured by DMA for the Various Hardener Compositions After 14 Days and 500
Days Aging in 45°C Water

Ratio of hardener to epoxy	After aging in 45°C water for 14 days		After aging in 45°C water for 500 days	
Weight : Weight	T_g by peak of phase angle	T_g by peak of loss modulus	T_g by peak of phase angle	T_g by peak of loss modulus
35 : 100	150.0	77.3	102.6	80.6
42 : 100	95.3	73.5	97.3	72.8
52 : 100	88.4	69.0	89.4	67.0
60 : 100	77.7	53.4	77.9	50.4

days. In region III of Figure 5(a) (the rubber status region), the storage modulus increases with the increase in temperature, indicating significant residual curing reaction during the DMA test. However, the curves of Figure 5(b), which are storage modulus curves of samples curing at room temperature for 507 days, are nearly level lines in region III, indicating that the samples are almost fully cured after 507 days. These results are consistent with DSC results. According to the result of isothermal curing at 80°C in DSC (Fig. 1), the initial reaction rate increases with the hardener amount. The same trend is expected while cured at room temperature; therefore, the sample with 60 phr of hardener should have the highest degree of cure among four compositions. The measurement of residual curing reaction for samples cured at room temperature for 7 days also proves that the two hardener-rich systems have less residual curing reaction, that is, a higher degree of cure, compared to the two epoxy-rich systems. However, the T_g of the sample with 60 phr of hardener listed in Table III is not obviously higher than other T_gs. Moreover, the storage modulus of the sample with 60 phr of hardener after 7 day curing [shown in Fig. 5(a)] is the lowest among the studied systems.

While T_g and modulus usually increase with the increase of degree of cure, the contradiction can be explained as follows: According to Ellis,[9] at 22°C, the rate of the reaction between secondary amine and epoxy is just equal to one-fourth of the rate of the reaction between primary amine and epoxy. Thus, during the initial curing stage at room temperature, the main reaction is the reaction between primary amines and epoxide unless there is not enough primary amine to react. The samples with 60 phr of hardener have a large excess of hardener. Therefore, the main reaction during the initial stage is the reaction between epoxide and primary amines, which are located at the two ends of the hardener molecule. Then, the whole length of the hardener molecule serves as a bridge between the epoxy molecules. This is a fairly loose structure, which may result in lower modulus and T_g. In addition, if there is an excess amount of hardener, some of the hardener molecules

did not have an opportunity to serve as bridges between the epoxy molecules. As such, the excess hardener molecules may serve as lubricating agents. This, in turn, has the effect of lowering the tightness of the network, resulting in lower modulus and T_g.

With the decrease of hardener amount, the secondary amines in the middle of the hardener molecule have more chance to be involved in the reaction, and then the bridge between the epoxy molecules is less than the length of the whole hardener molecule, which is the main bridge in the case of excess hardener. This is a tight structure, which may result in higher modulus and T_g. Both Figure 5(a) and Figure 5(b) show that the storage modulus for the two groups with hardener around stoichiometric composition (42 phr, 52 phr of hardener) are higher than the storage modulus for the other two groups (35 phr, 60 phr of hardener). The reason for low storage modulus for the samples with 60 phr of hardener has been discussed above. The samples with 35 phr of hardener have much less hardener than stoichiometric composition. The reaction rate is smallest among the four compositions according to DSC and FT-IR analysis, resulting in lower modulus and T_g. In addition, due to the excess number of epoxy molecules, some epoxy molecules may not be involved in the reactions or may be involved partially in the reactions (only one end of the epoxy ends are connected), which may serve as lubricating agents, resulting in lower modulus and T_g. It seems that the resins with hardener around stoichiometric composition have optimal properties while cured under dry environments.

Aging in 45°C water

Water can accelerate the curing reaction and increase the mobility of polymer chains, increasing the degree of cure over short time duration, consequently increasing glass transition temperature and crosslink density. However, the plasticizing effect of water can also lower glass transition temperature.

DMA tests were conducted after aging in 45°C water for 14 days and 500 days. The glass transition temperatures were obtained using the temperature at
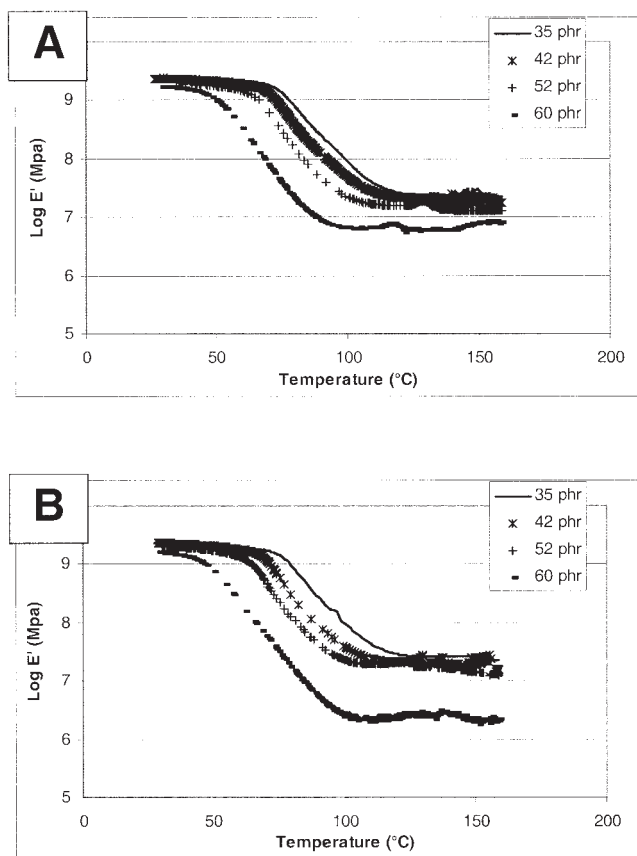
Figure 6 The storage modulus curves of an Epon 828/EPI 3046 system with different ratios of hardener to epoxy resin aging in 45°C water for 14 days (A) and 500 days (B).

peaks of both phase angle curves and loss modulus curves. The T_gs are listed in Table IV.

After aging in water, the phase angle curves become wide and it is not precise to get peak temperatures. Comparing the T_gs after aging in water listed in Table IV to T_gs of dry samples listed in Table III, surprisingly, for two epoxy-rich samples with 35 phr and 42 phr of hardener, after aging in 45°C water for just 14 days, the T_g increases by 90.5, 35.3°C by measuring the peak of the phase angle and 28.4, 22.8°C by measuring the peak of the loss modulus, respectively. Considering that two samples had already absorbed 2.56% and 2.79% water after aging in 45°C water for 14 days, the T_gs without the plasticizing effect of water could even be higher, indicating the strong accelerating effects of water on postcure. The T_g for the samples with 60 phr hardener do not show obvious increase compared to the T_g of the sample before immersion. The sample with high hardener content cures fast; therefore, there is no large room for postcure. Moreover, the samples with 60 phr hardener absorb more water, and the more plasticizing effect of water offsets the increasing of T_g by postcure. Figure 6 shows the storage modulus curves after aging in 45°C water for 14 days (a) and 500 days (b). The level line in the rubbery status region

indicates full cure after just 14 days aging in 45°C water. The modulus decreases with an increase of hardener amount. The water absorption curves (Fig. 7) show increased water absorption with an increase of hardener amount. The stronger plasticizing effect of water for samples with higher hardener content decreases the modulus. This results that the sample with 35 phr hardener, which is much less than stoichiometric composition, has the greatest storage modulus among the four compositions after aging in water.

The initial linear curves in Figure 7 indicate that diffusion of all specimens followed the Fickian law. The diffusion coefficients can be calculated with the Fickian diffusion equation:

$$\frac{M_t}{M_m} = 4\left(\frac{Dt}{h^2}\right)^{1/2}\left[\frac{1}{\pi^{1/2}} + 2\sum_{n=1}^{\infty}(-1)^n ierfc\frac{nh}{2(Dt)_{1/2}}\right] \quad (6)$$
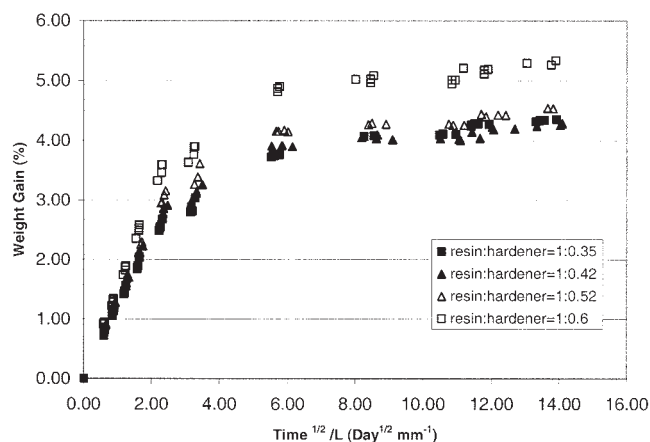
where M_t, the weight change in the specimen, is defined by:

$$M_t = \frac{\text{Weight of specimen} - \text{Weight of dry specimen}}{\text{Weight of dry specimen}} \times 100\% \quad (7)$$

and M_m is the maximum moisture content, D is the diffusion coefficient, and h is the thickness of the sample.

When M_t/M_m is less than about 0.5, eq. (6) can be approximated by the following:

$$\frac{M_t}{M_m} = \frac{4}{h}\sqrt{\frac{Dt}{\pi}} \quad (8)$$

Figure 7 Water absorption curves of an Epon 828/EPI 3046 system with different ratios of hardener to epoxy resin aging in 45°C water.

TABLE V
Density for Samples with the Various Hardener Compositions Aging in Dry Environment and Aging in 45°C Water for 500 Days

Ratio of hardener to epoxy (w/w)	Aging in dry environment for 500 days (g/cm^3)	Aging in 45°C water for 500 days (g/cm^3)	Volume expansion per volume resin (1)	Volume of water absorption per volume resin (2)	(2) − (1) (void volume)
35 : 100	1.1446	1.1497	3.88%	4.96%	1.08%
42 : 100	1.1339	1.1395	3.74%	4.83%	1.09%
52 : 100	1.1264	1.1306	4.14%	5.10%	0.96%
60 : 100	1.1182	1.1214	5.00%	5.92%	0.92%

Based on eq. (8), the diffusion coefficient D can be calculated as 3.36, 3.90, 4.08, and 4.24 mm · day$^{1/2}$ for the samples with 35 phr, 42phr, 52 phr, and 60 phr hardener, respectively. The diffusion coefficients increase with an increase of hardener amount.

The densities of samples aging in dry environment and aging in 45°C water for 500 days are listed in Table V. The volume expansion of resin α can be calculated by the following:

$$\alpha_\nu = \frac{\dfrac{(1 + M_t)}{\rho_i} - \dfrac{1}{\rho_0}}{\dfrac{1}{\rho_0}} \qquad (9)$$

where ρ_0 is the density of the dry specimen. ρ_i is the density of the resin after immersion in water for time t.

The calculated results are listed in Table V. It can be seen that the volume of resin expands 3.88%, 3.74%, 4.14%, and 5.00%, respectively, for samples with 35 phr, 42 phr, 52 phr, and 60 phr of hardener, while they absorb 4.96%, 4.83%, 5.10%, and 5.92% volume of water per volume of resin. The volume expansion increases with an increase of hardener amount. The water absorbed into the epoxy network causes expansion of the resin. However, water absorbed into the void volume of epoxy resin does not cause volume expansion. Suppose the difference between the volume of water absorption and the volume of expansion can be contributed to the void volume in epoxy resin, in which water can stay but does not cause volume expansion. Interestingly, while the volume expansion of resin varies from 3.74% to 5.00%, the void volume just varies from 1.09% to 0.92%. It seems that differences in moisture absorption for various hardener composition might be mainly due to differences of epoxy molecular network, but not void volume.

CONCLUSIONS

In a Epon 828 (DGEBA)/EPI-CURE 3046 (TETA) system, the curing rate increases with the amount of hardener. The epoxy groups are prone to reaction with primary amines with an increase of hardener amount. The epoxy with a large excess of hardener has a looser epoxy network. The optimal ratio of hardener to resin used for dry environment is around the stoichiometric ratio. In wet environment, the moisture can greatly accelerate postcure, and water absorption increases with an increase of hardener amount. The density measurements show that differences in moisture absorption for various hardener compositions are mainly due to differences of epoxy molecular network, but not void volume. When applied in moisture environments, the optimal ratio of hardener to resin is much less than the stoichiometric ratio.

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