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Study on Reaction Kinetics of Epoxy Resin Cured by a Modified Dicyandiamide

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ABSTRACT: To improve the disadvantage of the low reactivity and reduce the high curing temperature of epoxy resin cured by dicyandiamide (DICY), DICY is chemically modified with phenyl hydrazine and a new curing agent, LB-A, is developed in this research. The structure, the curing behavior, and reaction kinetics of LB-A curing epoxy resin are investigated. Results show that the DICY is modified successfully and the well-defined structure of DICY is destroyed after modification. Consequently, a new curing agent in a noncrystal form is resulted. Thereupon, the reactivity and compatibility between the epoxy resin and the curing agent are improved appreciably using LB-A instead of DICY. Meanwhile, the curing temperature and activation energy of the curing reaction decrease outstanding, whereas the rate constant increases remarkably. In addition, the compressive strength and the adhesive strength in shear by tension loading of the resulting epoxy resins have been increased using LB-A instead of DICY as the curing agent. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: epoxy resin; dicyandiamide; kinetics; modification; mechanism

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INTRODUCTION

Owing to the outstanding versatility and properties, such as good adhesion to various substrates, high-modulus and high-temperature performance, low shrinkage, and good corrosion resistance, etc.,[1–3] epoxy resin finds a broad spectrum of applications in adhesives, coatings, castings, modeling compounds, impregnation materials, high-performance composites, insulating materials, encapsulating and packaging materials for electronic devices, and so forth.[4–6] Just grounded on its great industrial significance, epoxy resin has received a lot of scientific and technical interests, especially its curing reaction and structure–property relationship.[7,8] To achieve well-balanced ultimate properties, the uncured epoxy must be converted into a crosslinked macromolecule in the presence of different kinds of curing agents under optimal processing conditions. Among frequently used curing agents, the latent curing agents have a long pot life in epoxy resin at ambient conditions, whereas they can cure epoxy resin quickly under the high temperature or irradiation with ultraviolet light.[9,10] Consequently, the mono-component epoxy adhesives, coatings, and castings can be prepared by the use of the latent curing agents.[11,12]

In practical applications, dicyandiamide (DICY) is one of the widely used latent curing agents for epoxy resin. However, a main disadvantage of DICY is that a high curing temperature, for example, 160–180°C, must be applied to improve the compatibility between DICY and epoxy resin to accelerate curing reactions because of the low reactivity and high-melting temperature of DICY.[13] This limits the wide use of DICY in some materials and products that cannot endure such high temperature. To meet this challenge and reduce the curing temperature of DICY, the crux of the problem is to develop new curing agents with high reactivity and good compatibility with epoxy resin. Generally, there are two kinds of routes to enhance the reactivity and compatibility between epoxy resin and DICY: one is to use the accelerant to promote the reactivity between DICY and epoxy resin,[14–16] and the other is to modify DICY chemically.[17] To the end, here DICY is modified with phenyl hydrazine and a new curing agent, LB-A, is developed. The reactivity and compatibility between DICY and epoxy resin has been improved significantly. As a result, the curing temperature has decreased ca. 50°C. Then, the curing behavior and kinetics of the curing reaction of epoxy resin E-44 are studied using LB-A as a curing agent. Finally, the mechanism of LB-A curing epoxy resin is discussed.

EXPERIMENTAL

Materials

DICY and phenyl hydrazine, provided by Sinopharm Group Chemical Reagent (China), are used as received. Epoxy resin E-44, one of the diglycidyl ethers of bisphenol-A (epoxy value: 0.41–0.47 mol/100 g, and M_w: 425–490 g/mol), purchased from Wuxi Resin Factory (China).

Modification of DICY and Synthesis of LB-A

The new curing agent, LB-A, is synthesized by chemically modifying DICY with phenyl hydrazine, and the detailed procedure is described as follows: first, 42 g of DICY, 54 g of phenyl hydrazine, and 50 mL of 6 mol/L hydrochloric acid together with 200 mL of distilled water are charged into a 500-mL three-necked flask, which is equipped with an N_2 inlet, a thermometer with temperature controller, and a Graham condenser. Second, the mixture is heated to 100°C under nitrogen atmosphere and vigorous stirring, and then continuously reacts at this temperature for 4 h. After the reaction is finished, the reactant solution is neutralized with 6 mol/L NaOH until the pH of the solution reaches 7.5. Third, the temperature is decreased to the room temperature and the precipitation is obtained after filtration. The crude product is further soaked clearing in distilled water. Finally, the product is dried at 40°C under vacuum to constant weight, and the resulting LB-A is a pink powder with a yield of over 85%.

Preparation of the Curing Samples of Epoxy Resins

The curing samples of epoxy resins are fabricated by the use of E-44 as the main resin while using DICY and LB-A as curing agents, respectively. The curing samples of E-44/DICY are prepared by curing 100 g of E-44 with 11 g of DICY at 160°C for 60 min (i.e., the ratio of the curing agent is 11 phr), whereas the curing samples of E-44/LB-A used for infrared spectroscopy analysis are prepared by curing E-44 with 20 phr of LB-A at 110°C for 40 min.

Characterization

FTIR Analysis. The chemical structure of the E-44/LB-A before and after curing is measured by Fourier transform infrared spectroscopy (FTIR) with an Avatar 370 FTIR spectrometer (Nicolet, USA) in the range of 400–4000 cm^{-1}, and the KBr pellet technique is adopted.

X-ray Diffraction Measurement. The phase structure identification is carried out using a Shimadzu XRD-7000LX X-ray diffraction (XRD) meter with Cu Kα irradiation ($\lambda = 1.5406$ Å) at a scanning rate of 0.02°/s in 2θ ranging from 10 to 70°.

Differential Scanning Calorimetry Measurement. Differential scanning calorimetry (DSC) measurements are conducted on a DSC-60 instrument (Shimadzu, Japan) calibrated with indium and *n*-octane. The stoichiometric E-44 and DICY or LB-A are mixed homogeneously as quickly as possible under vigorous stirring at room temperature (<15°C), and each prepared mixture was used only once. The fresh reaction mixture with a weight of about 10 mg is sealed in an aluminum DSC pan and

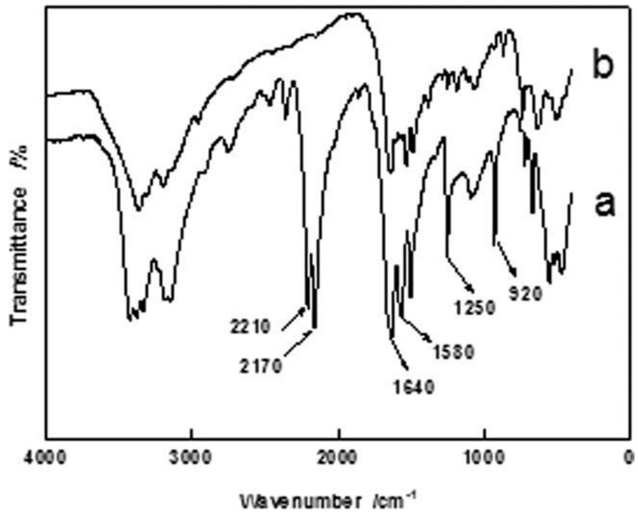


Figure 1. FTIR spectra of DICY (a) and LB-A (b).

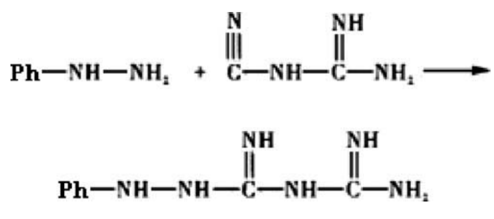
immediately performed from 25 to 300°C. The heating rate (β) in the curing behavior research is 10°C/min, whereas experiments of the curing reaction kinetics study are investigated under the nonisothermal condition at different scanning rates of 2, 5, 10, and 20°C/min.

Mechanical Properties Measurement. The compressive strength is measured according to China National Standard of GB/T 2567-2008 by using a hydraulic testing machine of YE-2000 (Jinan Testing, China). The measurement of the adhesive strength in shear by tension loading is operated by an electric universal testing machine of AG-10kN (Shimadzu, Japan) based on China National Standard of GB/T 7124-2008.

RESULTS AND DISCUSSION

Synthesis and Structure of the New Curing Agent of LB-A

To improve the low reactivity and reduce the temperature of DICY in curing epoxy resin, DICY is chemically modified with phenyl hydrazine. Consequently, a new curing agent, LB-A, is synthesized successfully according to the following chemical reaction:



That is, the chemical reaction between —NH_2 groups in phenyl hydrazine and the —C≡N groups in DICY molecules takes place successfully under the chosen reaction conditions. It can be found that there are diversified amidocyanogen groups with different reactivities in LB-A molecule, such as primary amine, secondary amine, and imine groups. These groups can all make the epoxy ring in epoxy resin open. As compared to DICY, there are two more active secondary amine groups and one more

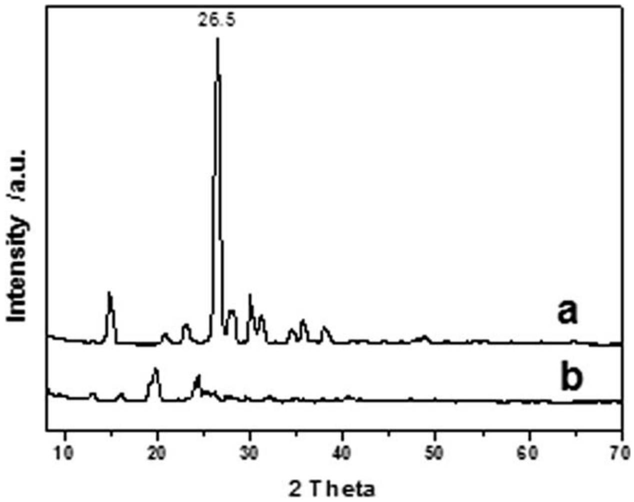


Figure 2. XRD patterns of DICY (a) and LB-A (b).

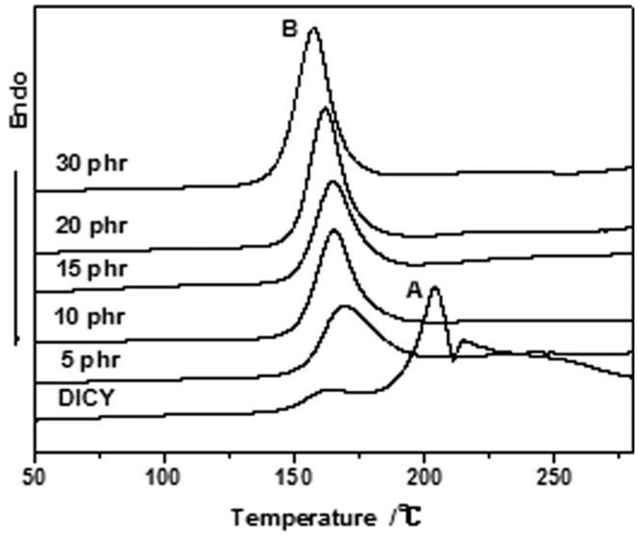


Figure 3. DSC curves of E-44 cured by DICY and different contents of LB-A.

active imine group in LB-A molecule. As a result, LB-A has higher reactivity than DICY does.

The structure of the resulting LB-A together with DICY is characterized by the techniques of FTIR and XRD, and results are shown in Figures 1 and 2, respectively.

Figure 1 is the FTIR spectra of DICY both before and after modification by phenyl hydrazine. As shown in Figure 1(a), the absorption peaks at 2210 and 2170 cm^{-1} are assigned to the characteristic stretching vibration of —C≡N groups in DICY, and the peaks at 1640 and 1580 cm^{-1} are ascribed to the stretching vibration of —C=N and —C—N groups, respectively. Meanwhile, the bending vibration peaks of —N—H groups present at 1250 and 920 cm^{-1}. By contrast, the FTIR spectrum of the modified DICY [Figure 1(b)] changes greatly. For instance, the absorption peaks at both 2210 and 2170 cm^{-1} assigned to the characteristic stretching vibration of —C≡N disappear completely, whereas the absorptions of —C=N, —C—N, and —N—H present distinctly all the same. These results show that the chemical reaction between —C≡N in DICY molecule and —NH_2 in phenyl hydrazine takes place successfully. As a result, the DICY is modified with phenyl hydrazine successfully and a new curing agent is synthesized.

It can be found from the XRD patterns in Figure 2(a) that distinct characteristic diffraction peaks of DICY with sharp and narrow shape appear, and the peak with the largest intensity presents at 2θ of 26.5°. These results indicate that DICY is a crystal with well-defined structure. Therefore, the compatibility between epoxy resin and DICY is quite poor. As compared to DICY, the XRD patterns of DICY after modification with phenyl hydrazine [Figure 2(b)] changes enormously, and the intensity of the diffraction peaks decreases greatly. Meanwhile, there exist a few discernible crystalline peaks, demonstrating that the well-defined structure of DICY is destroyed by the chemical modification with phenyl hydrazine. Consequently, a new curing agent in more poorly packed order is synthesized. As a result, the poor compatibility between epoxy resin and DICY is expected to be improved by chemically modifying DICY with phenyl hydrazine.

The Behavior of LB-A Curing E-44. DICY is a good latent curing agent for epoxy resin; however, the curing temperature is very high (about 160–180°C), and which limits its wide use in some products and apparatus.[13–15] Generally, the chemical modification is a very good method to reduce the high curing temperature. Here, DICY is chemically modified and a new curing agent, LB-A, is developed by the modification with phenyl hydrazine. The behavior of LB-A curing epoxy resin is investigated using E-44 as a model epoxy resin via DSC and FTIR techniques.

The DSC curves of E-44 cured by different contents of LB-A together with 11 phr of DICY are shown in Figure 3, and the corresponding heating effect parameters are listed in Table I. As shown in Figure 3 and Table I, there are three exothermic peaks in DSC curve of E-44 cured by DICY, and the main exothermic peak A is quite small with an heat release (ΔH) of only 168.8 J/g, whereas the starting point temperature (T_{onset}), peak temperature (T_p), and the final temperature (T_f) of peak A are 193.4, 204.1, and 209.5°C, respectively. By contrast, there is only one exothermic peak, namely, peak B, in DSC curves of E-44 cured by LB-A. The heat release in E-44 /LB-A system is higher than that of in E-44/DICY system when the amount of LB-A reaches 10 phr. All characteristic temperatures, T_{onset}, T_p, and T_f, in E-44/LB-A system are lower than those in E-44/DICY system, correspondingly. This indicates that the curing temperature of E-44 cured by LB-A decreases remarkably as compared to that of cured by DICY. Furthermore, all the corresponding temperature of T_{onset}, T_p, and T_f in E-44/LB-A system are decreased gradually, respectively, with the increase of the amount of LB-A from 5 to 30 phr. Meanwhile, the exothermic peak becomes more and more sharpen while the heat release increases gradually. These results show that the rate of curing reaction in E-44/LB-A system speeds up and the curing time shortens with the increase of the content of LB-A.

The Temperature of LB-A Curing E-44

The aim of modifying DICY is to improve the reactivity and compatibility between epoxy and DICY, and the DSC technique

Table I. The Thermal Effect Parameters of E-44 Cured by DICY and Different Contents of LB-A

		E-44 cured by different contents of LB-A (phr) (Peak B)				
Parameters	E-44/DICY (Peak A)	5	10	15	20	30
ΔH (J/g)	168.8	103.9	188.3	189.4	207.4	209.8
T_{onset} (°C)	193.4	153.9	152.1	151.9	150.6	144.4
T_p (°C)	204.1	169.3	165.3	164.8	161.8	157.5
T_f (°C)	209.5	190.3	179.1	178.0	173.6	168.8

is used to confirm the curing temperature of E-44/LB-A system, whereas the FTIR is used to substantiate the decided curing temperature. The DSC curves of E-44 cured by 20 phr of LB-A at different scanning rates of 2, 5, 10, and 20°C/min are shown in Figure 4, and the corresponding heating effect parameters are listed in Table II. As shown in Figure 4, the exothermic peak in DCS curves moves to the high temperature gradually with the increase of the scanning rate. At the same time, the heat release (ΔH) increases gradually.

By plotting of T_{onset} against the scanning rate, a functional equation can be fitted. Treating the fitting equation with extrapolation method, and then the value of T_{onset} at the scanning rate of 0°C/min can be estimated, which can reflect the curing effect of epoxy resin on isothermal condition. Similarly, the values of T_p and T_f at the scanning rate of 0°C/min can be estimated as well. The values of T_{onset}, T_p, and T_f in our experiment are 110.0, 117.5, and 132.5°C, respectively. Therefore, it can be deduced that the curing temperature of E-44/LB-A system is between 110 and 132.5°C. This curing temperature is about 50°C lower than that of E-44/DICY system, indicating that the reactivity and compatibility between epoxy and DICY have been improved greatly via modifying DICY with phenyl hydrazine. Consequently, the curing temperature has decreased significantly.

The effect of LB-A curing E-44 is also investigated by the FTIR technique, and the measured infrared spectra of E-44 before and after cured with 20 phr of LB-A are shown in Figure 5. It

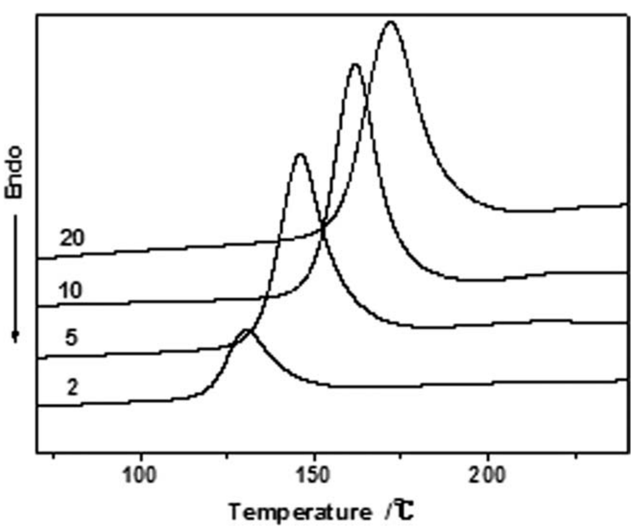


Figure 4. DSC curves of E-44/LB-A system at different scanning rates.

can be found that there is a distinct absorption peak at 910 cm^{-1} in the IR spectrum of E-44 before cured by LB-A [Figure 5(a)], and this peak is assigned to the characteristic absorption of epoxy groups. By contrast, the absorption peak disappears completely for E-44 after cured by LB-A [Figure 5(b)], indicating that the chemical reaction between E-44 and LB-A happens indeed under the selected curing conditions, and the ring in epoxy groups has been opened. Therefore, it proves that the epoxy resin of E-44 can be cured by LB-A completely at 110°C for 40 min, indicating that the DICY has been modified successfully and the curing temperature has decreased markedly.

Additionally, our experiment also shows that E-44 can be cured by LB-A completely at 90°C when the curing time extends to 8 h, and the resulting epoxy resin samples have excellent mechanical property. For instance, the compressive strength and the adhesive strength in shear by tension loading can reach 104.0 and 34.5 MPa, respectively. By contrast, the compressive strength and the adhesive strength in shear by tension loading can only reach 87.5 and 24.3 MPa, respectively, for E-44/DICY system cured at 170°C. It can be found that the mechanical properties of the cured epoxy resin increase using LB-A instead of DICY as the curing agent. The reason is that the phenyl group, which is a rigid group, is incorporated into the cured epoxy resins.

Results from these characterizations manifest that as compared to the curing temperature of DICY in cuing epoxy resin, that is 160–180°C, the curing temperature of LB-A in cuing epoxy resin decreases markedly, and the epoxy resin can be cured completely at 90–110°C by the use of the modified DICY (i.e., LB-A) as the curing agent.

Curing Kinetics Analysis

Kinetic models developed from kinetic analysis of DSC data have been widely applied to the curing of epoxy resins.[18–20] Under the nonisothermal condition, the Kissinger–Akahira–Sunose (KAS) method[21,22] can be used to give the activation energy (E_a) from the plot of $\ln(\beta/T^2)$ versus T^{-1} (here β is the

Table II. The Thermal Effect Parameters of E-44/LB-A System at Different Scanning Rates

	The scanning rate (β, °C/min)			
Parameters	2	5	10	20
T_{onset} (°C)	119.9	134.7	150.6	157.9
T_p (°C)	130.5	146.1	161.8	171.9
T_f (°C)	143.7	158.6	173.6	187.0

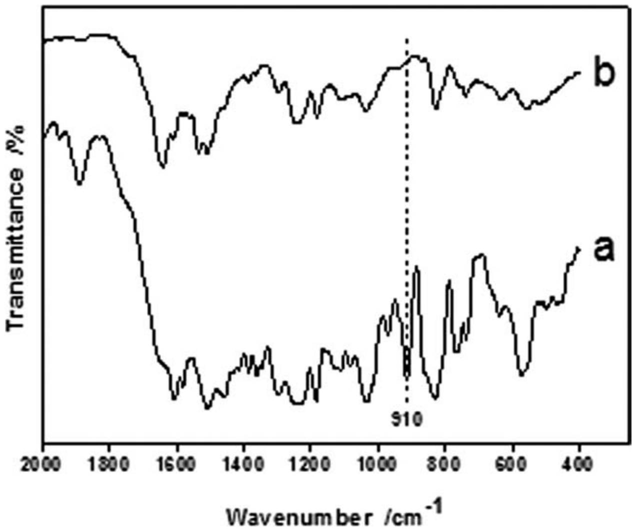


Figure 5. IR spectra of E44/LB-A before (a) and after (b) cured.

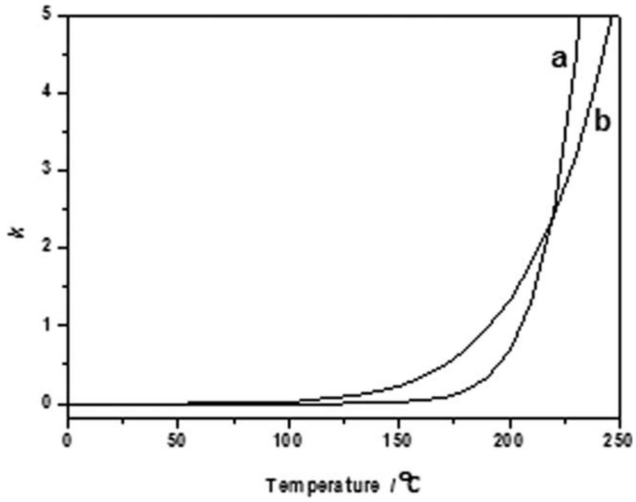


Figure 6. The rate constant of E-44 cured by DICY (a) and LB-A (b) at different curing temperatures.

different heating rate and T denotes the temperature). The use of KAS function is obtained as follows:

$$-\ln\frac{\beta}{T^2}=\frac{E_a}{R}\frac{1}{T}-\ln\left[\frac{AR}{E_a}\right] \quad (1)$$

where R is the gas constant, and A is the pre-exponential factor. In our research, the peak temperature (T_p) is used to estimate the E_a and which can be obtained at the different scanning rate (β), and the measured data are summarized in Table II. Then, the kinetic parameters can be calculated based on eq. (1) and Crane equation[23] (eq. 2), respectively.

$$-\ln\beta=\frac{E_a}{nR}\times\frac{1}{T_p}+C \quad (2)$$

where n is the reaction order, and C denotes the integration constant.

By using the experimental data of β and T_p in Table II, the linear plot of $-\ln(\beta/T_p^{\,2})$ versus T_p^{-1} can be obtained according to the Kissinger equation. Then, the value of E_a can be worked out from the slope of E_a/R, and the value of the pre-exponential factor (A) can also be obtained from the intercept of $-\ln(AR/E_a)$. Meanwhile, the linear plot of $-\ln(\beta)$ versus T_p^{-1} can be obtained according to the Crane equation, and the reaction order of n can be obtained combining the gained E_a. In our experiment, the calculated kinetic parameters of E_a, n, and A are listed in Table III.

As listed in Table III, as compared to the E-44/DICY system, the E_a in E-44/LB-A system decreases significantly, and the value of E_a in the E-44/LB-A system has not reached a half of that in the E-44/DICY system. This indicates that the reactivity of the modified DICY (namely, LB-A) increases as compared to the primal DICY. As a result, the modified DICY can react with epoxy resin easier than the pristine DICY does. On the other hand, the reaction order of n in E-44/LB-A system decreases as compared to that in E-44/DICY system, showing that the reaction mechanism in the process of the curing epoxy resin has changed after the DICY is modified with phenyl hydrazine. Consequently, the heat course has also changed. Meanwhile, the reaction order is not the integer, manifesting that the curing reaction in E-44/LB-A is quite complicated, and several elementary reactions occur in the curing course.

Table III. The Curing Kinetics Parameters in Curing Reaction

Curing system	E_a (kJ/mol)	n	A
E-44/DICY	123.8	0.941	3.19×10^{13}
E-44/LB-A	57.8	0.912	3.20×10^{6}

The relationship between the reaction rate constant of k and the temperature of T can be expressed by the Arrhenius equation[24]:

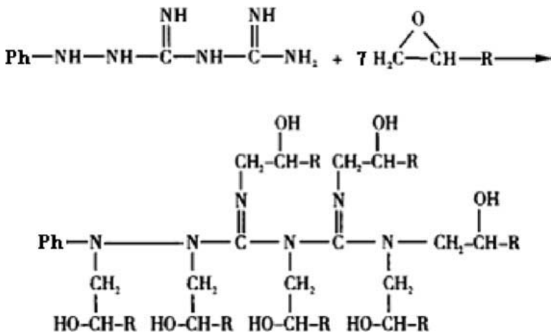
$$k=A\exp(-E_a/RT) \quad (3)$$

where A is the pre-exponential factor, R is the gas constant, and E_a is the activation energy.

By substituting the values of A and E_a in Table III into the Arrhenius equation, the value of k at the different temperatures can be obtained. Turn the unit of temperature from Kelvin to centigrade, and then the curves of k versus T(°C) in both E-44/LB-A and E-44/DICY systems can be obtained, as shown in Figure 6. As shown in Figure 6(a), the reaction rate constant of E-44/DICY system almost keeps zero before 175°C, whereas k increases quickly with the increase of the temperature after the reaction temperature reaches 175°C. These show that DICY has no reactivity for curing epoxy resin before 175°C, whereas it takes on very high reactivity after 175°C. By contrast, Figure 6(b) shows that LB-A can cure epoxy resin at lower temperature. Meanwhile, it can also be found from Figure 6 that E-44/LB-A system has a higher k-value than E-44/DICY system does before 220°C, indicating that as compared with DICY, LB-A has higher reactivity at the low–medium temperature. These results show that the curing reactivity of DICY increases greatly and the curing temperature decreases significantly by the modification with phenyl hydrazine.

Reaction Mechanism of LB-A Curing Epoxy Resin

There are diversified amidocyanogen groups with different reactivities in LB-A molecule, such as primary amine, secondary amine, and imine groups. These groups can all make the epoxy ring in epoxy resin open. Therefore, the reaction process is quite complicated between LB-A and epoxy resin. Generally speaking, the curing reaction process in E-44/LB-A is as follows: first, the reaction between the active hydrogen in aliphatic primary amine and the epoxy group in epoxy resin takes place and results in the aliphatic secondary amine. Second, the active hydrogen in the aliphatic secondary amine, aromatic secondary amine, and imine groups can react with epoxy groups, respectively. As a result, the crosslinked netlike structure in epoxy resin comes into existence. If all kinds of amidocyanogen groups in LB-A react with epoxy groups, the structure of the cured epoxy resin can be described as follows:



In addition, the results from XRD show that DICY has typical crystal structure, whereas LB-A exists in a noncrystal form, which indicates that the well-defined structure and strong crystallizability of DICY are destroyed by the modification with phenyl hydrazine. As a result, the problem of the bad miscibility between DICY and epoxy resin can be improved basically. Moreover, there are two more active secondary amine groups and one more active imine group in LB-A molecule than in DICY. Therefore, LB-A has higher reactivity than DICY. Just based on the good compatibility and high reactivity between LB-A and epoxy resin as compared to E-44/DICY system, the curing temperature of E-44/LB-A system decreases dramatically.

CONCLUSIONS

DICY has been modified with phenyl hydrazine and a new curing agent of LB-A is developed. As compared to the curing reaction of DICY in cuing epoxy resin, the activation energy and the curing temperature of LB-A cuing epoxy resin decrease dramatically, and the epoxy resin can be cured completely at moderate temperature, that is, 90–110°C, by the use of LB-A as a curing agent. Meanwhile, the cured epoxy samples have excellent mechanical property, and the tensile shear strength and compressive strength can reach 34.5 and 104.0 MPa, respectively.

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