DOI https: //doi. org/10.1007/s11595-018-1960-3

Curing Kinetics and Properties of Epoxy Resin with 1, 4-bis (2, 4-diaminophenoxy)benzene

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Abstract: A multifunctional amine, 1,4-bis(2,4-diaminophenoxy)benzene (14BDAPOB), was prepared and used as a novel hardener for novolac epoxy resin (ER). The structure of 14BDAPOB was characterized with Fourier transform infrared (FT-IR) spectroscopy and differential scanning calorimetry (DSC). The curing kinetics of the novolac epoxy resin/1,4-bis(2,4-diaminophenoxy)benzene (ER/14BDAPOB) system was studied by means of non-isothermal DSC experiments at five heating rates and determined by the Kissinger, Ozawa and Crane methods. The results showed that the activation energy E_a of the ER/14BDAPOB (74.56 kJ/mol) system was higher than that of the epoxy resin/LCA-30 (ER/LCA-30, 68.85 kJ/mol), where LCA-30 is a commercial modified diamine. The reaction order, frequency factor and the reaction rate constant at peak temperature of the two systems were calculated. The initial decomposition temperatures (T_{onset}) were 398.8 ℃ (ER/14BDAPOB) and 334.3 ℃ (ER/LCA-30). The tensile shear strengths were 21.63 MPa (ER/14BDAPOB) and 21.28 MPa (ER/LCA-30). The results showed that the two cured systems exhibited good thermal and mechanical properties.

Key words: epoxy resin; reaction kinetics; hardener; thermal properties; mechanical properties

1 Introduction

Epoxy resins are widely used to formulate moulding compounds for microelectronics packaging.[1, 2] This is because of their superior performance at elevated temperatures, excellent mouldability, superior mechanical and electrical properties, and heat and humidity resistance. Aliphatic[3-11] and aromatic amines[12-18], as curing agents, can improve the thermal, chemical, and mechanical properties of the cured epoxy resin which have attracted extensive research interests during the past few years. Wan *et al*[19], for instance, reported that the N,N,N,N-tetra(3-aminopropyl)-1,6-diaminohexane (TADH) they prepared was an effective curing reagent for diglycidyl ether of bisphenol-A (DGEBA). However, we know of no reports of aromatic tetraamine being used as a curing agent of epoxy resin, with four reactive amino groups that can react with the epoxy groups to get a high cross-linking density network[20, 21].

In the present study a new aromatic functional amine (14BDAPOB) was first synthesized and then used as the curing agent of an epoxy resin. 14BDAPOB has four amine groups in its structure and thus it was used in order to achieve the high cross-link density expected to result in excellent thermal properties, high cohesional strength, and chemical solvent resistance. A non-isothermal method[22-28] was used to evaluate the kinetic parameters of the curing reaction by introducing the Kissinger[29], Ozawa[30] and Crane[31] methods in this study. When analyzing the non-isothermal DSC data, an assumption can be made that E_a (apparent activation energy) is constant or it could be considered to be variable during the process. In this work it was supposed that E_a was constant. In addition, the thermal stability and dynamic mechanical properties of the cured systems were evaluated.

2 Experimental

2.1 Materials

Hydroquinone, 2,4-dinitrochlorobenzene, potassium carbonate (K_2CO_3), toluene, N,N-dimethylformamide (DMF), hydrazine hydrate (HHA), anhydrous ethyl alcohol, novolac epoxy resin (epoxy value: 0.526-0.588, Scheme 1(a)), epoxy E-51 (epoxy value: 0.51, Scheme 1(b)), LCA-30 (a modified

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(Received: Feb. 18, 2016; Accepted: May 17, 2018)

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diamine, structure unknown), palladium on activated carbon (Pd/C) (10%) and 4,4'-Diaminodiphenyl ether (DDE) were all obtained from Shanghai Electronic Material Co., Ltd. (China).

2.2 Measurements

The thermal analysis was done by using DSC-204F1 and TG-209F1 instruments in N_2, both from the German Netzsch Instrument Co., Ltd. The heating rate was 10 ℃/min, and the weight range was 3-5 mg. The cohesional strength was measured on a tensile shear strength tester HSK-S (Hounsfield, England). The FTIR spectra were recorded on a Varian 640-FT-IR infrared spectrometer (USA). ^{1}HNMR spectrum was recorded on a Avance 400 (Bruker, Switzerland) instrument.

2.3 Synthesis and characterization of 1, 4-bis (2, 4-dinitrophenoxyl) benzene (14BDNPOB)

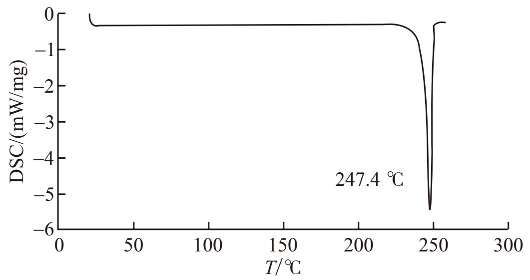


Fig.1 DSC scan of 14BDNPOB

Hydroquinone (HQ) 5.5 g (0.05 mol), potassium carbonate (K_2CO_3) 13.8 g (0.105 mol), 2,4-dinitrochlorobenzene (24DNCB) 21.3 g(0.105 mol) and N,N-dimethylformamide (DMF) 80 mL were added into a 250 mL three-necked flask, and the mixture was heated to reflux until no further water was separated. After the reaction was finished, the reaction mixture was poured into 400 mL of distilled-water and the crude product (yellow solid) crystallized to obtain the product 20.8 g (yield: 93.3%). The melting point of 14BDNPOB was 247.4 ℃(DSC, Fig.1).

The structure of 14BDNPOB was characterized by FT-IR spectroscopy (Fig.2). FT-IR results (KBr, cm^{-1}): 1 531 and 1 350 (N-O), 3 105 (C-H of benzene), 1 610 and 1 499 (benzene), 1 269 (C-O).

2.4 Synthesis and characterization of 1, 4-bis (2, 4-diaminophenoxyl)benzene (14BDAPOB)

14BDNPOB 8.8 g (0.02 mol, pure product), Pd/C (10%) 0.5 g and ethanol 80 mL were added into a 250 mL three-necked flask, and the mixture was heated to 70 ℃ followed by hydrazine hydrate 25 mL being added dropwise. When the reaction was finished the mixture was filtered and the white solid 5.1 g (yield: 80.0%) crystallized from the filtrate. The reaction route is also shown in Scheme 1. The melting point of 14BDAPOB was tested by DSC (222.4 ℃, Fig.3).

The structure was characterized by FT-IR spectroscopy (Fig.4). FT-IR (KBr, cm^{-1}): 3 449 (N-H), 1 618, 1 510 and 1 495 (benzene), 1 190 (C-O). ^{1}HNMR (DMSO-d_6, ppm) (Fig.5): 4.8(br, 8H), 5.8 (d,2H), 6.0 (s,2H), 6.4 (d, 2H), 6.7 (s, 4H).

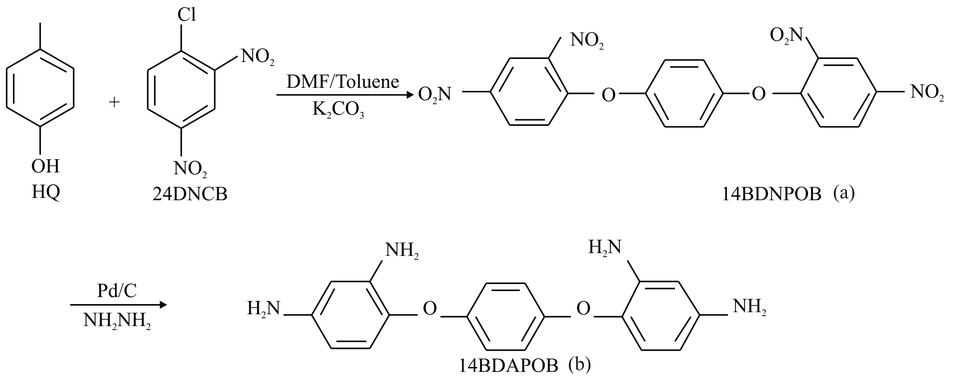
2.5 Sample preparation

Novolac epoxy resin, epoxy E-51 and hardener were mixed at a 60: 40: 20 weight ratio. The mixture was stirred until dissolved completely at room temperature. 3-10 mg of the uniform viscous liquid was put into a DSC sample pan for curing. The heating rates were 2.5, 5, 10, 15 and 20 K/min in nitrogen atmosphere.

3 Results and discussion

3.1 Synthesis and characterization of 14BDNPOB

14BDNPOB was synthesized from hydroquinone (HQ) and 2,4-dinitrochlorobenzene (24DNCB) by nucleophilic substitution reaction as shown in Scheme 1. Fig.2 clearly shows the asymmetric and symmetric



Scheme 1 Synthesis route for 14BDNPOB and 14BDAPOB

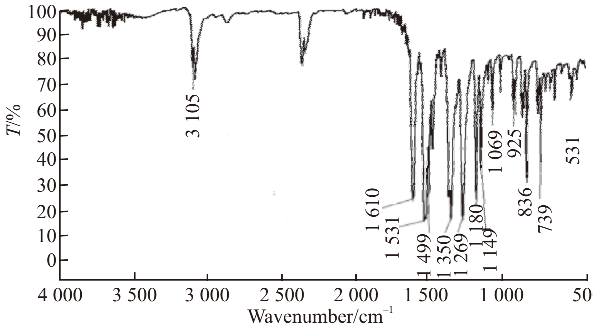


Fig.2 FT-IR spectrum of 14BDNPOB

characteristic absorption peaks of nitro groups at around 1 531 cm^{-1} and 1 350 cm^{-1}, the C-H of benzene group peak at 3 105 cm^{-1}, while the characteristic absorption peaks of benzene (C=C) were at 1 610 and 1 499 cm^{-1}. The absorption peak of C-O was at 1 269 cm^{-1}. The melting point and FT-IR spectrum confirmed the expected chemical structures of 14BDNPOB.

3.2 Synthesis and characterization of 14BDAPOB

The new tetraamine 14BDAPOB was synthesized from 14BDNPOB by reduction. The measured melting point of 14BDAPOB was 222.4 ℃ in Fig.3. In Fig.4 for 14BDAPOB, peaks at 3 449 cm^{-1} and 3 406 cm^{-1} were attributed to the aromatic primary amino functional groups. Peaks at 1 618 cm^{-1}, 1 510 cm^{-1} and 1 495 cm^{-1} showed obvious benzene functional groups and 1 190cm^{-1} was the characteristic absorption peak of C-O.

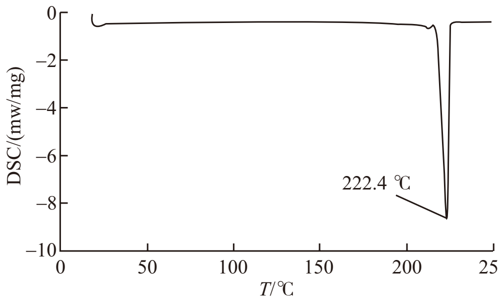


Fig.3 DSC scan of 14BDAPOB

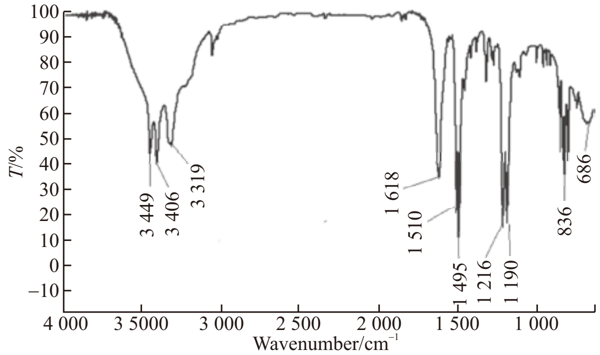


Fig.4 FT-IR spectrum of 14BDAPOB

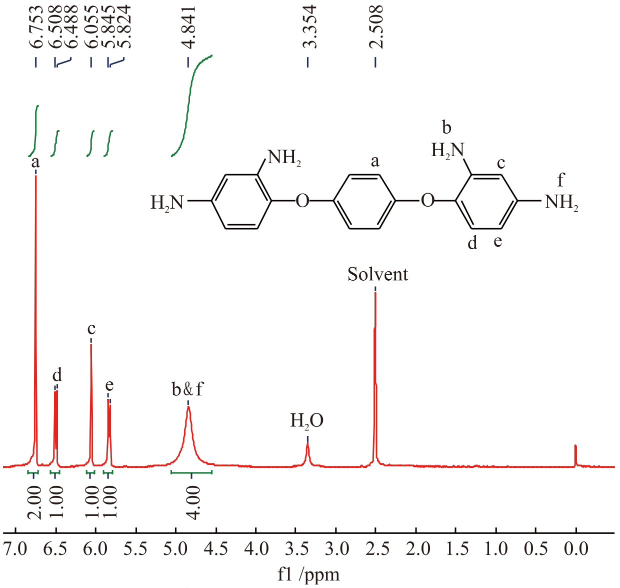


Fig.5 ^{1}HNMR spectrum of 14BDAPOB

3.3 Curing kinetics of ER/14BDAPOB and ER/LCA-30

Non-isothermal kinetics, which is an important method for the characterization of the curing kinetics of epoxy resin, has been studied for more than half a century. With this method, the basic assumption is that the curing process (d*α*/d*t*) is proportional to the heat flow. All kinetic models start with the following basic Eq.(1):

$$\frac{d\alpha}{dt}=k(T)f(\alpha)=A\exp(-E_a/RT)f(\alpha) \qquad (1)$$

where d*α*/d*t* is the instant curing rate, *α* is the fractional conversion at time *t*, *k* is the Arrhenius rate constant, and *f(α)* is a functional form of α that depends on the reaction mechanism. *R* is the gas constant, E_a is the activation energy and *A* is the frequency factor.

Kissinger took the derivative of Eq.(1) and assumed that the reaction rate (d*α*/d*t*) reaches a maximum at a temperature (T_p), where the *DSC* curve displays a peak, to obtain Eq.(2):

$$\frac{-\mathrm{d}\ln(\beta/T_p^2)}{\mathrm{d}(1/T_p)}=\frac{E_a}{R} \qquad (2)$$

where *β* is the heating rate and T_p is the temperature at which d*α*/d*t* is the maximum. By use of the given DSC curves with different heating rates (*β*), the Kissinger plot of $\ln(\beta/T_p^2)$ against $1/T_p$ was obtained. From the slope of the Kissinger plot, the activation energy (E_a) can be calculated.

The Ozawa-Flynn-Wall method, based on Doyle’s approximation, is an alternative method for the calculation of E_a and is expressed as Eq.(3):

$$\ln\beta = A' - 1.052\frac{E_a}{RT_p} \tag{3}$$

A plot of $\ln(\beta)$ *versus* $(1/T_p)$ should give a straight line with a slope of $-1.052E_a/R$. This can give the activation energy for different levels of conversion. Furthermore, the curing reaction order (n) can be obtained when the Crane method, as depicted in Eq.(4), is applied.

$$\frac{\mathrm{d}\ln\beta}{\mathrm{d}(1/T_p)} = -(\frac{E_a}{nR} + 2T_p) \tag{4}$$

When E_a is the activation energy calculated by the Kissinger or Ozawa method, n can be derived from the slope of $\ln(\beta)$ *versus* $1/T_p$ plot when E_a/nR is much higher than $2T_p$ through Eq.(5):

$$\frac{\mathrm{d}\ln\beta}{\mathrm{d}(1/T_p)} = -\frac{E_a}{nR} \tag{5}$$

The frequency factor (A) in Eq.(1) was calculated by use of Eq.(6):

$$A = \frac{\beta E_a \exp(E_a / RT_p)}{RT_p^2} \tag{6}$$

Furthermore the reaction rate constant at peak temperature (K_p) was calculated by use of the Arrhenius equation (7):

$$K_p = A\exp(-E_a / RT) \tag{7}$$

The *DSC* curves of ER/14BDAPOB and ER/LCA-30, for five different heating rates, are shown in Figs.6 and 7.

All curves showed only one exothermic peak, regardless of the heating rate. The exothermic peaks became larger and sharper and the peaks also shifted towards higher temperatures as the heating rate was increased. The temperature at which the instant conversion rate was the maximum (T_p) and the heating rate (β) (Table I) were used for the calculation of the kinetic parameters by using the Kissinger, Ozawa, and Crane methods.

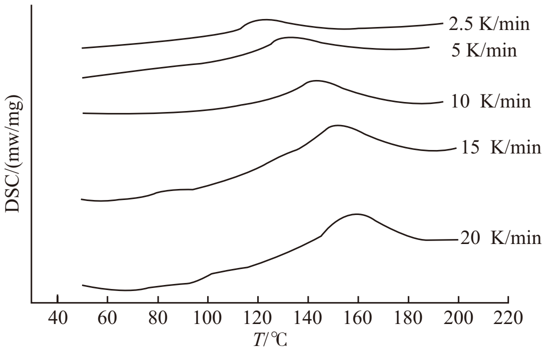


Fig.6 Non-isothermal DSC curves of ER/14BDAPOB

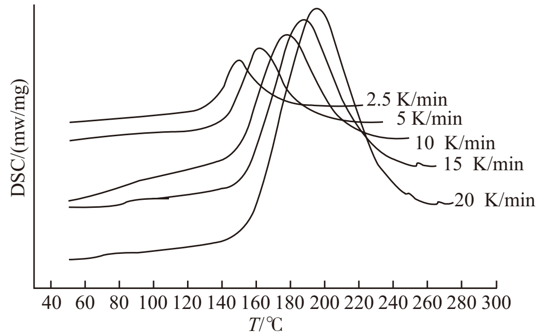


Fig.7 Non-isothermal DSC curves of ER/LCA-30

The data in Table 1 were introduced into the Kissinger equation, and $-\ln(\beta/T_p^{\ 2})$ *versus* $1/T_p$ was plotted (Fig.8), from which an excellent linear correlation was found ($R_{\mathrm{ER/14BDAPOB}}$=0.994 1, $R_{\mathrm{ER/LCA\text{-}30}}$=0.997 0). The linear plots were expressed by the following equations for ER/14BDAPOB and ER/LCA-30:

Y=8.790 6x−11.248 (ER/14BDAPOB)

Y=8.055 2X−7.953 4 (ER/LCA-30)

Table 1 DSC data of ER/14BDAPOB and ER/LCA-30

System	β /(K/min)	T_p/K	$\ln\beta$	$1/T_p$ ($\times10^3$)/K^{-1}	$-\ln(\beta/T_p^2)$	$-\Delta H$/(J/g)
ER/14BDAPOB	2.5	395.5	0.916	2.528	11.044	72.74
	5	404.7	1.609	2.471	10.397	75.73
	10	417.6	2.302	2.394	9.766	80.70
	15	425.6	2.708	2.350	9.399	91.26
	20	432.2	2.996	2.314	9.142	100.62
ER/LCA-30	2.5	422.1	0.916	2.369	11.174	255.0
	5	434.3	1.609	2.302	10.538	266.2
	10	450.4	2.302	2.220	9.918	270.3
	15	459.6	2.708	2.176	9.553	265.0
	20	467.9	2.996	2.137	9.301	287.4

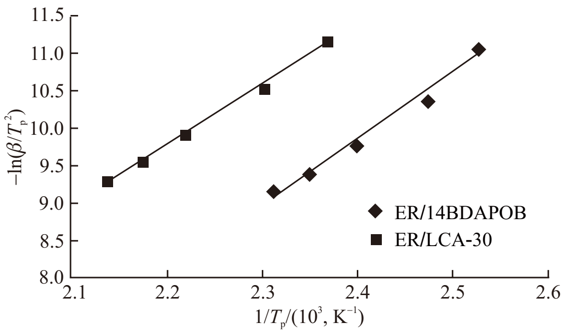


Fig.8 $-\ln(\beta/T_p^2)$ *vs* $(1/T_p)\times10^3$ of the epoxy resin/curing agent

The activation energies of ER/14BDAPOB and ER/LCA-30 were calculated from the slopes of the linear plots and are listed in Table 2.

Table 2 Activation energies of ER/14BDAPOB and ER/LCA-30 with different kinetics model and reaction orders

System	E_a /(kJ/mol)			
	Kissinger	Ozawa	Average	Reaction order *n*
ER/14BDAPOB	73.1	76.0	74.6	0.93
ER/LCA-30	67.0	70.7	68.9	0.93

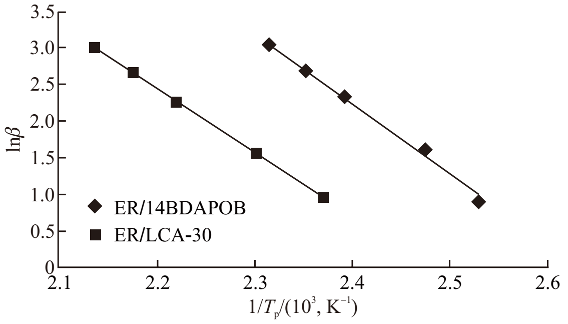


Fig.9 Slopes of lnβ *vs* $(1/T_p)$

The other method to calculate the activation energy of the curing reaction is the Ozawa equation. The data in Table 1 were also introduced into the Ozawa equation (3), and plots of ln (β) *versus* ($1/T_p$) gave straight lines with slopes of $-1.052E_a/R$, as shown in Fig.9.

The activation energies calculated from the slopes are also listed in Table 2. Although the activation energies obtained by using the Ozawa method were higher than those by the Kissinger method, the agreements between the values were reasonably good. The reaction orders of ER/14BDAPOB and ER/LCA-30 were calculated by introducing the activation energy into Eq.(5), and the values are also listed in Table 2. The results suggested that the curing reactions of epoxy resin with 14BDAPOB and LCA-30 were complicated reactions. For the curing reaction of the epoxy resin, the reaction process is complicated such as the reaction of amino- with epoxide group, hydroxyl- with epoxide groups and so on, the reaction order is not an integer. The reaction mechanisms are similar so the reaction orders of the two systems are the same.

From Table 2, it can be seen that the activation energy of ER/14BDAPOB was higher than that of ER/LCA-30, which can be attributed to the fact that 14BDAPOB has four active amines while LCA-30 has just two active amines. This increased the crosslink density which hindered diffusion in the curing system.

The frequency factors were calculated by introducing the activation energy into Eq.(6), and the values are listed in Table 3.

Table 3 Curing kinetics parameters of ER/14BDAPOB

System	β/(K/min)	Frequency factor $A/(\times10^{-8})$	K_p
ER/14BDAPOB	2.5	6.31	0.140
	5	7.27	0.268
	10	6.98	0.504
	15	6.79	0.728
	20	6.40	0.941
ER/LCA-30	2.5	21.9	0.113
	5	24.2	0.214
	10	23.2	0.397
	15	23.4	0.572
	20	22.0	0.736

The frequency factors of ER/LCA-30 were higher than those of ER/14BDAPOB. From the results in Table 3 it can be seen that the frequency factors of ER/14BDAPOB were lower than those of ER/LCA-30 which means that the reaction of the former is more difficult than the latter which can be proved by the reactive energy of the two systems, the reactive energy of the former is higher than the latter.

3.4 Properties of ER/14BDAPOB and ER/LCA-30

3.4.1 Thermal properties of curing epoxy adhesives

The degradation of the two epoxy adhesives was evaluated with TGA. Figs.10 and 11 illustrate the mass change at a heating rate of 10 ℃/min in N_2.

Table 4 Thermal properties of epoxy resin

System	Mass change /%(180 ℃)	Mass change /%(300 ℃)	T_{onset}/℃
ER/14BDAPOB	−1.17	−7.59	398.3
ER/LCA-30	−1.30	−4.49	334.3

The data of the TGA results are listed in Table 4. There was no significant mass loss up to 180 ℃, then the mass loss changed slowly between 180 and 300

℃, after which a quick mass loss appeared within the temperature range of 300-500 ℃. The initial decomposition temperature of the ER/14BDAPOB resin (398.8 ℃) was higher than that of ER/LCA-30 resin(334.3 ℃). The result suggested that the multifunctional hardener of 14BDAPOB can improve the heat resistance of the epoxy resin. A probable reason for the observation is that 14BDAPOB has four reactive amino groups which can enhance the crosslink density of the resulting epoxy network to improve the heat resistance of the prepared epoxy resin.

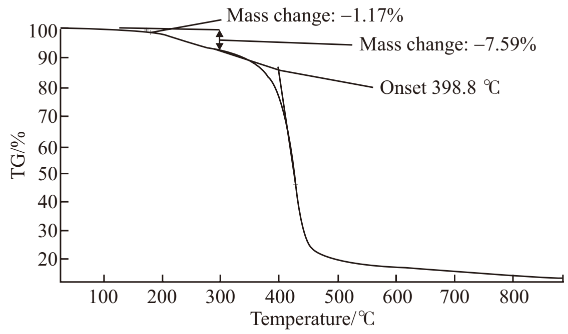


Fig.10 Thermal analysis of ER/14BDAPOB resin

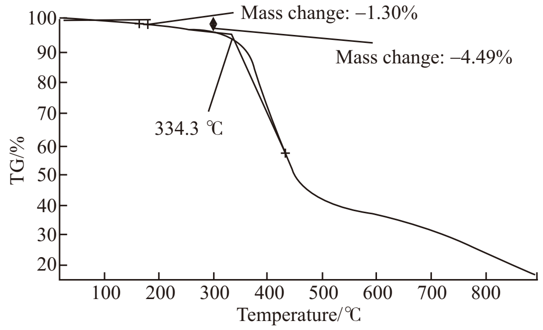


Fig.11 Thermal analysis of ER/LCA-30 resin

3.4.2 Mechanical properties of curing epoxy adhesives

The tensile shear strength is important for the application of epoxy resins. For understanding of the mechanical properties of the epoxy resin cured with 14BDAPOB, the tensile shear strengths of ER/14BDAPOB and ER/LCA-30 were measured and the results were compared with that of ER/ 4,4'-diaminodiphenyl ether(DDE). The results are summarized in Table 5.

Table 5 Mechanical properties of epoxy resin systems

Curing system	ER/14BDAPOB	ER/LCA-30	DDE
Tensile shear strength/MPa	21.63	21.28	17.64

The tensile shear strength increased in the order of 14BDAPOB>LCA-30>DDE. The cured ER/14BDAPOB had the highest tensile shear strength because, we suggest, 14BDAPOB has four active amino groups which react with the epoxy resin to improve the cross-link density.

4 Conclusions

14BDAPOB was prepared and characterized. Then 14BDAPOB and LCA-30 were used to cure epoxy resin. The kinetics of the curing reaction of ER/14BDAPOB and ER/LCA-30 were studied by using non-isothermal DSC and two kinetic models: Kissinger and Ozawa equations. The activation energy increased, presumably because of an increase in the crosslink density. The activation energies were calculated by use of the Kissinger and Ozawa methods and the results were similar. The kinetic parameters of ER/14BDAPOB and ER/LCA-30 were calculated by the Kissinger, Ozawa and Crane methods. The results showed that T_{onset} values of the cured epoxy resin systems were 398.8 ℃ (ER/14BDAPOB) and 334.3 ℃ (ER/LCA-30); The tensile shear strengths of the cured epoxy resin were 21.63 MPa (ER/14BDAPOB) and 21.28 MPa (ER/LCA-30).

References

[1] May CA. *Epoxy Resins Chemistry and Technology*[M]. second ed. Yew York: Marcel Dekker, Inc, 1988

[2] Musto P, Abbate M, Ragosta G, *et al*. A Study by Raman, Near-infrared and Dynamic-mechanical Spectroscopies on the Curing Behaviour, Molecular Structure and Viscoelastic Properties of Epoxy/Anhydride Networks[J]. *Polymer,* 2007, 48: 3 703-3 716

[3] Wan J, Bu ZY, Xu CJ, *et al*. Model-fitting and Model-Free Nonisothermal Curing Kinetics of Epoxy Resin with a Low-volatile Five-armed Starlike Aliphatic Polyamine[J]. *Thermochim. Acta* , 2011, 525: 31-39

[4] Wan J, Li BG, Fan H, *et al*. Nonisothermal Reaction Kinetics of DGEBA with Four-armed Atarlike Polyamine with Benzene Core (MXBDP) as Novel Curing Agent[J]. *Thermochim. Acta*, 2010, 510: 46-52

[5] Wan J T, Li C, Bu ZY, *et al*. A Comparative Study of Epoxy Resin Cured with a Linear Diamine and a Branched Polyamine[J]. *Chem. Eng. J.*, 2012, 188: 160-172

[6] Montserrat S, Martin JG. Non-isothermal Curing of Diepoxide-Cycloaliphalic Diamine System by Temperature Modulated Differential Scanning Calorimetry[J]. *Thermochim. Acta* , 2002, 388: 343-354

[7] Cai HY, Li P, Sui G, *et al*. Curing Kinetics Study of Epoxy Resin/Flexible Amine Toughness Systems by Dynamic and Isothermal DSC[J]. *Thermochim. Acta*, 2008, 473: 101-105

[8] Wang HM, Zhang YC, Zhu LR, *et al*. Curing Behaviors and Kinetics of Epoxy Resins with a Series of Biphenyl Curing Agents Having Different Methylene Units[J]. *Thermochim. Acta*, 2011, 521: 18-25

[9] Wan JT, Bu ZY, Xu CJ, *et al*. Preparation, Curing Kinetics and Properties of a Novel Low-volatile Starlike Aliphatic-Polyamine Curing Agent for Epoxy Resins[J]. *Chem. Eng. J.*, 2011, 171: 357-367

[10] Li C, Fan H, Hu JJ, *et al*. Novel Silicone Aliphatic Amine Curing Agent for Epoxy Resin: 1,3-Bis(2-aminoethylaminomethyl) tetramethyldisiloxane. 2. Isothermal Cure, and Dynamic Mechanical Property [J]. *Thermochim. Acta*, 2012, 549: 132-139

[11] Maity T, Samanta B, Banthia A, *et al*. Synthesis, Characterisation, Curing Reaction of Aniline Acetaldehyde Condensate with Epoxy Resin[J]. *Resin Technol.*, 2011, 40: 285-291

[12] Ghaemy M, Barghamadi M, Behmadi H. Nonisothermal Cure Kinetics of DGEBA with Novel Aromatic Diamine[J]. *J. Appl. Polym. Sci.*, 2007, 103: 3 076-3 083

[13] Hu JH, Shan J Y, Zhao J, *et al*. Water Resistance and Curing Kinetics of Epoxy Resins with a Novel Curing Agent of Biphenyl-containing Amine Synthesized by One-pot Method[J]. *Thermochim. Acta*, 2015, 606: 58-65

[14] Tang XP, Huang CH. Curing Kinetics of Epoxy Resin by Amine-containing Agents[J]. *Guangzhou Huagong*, 2013, 41(8): 86-87, 204

[15] Liu XD, Cheng J, Lin X, *et al.* Curing Kinetics of Epoxy Resins/Amine System and Epoxy/Episulfide Resin/Amine System[J]. *Huagong Xuebao (Chinese Edition)*, 2013, 64(11): 4 046-4 053

[16] Mustafa MF, Cook WD, Schiller TL, *et al*. Curing Behavior Andthermal Properties of TGDDM Copolymerized with a New Pyridine-containing Diamine and with DDM or DDS [J]. *Thermochim. Acta*, 2014, 575: 21-28

[17] Bhuvana S, Sarojadevi MJ. Synthesis and Characterization of Epoxy/Amine Terminated Amide-Imide-Imide Blends[J]. *J. Appl. Polym. Sci.*, 2008, 108: 2 001-2 009

[18] Supriya N, Catherine KB. DSC-TG Studies on Kinetics of Curing and Thermal Decomposition of Epoxy-Ether Amine Systems[J]. *J. Therm. Anal. Calorim.*, 2013, 112: 201-208

[19] Wan JT, Li BG, Fan H, *et al*. Nonisothermal Reaction, Thermal Stability and Dynamic Mechanical Properties of Epoxy System with Novel Nonlinear Multifunctional Polyamine Hardener[J]. *Thermochim. Acta*, 2010, 511: 51-58

[20] Luda MP, Balabanovich AI, Zanetti M, *et al*. Thermal Decomposition of Fire Retardant Brominated Epoxy Resins Cured with Different Nitrogen Containing Hardeners[J]. *Polym. Degrad. Stab.*, 2007, 92: 1 088-1 100

[21] Woo EM, Seferis JC, Schaffnit RS. Viscoelastic Characterization of High Performance Epoxy Matrix Composites[J]. *Polym. Compos*., 1991, 12: 273-280

[22] Tripathi G, Srivastava D. Cure Kinetics of Ternary Blends of Epoxy Resins Studiedby Nonisothermal DSC Data[J]. *J. Appl. Polym. Sci.*, 2009, 112: 3 119-3 126

[23] Jagadeesh KS, Gururaja RJ. Effect of Type of Substitution in 4,4’-Bis-(diaminodiphenyl) Methane Hardener on Cure Kinetics, Mechanical, and Flame Retardant Properties of Tetrafunctional Epoxy Resins[J]. *J. Appl. Polym. Sci.*, 2006, 101: 480-491

[24] Wan JT, Bu ZY, Xu CJ, *et al*. Model-fitting and Model-free Nonisothermal Curing Kinetics of Epoxy Resin with a Low-volatile Five-armed Starlike Aliphatic Polyamine[J]. *Thermochim. Acta*, 2011, 525: 31-39

[25] Van AG, Van HA, Rahier H, *et al*. Modulated Differential Scanning Calorimetry: Isothermal Cure and Vitrification of Thermosetting Systems[J]. *Thermochim. Acta*, 1996, 286: 209-224

[26] Girard-Reydet E, Riccardi C, Sautereau CH, *et al*. Epoxy -Aromatic Diamine Kinetics. 1. Modeling and Influenceof the Diamine Structure[J]. *Macromolecules*, 1995, 28: 7 599-7 607

[27] Ghaffaria M, Ehsania M, Khonakdara HA, *et al*. Evaluation of Curing Kinetic Parameters of an Epoxy/Polyaminoamide/Nano-Glassflake System by Non-isothermal Differential Scanning Calorimetry[J]. *Thermochim. Acta*, 2012, 533: 10-15

[28] Zvetkov VL. Comparative DSC Kinetics of the Reaction of DGEBA with Aromatic Diamines. I. Non-isothermal Kinetic Study of the Reaction of DGEBA with m-Phenylene Diamine[J]. *Polymer*, 2001, 42: 6 687-6 697

[29] Kissinger HE. Reaction Kinetics in Differential Thermal Analysis[J]. *Anal. Chem.*, 1957, 29: 1 702-1 706

[30] Ozawa T. Kinetic Analysis of Derivative Curves in Thermal Analysis[J]. *Bull. Chem. Soc. Jpn.*, 1965, 38: 1 881-1 886

[31] Crane LW, Dynes PJ, Kaelble DH. Analysis of Curing Kinetics in Polymer Composites[J]. *J. Polym. Sci. Polym. Lett. Ed.*, 1973, 11: 533-540