

Toughening of Epoxy Resins by Modified *m*-Phenylene Diamine Having Soft Ether Chain

Chunhua Lou,¹ Kong Xianzhi,² Wang Jianxin,¹ Ma Liqun¹

¹Department of Material Science and Engineering, Qiqihar University, Qiqihar 161006, China

²Institute of Petrochemistry, Heilongjiang Academy of Science, Harbin 150040, China

Received 22 December 2010; accepted 26 September 2011

DOI 10.1002/app.36264

Published online 22 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A new softening curing agent for toughening epoxy resins was synthesized by *m*-phenylene diamine modified with epoxypropyl butyl ether. The curing processes of epoxy resin/modified *m*-phenylene diamine were traced by differential scanning calorimetry (DSC), then kinetic parameters, ΔE and n , were deduced. Fourier transform infrared (FTIR) analysis showed that the longer the reaction time was, the smaller the absorption peaks of epoxy group were. The results of the mechanical properties

demonstrated that the impact property of the epoxy resin cured by modified *m*-phenylene diamine at the moderate temperature was better than that of cured by unmodified one because of the introduction of soft ether chain. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 578–583, 2012

Key words: epoxy resin; kinetics; *m*-phenylene diamine; toughness; mechanical properties

INTRODUCTION

Epoxy resins have high chemical and corrosion resistance, outstanding adhesion properties, low shrinkage upon curing, and good electrical properties. Principal applications for these resins include protective coatings, composite matrices, and adhesives. But, as a consequence of their highly cross-linked structure, these materials tend to suffer from brittleness, poor crack resistance, and low fracture toughness.¹ It is necessary that toughening epoxy resins to adapt to the various aspects of needs.

Epoxy resins can be cured by catalytic or coreactive curing agents. The ultimate properties of cured resins can be controlled according to end use by proper choice of curing agent and curing conditions. Although epoxy resins are used for a wide range of applications, their inability to withstand impact is a serious drawback for several advanced applications. Four methods of toughening brittle epoxy resins are known: Type 1—chemically modify with a more flexible backbone; Type 2—increase molecular weight of the epoxy backbone resin; Type 3—decrease crosslinking density of the matrix; Type 4—incorporate a dispersed toughener phase in the epoxy matrix.^{2–4} Major investigations focused on forming blends by adding thermoplastic polymers or rubbers into epoxy resin in order to improve

toughness of epoxy resins.^{5–11} The methods of toughened epoxy generally lead to the loss of modulus, glass transition temperature, and solvent resistance, thus limiting the number of high-performance application of these resins. The most effective approach is the introduction of a second component which is capable of phase separation as reactive liquid rubber,^{12–14} thermoplastic,^{15–17} or core-shell particles.^{18–23} Considerable attention has been paid to the use of functionalized curing agents for epoxy resins. By designing molecules' structure of curing agents or synthesizing flexible curing agents, the toughness, crack resistance, and other properties of the epoxy resins could be improved,^{24,25} what is popular increasingly from now on.

Amine curing agents are the most widely used in the epoxy resins. But the unmodified amines can not meet the needs of developments, since they are of defects as follows: (a) some have volatility and toxicity; (b) some have bad blend with epoxy resin; (c) some have fast curing speed; (d) some are solid using inconveniently; (e) some are easy to absorb damp and CO₂ which make the surface of the solidification white; (f) some are brittle; etc. Thus, a great many of modified amines are developed to play down volatility and toxicity, regulate curing speed and reaction heat, reduce viscosity or make them liquefy, amend soakage and blend with epoxy, enhance strength and toughness, ameliorate curing performances at low temperature, humidity, underwater and some other extreme conditions. The modified amines have already become major variety of amine curing agent, its applications are more and more widely. The

Correspondence to: C. H. Lou (chunhualou@163.com).

TABLE I
Raw Materials List

Chemical description	Abbreviation	Suppliers
E51(DYD-128): bisphenol-A type epoxy resin (liquid, average epoxy value is 0.51)	E51	Dalian Qihua Chemical Co. Ltd.
<i>m</i> -phenylene diamine	<i>m</i> -PDA	Tianjin Kermel Chemical Reagent Exploiture Center
epoxypropyl butyl ether	EPBE	Tianjin Kermel Chemical Reagent Exploiture Center

modified methods are either chemical or physical, in which the chemical ways are major. The modified amine was synthesized by utilizing additions or condensations of the activate H or other groups of amine curing agents with modifier in the chemical modifications.²⁶ Now, developing new curing agents is more important than exploiting new epoxy resins, and which also acquires economic benefits easily.

The curing agent having polyfunctionality is the most ideal product due to its excellent curing property. In this article, in order to prepare a kind of polyfunctional curing agents of epoxy resins, epoxypropyl butyl ether (EPBE) was selected to modify *m*-phenylene diamine (*m*-PDA). Thus, the epoxy resin could be toughened by the introduced long ether chain of EPBE.

EXPERIMENTAL

Materials

The raw materials used in this study are listed in Table I. All these materials except epoxy resin were laboratory grade chemicals and were used without further purification.

Preparation of PDAE

The modified *m*-PDA having soft ether chain of EPBE (PDAE) was synthesized by the nucleophilic

substitution reaction of *m*-PDA with EPBE as show in Scheme 1. A typical procedure for the synthesis of PDAE is as follows. The *m*-PDA was introduced into a 250 mL four-necked flask equipped with a mechanical stirrer, an inlet of nitrogen, a condenser and a thermometer. The reactant was heated to melt in a constant temperature water bath. EPBE was added dropwise with stirring; the dropping rate was controlled. The reaction has been at 70°C for 5 h.

Measurements

FTIR spectra for the samples were recorded using Spectrum 100 FTIR (PekinElmer Corporation, USA) analyzer in the range of 4000–400 cm⁻¹; the samples were dissolved in acetone and evaporated on potassium bromide (KBr) disc under infrared (IR) lamp.

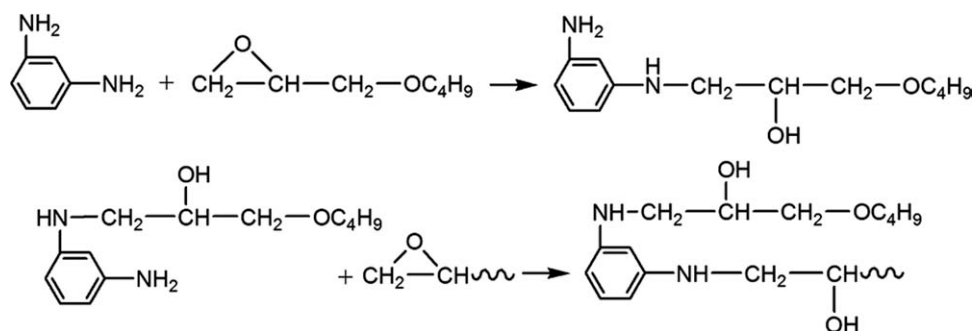
Differential scanning calorimetric (DSC) analyses were performed on a Netzsch DSC 204F1 in a nitrogen atmosphere. Calibration was achieved using indium standard samples. Scans were run at heating rate of 10°C/min. Reported values were obtained from a second heating after a quick cooling.

For mechanical characterization, five specimens were prepared by casting the resin onto PTFE molds having precise size and shape.

Impact tests were carried out on a JJ-20 memorable impact tester at room temperature. Specimens were molded with dimension of 80 ± 2 mm² length, 10 ± 0.5 mm² width and 4 ± 0.2 mm² thickness.

Tensile shear tests were put into practice on a NLW-20 shear tester of adhesive at room temperature. Joint areas of aluminum alloy specimen were 15 × 15 mm².

Tensile tests were accomplished on a CSS-2200 universal testing machine at room temperature. In a typical tensile test, a polymer sample, in the form of a dogbone (Fig. 1 and Table II), is clamped at one end and pulled at a constant speed of 2 mm/min of elongation at the other clamped end. The thinner portion of the tensile specimen encourages the sample to fail at the center of the bar, where the stress is the highest, and not at the grip sites, where stress concentration may otherwise result in premature failure.



Scheme 1 Reactions involved in the synthesis of *m*-PDA having soft ether chain.

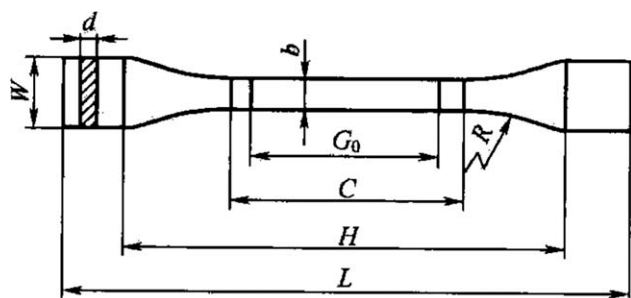


Figure 1 Dimension of the samples of tensile tests.

RESULTS AND DISCUSSION

FTIR analysis

In epoxy/PDAE blends, curing reaction was done at 80°C. FTIR studies were conducted to examine the curing degree of curing reaction. The analyses of the samples were performed every 20 min, and then the FTIR spectra were depicted in Figure 2.

From Figure 2, the absorption characteristic of epoxy group was at 915 cm⁻¹. According to Lambert-beer law:

$$A = \varepsilon \cdot b \cdot C \quad (1)$$

where, A is the absorbency, ε is the absorption coefficient, b is the sample width of light passes through, C is the concentration of sample. The film thickness was adjusted to make the A value less than 1 at 915 cm⁻¹ during experiment, which make it preferably linear. The absorption intensity of epoxy groups decreased in slightly with increasing time. This indicated that epoxy groups were reacted with the primary amine. Because it is a slender absorption peak, reading straight forwards would be prone to even greater errors. Chosen the characteristic peak of benzene ring at 1508 cm⁻¹ to be a reference peak, the ratio of $\frac{A_{915\text{ cm}^{-1}}}{A_{1508\text{ cm}^{-1}}}$ is described the degree of curing. Thus, degree of curing at time t is:

TABLE II
Dimensions of Tensile Specimens

Designation	Description	Dimension (mm)	Tolerance (mm)
L	Total length (the least)	150	—
H	Space between clamp	115	±5.0
C	Length of middle parallel part	60	±0.5
G_0	Valid part	50	±0.5
W	Width of end part	20	±0.2
d	thickness	4	—
b	Width of middle parallel part	10	±0.2
R	Radius (the least)	60	—

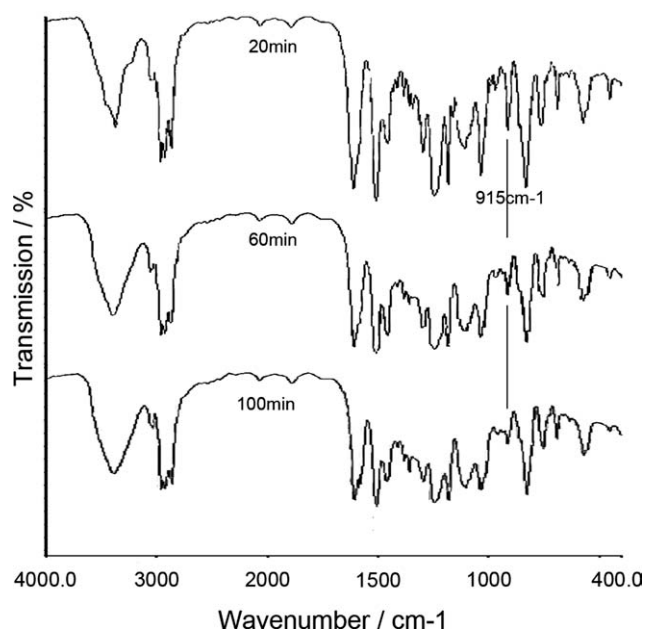


Figure 2 FTIR spectra of curing reaction at 80°C.

$$D_t = 1 - \frac{(A_{915}/A_{1508})_t}{(A_{915}/A_{1508})_0} \quad (2)$$

where, D_t is the degree of curing at time t , $(A_{915}/A_{1508})_t$ is the ratio of $\frac{A_{915\text{ cm}^{-1}}}{A_{1508\text{ cm}^{-1}}}$ at time t , $(A_{915}/A_{1508})_0$ is the ratio of $\frac{A_{915\text{ cm}^{-1}}}{A_{1508\text{ cm}^{-1}}}$ at time 0. The absorbencies are represented in Table III and the degree of curing is shown in Figure 3.

From Figure 2, strong absorptions at 3400 cm⁻¹ (—OH forms hydrogen bend) increased gradually. The mechanism of amine cured epoxy resins is presented in Scheme 2.

From Scheme 2, the secondary amine group formed in this reaction can react further to give a tertiary amine. Therefore, the percentage of unreacted epoxy groups decreased and the hydroxyl groups increased with increasing time.

Thermal properties

DSC analysis

The activities of the epoxy resin systems cured by PDAE are related to both epoxy resins and curing

TABLE III
Absorbency of Curing

Reaction time/min	$A_{915\text{ cm}^{-1}}$	$A_{1508\text{ cm}^{-1}}$	$\frac{A_{915\text{ cm}^{-1}}}{A_{1508\text{ cm}^{-1}}}$	D_t
0	0.205	0.655	0.313	0
20	0.158	0.534	0.296	0.054
40	0.125	0.466	0.268	0.144
60	0.095	0.377	0.252	0.195
80	0.066	0.35	0.189	0.396
100	0.062	0.35	0.177	0.434

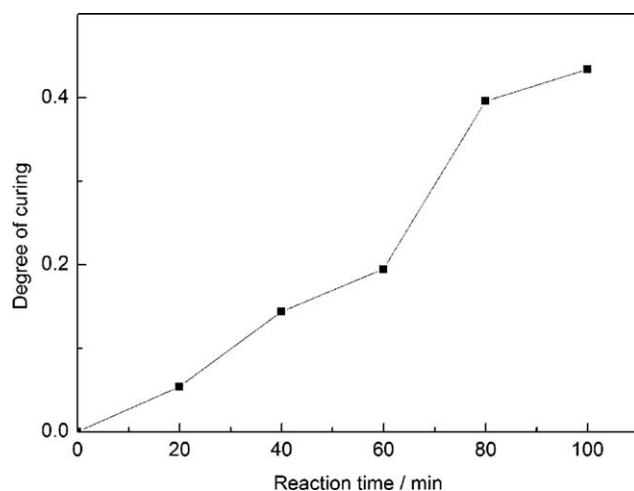
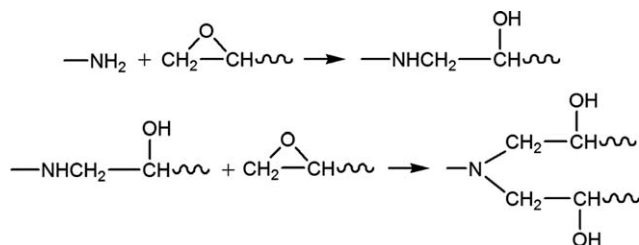


Figure 3 Degree of curing reaction at 80°C.

agents. Figure 4 shows the DSC curves of cured epoxy resins with different contents of PDAE.

As seen in Figure 4, the weight ratios of PDAE and epoxy resins are 1 : 1.6, 1 : 2, and 1 : 2.5, respectively. There is only one exothermic on every DSC curve. However, the location of each peak and the value of reaction heat are different from the others. The damping peak corresponding to the temperature is displaced to higher temperatures as addition of PDAE. The exothermic enthalpy (ΔH) of each peak indicates the degree of curing. The curing is not completed and the value of ΔH is low with less curing agent or at lower curing temperature. As a result, the system is not cured completely unless it is at higher curing temperature and for longer curing time. On the contrary, excessive amounts of curing agents may promote excessive curing so that the reaction would be carried out under more violent conditions and generally the molded products would become hard and fragile. In Figure 4, the temperature of the exothermic peak is the lowest when the ratio of PDAE and epoxy resin was 1 : 1.6.

DSC curves of different heating rates are shown in Figure 5 when the ratio of PDAE and epoxy resins was 1 : 2. There is only one exothermic peak each, which indicates that the curing is an exothermic and one-step reaction. However, the peaks are displaced to higher temperatures as increased heating rates.



Scheme 2 Mechanism of amine cured epoxy resins.

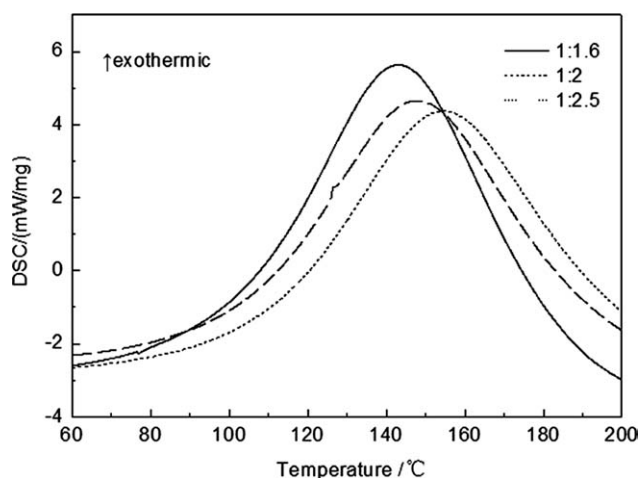


Figure 4 DSC curves of curing systems with different content of modified curing agents.

The reason is that the curing time is decreased and the exothermic enthalpy per unit time is increased as increased the heating rate, thus, the exothermic peak turned peakedly and produced caloric hysteresis.²⁷

Kinetic parameters deduction

The kinetic parameters, such as apparent activation energy and reaction order, are important to understand the resin curing. The curing reaction would have completed only if the energy of reactive molecules was more than the activation energy. The reaction order might be expected the mechanism of the curing reaction.

Curing kinetics of epoxy resins would be studied according to Kissinger equation (3)²⁸⁻³⁰ (the data see Fig. 5):

$$\frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} = -\Delta E/R \quad (3)$$

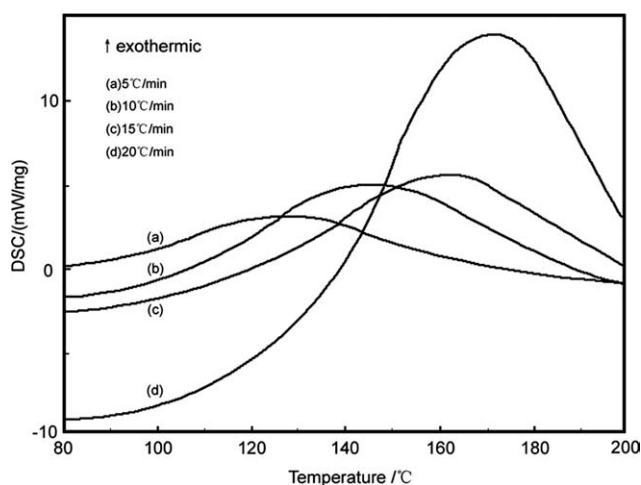


Figure 5 DSC curves at different heating rates.

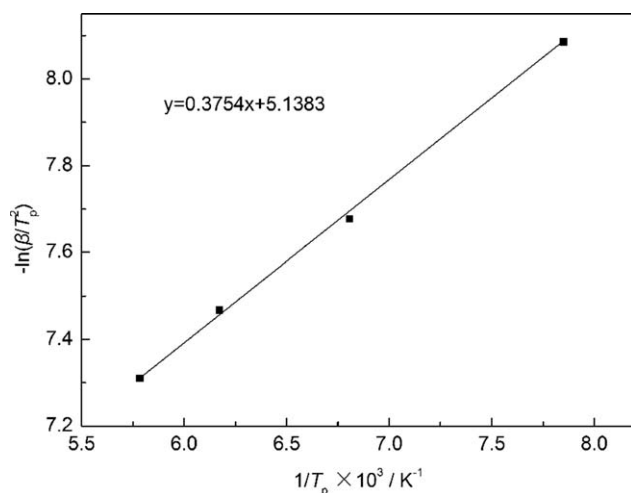


Figure 6 Curve of $-\ln(\beta/T_p^2)$ versus $1/T_p$.

where β is the constant heating rate (K/min), T_p is the top-peak temperature (K), R is the ideal gas constant (8.314 J/mol K), ΔE is the apparent activation energy (kJ/mol).

The curve of $-\ln(\beta/T_p^2)$ versus $1/T_p$ is shown in Figure 6.

From Figure 6, the slope of the line is 3.754×10^2 K from which the apparent activation energy (ΔE) of E51/*m*-PDA/EPBE can be calculated as 3.121 kJ/mol.

The reaction order could be calculated according to Crane equation (4)^{28–30}:

$$\frac{d(\ln \beta)}{d(1/T_p)} = -\left(\frac{\Delta E}{nR} + 2T_p\right) \quad (4)$$

where, n is the reaction order.

The curve of $\ln \beta$ versus $1/T_p$ is shown in Figure 7. Crane deemed that the slope of the beeline is $-\Delta E/nR$ when $\Delta E/nR \gg 2T_p$. The slope value is -6.711×10^2 K, then $\Delta E/nR = 6.711 \times 10^2$ where ΔE has obtained from eq. (3), so the reaction order could be calculated and its value was 0.56, not an integer, which indicates the curing reaction is a complicated course.

Mechanical properties

The system of *m*-PDA cured epoxy resins suffered the drawbacks of brittleness, which limits its appli-

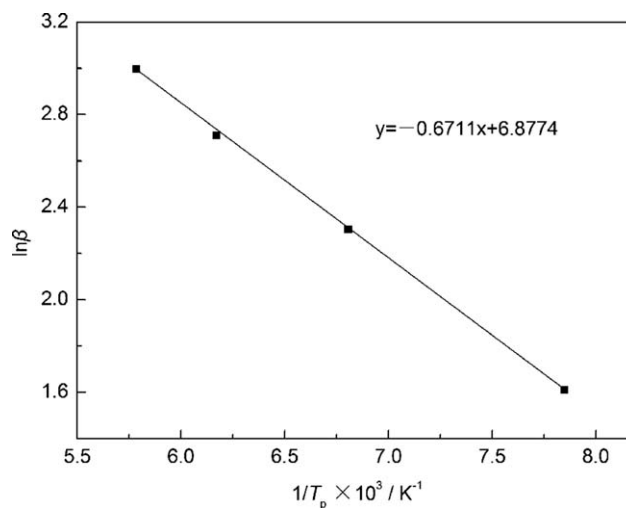


Figure 7 Curve of $\ln \beta$ versus $1/T_p$.

cations. The introduction of EPBE groups into curing agents can always improve their toughness effectively. To determine the effect of toughening mechanism on the mechanical properties of epoxy resin system, various formulations were performed by the incorporation of PDAE in different weight ratios. The mechanical properties of epoxy resins which were cured with *m*-PDA or PDAE are given in Table IV. The impact, tensile, and tensile shear strengths of the cured resins increased on addition of PDAE but the weight ratio more than 1 : 3, all strength properties of cured resins effected adversely. And they reach a maximum value by using weight ratio of 1 : 3. The impact strength increases from 4.22 kJ/m² to 7.43 kJ/m², the tensile strength increases from 8.19 MPa to 21.89 MPa, and the tensile shear strength increases from 5.53 MPa to 17.53 MPa. These maximum values all exceed the ones which cured with *m*-PDA.

The properties are also depended on the amount of curing agents. Since the molecule of the curing agent was smaller than that of epoxy resin, further addition of curing agents could influence on the viscosity of curing system which made it difficult to get polymer; while decrease could make the curing reaction incomplete, consequently, the values of mechanical properties are lower. Therefore, the solidifier of excellent properties would be

TABLE IV
Mechanical Properties of Epoxy Resins of Different Curing Agents

Curing agent	<i>m</i> -PDA	Modified <i>m</i> -PDA ^a		
<i>m</i> (curing agent) : <i>m</i> (resin) ^b	1 : 6	1 : 2	1 : 3	1 : 4
Impact strength (kJ/m ²)	3.59 ± 0.20	4.22 ± 0.20	7.43 ± 0.25	3.97 ± 0.20
Tensile shear strength (MPa)	10.78 ± 1	5.53 ± 0.2	17.53 ± 1	3.36 ± 0.2
Tensile strength (MPa)	13.56 ± 1	8.19 ± 0.5	21.89 ± 1	7.64 ± 0.5

^a Modified *m*-PDA was synthesized when the molar ratio of EPBE and *m*-PDA was 1 : 1, curing conditions: 100°C, 3.5 h.

^b *m*(curing agent) : *m*(resin) means weight ratio of curing agent and resin.

obtained only if the amount of curing agents were appropriate. On the basis of mechanical properties tested, it can be said that PDAE is the better one as a toughener and the weight ratio of curing agents in the epoxy resin formulations is the key factor to determine the efficiency of PDAE as the toughener.

Toughening mechanism analysis

In conclusion, the PDAE is synthesized by EPBE reacting to *m*-PDA, and the toughening mechanism is presented in Scheme 1.

EPBE being introduced into *m*-PDA, the primary amidocyanogen is decreased while molecular weight is increased. The structure of the PDAE is of long ether chain, which made the solidifier toughened.

CONCLUSION

E51 was toughened, which was cured with EPBE modified *m*-PDA. The mechanism of amine curing agents cured epoxy resin was deduced from FTIR of curing process. Kinetic parameters can be calculated using DSC analysis: the apparent activation energy $\Delta E = 3.121$ kJ/mol and the reaction order $n = 0.56$, which indicates the curing reaction was a complicated course. The mechanical properties as impact, tensile, and tensile shear strength of E51/*m*-PDA or PDAE system were measured. No gap impact strength of molded epoxy which was cured with *m*-PDA was only 3.59 kJ/m² while that of done with PDAE was 7.43 kJ/m², increased by 107%. Moreover, the tensile and tensile shear strength of this cured system present a trend same as the impact strength, their maximum values were 21.89 MPa and 17.53 MPa, respectively, these maximum values all exceed the ones which cured with *m*-PDA. The weight ratio of curing agent was key factor for the mechanical properties of toughened resins. Take the impact strength, tensile strength and tensile shear strength of the cured systems as a whole into account, the most suitable composition to improve the mechanical properties of the epoxy matrix was obtain at 1/3 w/w. Finally, toughening mechanism has been indicated that the curing agent, PDAE, made the epoxy resins toughened because EPBE was introduced.

The authors thank Dalian Qihua Chemical Co. Ltd., China, for the generous gift of epoxy resin.

References

- Emel, Y.; Özdemir, Ö.; Tülay, Y. İ.; Abdülkadir, K.; Attila, G. *Polym Bull* 2007, 58, 503.
- Abdolreza, M.; Siamak, Z. *J Polym Res* 2010, 17, 191.
- Francis, B.; Rao, V. L.; Jose, S.; Catherine, B. K.; Ramaswamy, R.; Jose, J.; Thomas, S. *J Mater Sci* 2006, 41, 5467.
- Raghavachar, R.; Letasi, R. J.; Kola, P. V.; Chen, Z.; Massingill, J. L. *JAACS* 1999, 76, 511.
- Shailesh, K. S.; Deepak, S. *J Mater Sci* 2007, 42, 3215.
- Lee, J.; Yee, A. F. *J Mater Sci* 2001, 36, 7.
- Krzysztof, S.; Dariusz, B. *J Polym Res* 2009, 16, 401.
- Auad, M. L.; Proia, M.; Borrajo, J.; Aranguren, M. I. *J Mater Sci* 2002, 37, 4117.
- Liu, P. G.; He, L. H.; Ding, H. Y.; Liu, J. N.; Yi, X. S. *J Polym Res* 2005, 12, 139.
- Ratna, D.; Varley, R.; Singh Raman, R. K.; Simon, G. P. *J Mater Sci* 2003, 38, 147.
- Li, J. B. *Polym Bull* 2006, 56, 377.
- Cengiz, C.; Guneri, A.; Cevdet, K. *Polym Bull* 2004, 51, 429.
- Kong, J.; Ning, R. C.; Tang, Y. S. *J Mater Sci* 2006, 41, 1639.
- Kong, J.; Tang, Y. S.; Zhang, X. J.; Gu, J. W. *Polym Bull* 2008, 60, 229.
- Kinloch, A. J.; Taylor, A. C. *J Mater Sci* 2006, 41, 3271.
- Wang, M. H.; Yu, Y. F.; Li, S. J. *Sci China Ser B-Chem* 2007, 50, 554.
- Zhang, B. Y.; Li, P.; Chen, X. B. *J Mater Sci* 1998, 33, 5683.
- Yan, C.; Xiao, K. Q.; Ye, L.; Mai, Y. W. *J Mater Sci* 2002, 37, 921.
- Sue, H. J.; Bertram, J. L.; Garcia-Meitin, E. I.; Wilchester, J. W.; Walker, L. L. *Colloid Polym Sci* 1994, 272, 456.
- Becu, L.; Taha, M.; Maazouz, A.; Merle, G. *J Mater Sci* 2002, 37, 41.
- Lu, F.; Cantwell, W. J.; Kausch, H. H. *J Mater Sci* 1997, 32, 3055.
- Ormaetxea, M.; Forcada, J.; Mugika, F.; Valea, A.; Martin, M. D.; Marieta, C.; Goyanes, S.; Mondragon, I. *J Mater Sci* 2001, 36, 845.
- Sue, H. J.; Garcia Meitin, E. I.; Pickelman, D. M.; Bott, C. J. *Colloid Polym Sci* 1996, 274, 342.
- Tian, X. H. *Thermosetting Resin* 1987, 4, 41.
- Zhou, J. L.; Fan, H. P. *Chem Propellants Polym Mater* 2006, 4, 13.
- Tian, X. H.; Gao, F. S.; Ye, L. H. *China Plast Industry* 1981, 5, 23.
- Chen, X. Q.; Wang, L.; Huang, P.; Shi, J. *Thermosetting Resin* 2005, 20, 23.
- Wang, Q.; Wang, T. W.; Wei, W. J. *Chem React Eng Technol* 2005, 21, 492.
- Zeng, X. N.; Duan, Y. X. *Acta Mater Compos Sin* 2007, 24, 100.
- Yi, C. H.; Yin, Y. G.; Li, J. Z.; Cheng, S. Y. *Thermosetting Resin* 2000, 15, 13.