

Effect of Reactive Poly(ethylene glycol) Flexible Chains on Curing Kinetics and Impact Properties of Bisphenol-A Glycidyl Ether Epoxy

Dahu Yao,^{1,2} Tapas Kuila,¹ Kyung-Bok Sun,¹ Nam-Hoon Kim,³ Joong-Hee Lee^{1,4}

¹*BIN Fusion Research Team, Department of Polymer and Nano Engineering, Chonbuk National University, Jeonju, Jeonbuk, 561-756, Korea*

²*College of Chemical Engineering and Pharmaceuticals, Henan University of Science and Technology, Luoyang 471003, Peoples' Republic of China*

³*Department of Hydrogen and Fuel Cell Engineering, Chonbuk National University, Jeonju, Jeonbuk, 561-756, Korea*

⁴*WCU Program, Department of BIN Fusion Technology, Chonbuk National University, Jeonju, Jeonbuk, 561-756, Korea*

Received 30 September 2010; accepted 18 July 2011

DOI 10.1002/app.35275

Published online 26 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Bisphenol-A glycidyl ether epoxy resin was modified using reactive poly(ethylene glycol) (PEO). Dynamic mechanical analysis showed that introducing PEO chains into the structure of the epoxy resin increased the mobility of the molecular segments of the epoxy network. Impact strength was improved with the addition of PEO at both room (RT) and cryogenic (CT, 77 K) temperature. The curing kinetics of the modified epoxy resin with polyoxypropylene diamines was examined by differential scanning calorimetry (DSC). Curing kinetic parameters were deter-

mined from nonisothermal DSC curves. Kinetic analysis suggested that the two-parameter autocatalytic model suitably describes the kinetics of the curing reaction. Increasing the reactive PEO content decreased the heat flow of curing with little effect on activation energy (E_a), pre-exponential factor (A), or reaction order (m and n). © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2325–2332, 2012

Key words: toughness; modification; differential scanning calorimetry; mechanical properties

INTRODUCTION

Epoxy resin is one of the most important thermosetting materials owing to its low cost, ease of processing, and good thermal, mechanical, and electrical properties. They are used widely in aerospace, electrical, electronic, and automobile industries,^{1–3} as structural adhesives^{4,5} and as matrices for composites. However, these resins are quite brittle showing poor resistance to crack propagation. In particular, dramatic changes in the structure and properties can occur when they are exposed to thermal cycles at cryogenic temperatures. When the temperature is decreased to cryogenic temperatures, internal stress due to thermal contraction is generated in a matrix resin. However, the performance of epoxy resins

and their composites at cryogenic temperatures is very important when they are used in the aerospace and superconductor industries.^{6–8} Therefore, it is essential to give the epoxy resin fracture resistance at cryogenic temperatures (CT).

Most polymer segments are frozen at CT. Hence, the toughening of the epoxy resin is quite difficult under this condition. Different chemical units are present in epoxy resins, such as diphenylol propane, diphenylol methane, tetrabromo-diphenylol propane, phenol novolac, diamines, diacids, diols, etc. Based on these chemical units, different types of toughening agents and hardeners, such as engineering thermoplastics, hyperbranched polymer, reactive diluents, fillers, acid anhydride, amine, phenol, etc.,^{9–20} have been used to induce a change in the performance of epoxy resins. It was suggested that the different network structures impart different properties even if the polymers have the same chemical structure. On the other hand, the network structure can be controlled by a chemical reaction. Ueki et al. proposed that low molecular weight plasticizers can also be used to improve the fracture toughness of epoxy resin.²⁰ More commonly, ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, and polyethylene glycol (PEO) have been used as plasticizers for

Correspondence to: J.-H. Lee (jhl@chonbuk.ac.kr).

Contract grant sponsor: Human Resource Training Project for Regional Innovation and the World Class University program; contract grant number: R31-20029.

Contract grant sponsor: National Research Foundation of Korea funded by the Ministry of Education, Science and Technology, South Korea.

polymer modification.²¹ Among these plasticizers, the chain segments of PEO are more flexible, sterically less hindered, and hence, the rotational movement of the chain segments are allowed at cryogenic temperatures.¹⁵ Therefore, PEO can be used to toughen epoxy resin at cryogenic temperatures. In this study, epoxy resin was toughened by reactive PEO flexible chains. The modifications can affect the processability of the epoxy resin, and the curing condition has a large effect on the physical properties of cured epoxy resins.^{22,23} Therefore, it is essential to control the curing condition for thermosetting materials to achieve the desired end-properties. The cure kinetics of modified epoxy resins was examined using a nonisothermal DSC method. The impact strength of the modified epoxy resins was investigated at room temperature (RT) and cryogenic temperatures.

EXPERIMENTAL

Material

The epoxy resin used in this study was diglycidyl ether of bisphenol-A (DGEBA, YD-128, Kukdo Chemical Ind. Co., Korea) with an epoxide weight equivalence in the 184–190 g/mol range. The curing agent (D-230) (polyoxypropylene diamines, $M_w = 230$) was purchased from New Seoul Chemical Co. Ltd., South Korea. PEO-1000 (poly(ethylene glycol), $M_n = 1000$) was purchased from Aldrich Co. and isophorone diisocyanate (IPDI) was obtained from TCI, Japan.

Modification of epoxy resin

Different NCO terminated-polyurethane prepolymers were prepared by reacting 1.8 equivalents of IPDI with 1 equivalent of PEO-1000. PEO-1000 was first heated under vacuum at 120°C for 90 min in an oil bath to remove moisture. IPDI was added at a reduced temperature of 80°C, at which the reaction progressed with constant stirring by a mechanical stirrer under a dry nitrogen atmosphere until the isocyanate content (determined by di-*n*-butylamine titration) reached the theoretical value. Dry DGEBA was subsequently added to the prepolymers and the reaction occurred at 80°C for 4 h with a dibutyl tin dilaurate catalyst. The resulting product after modification was designated as modified epoxy resin. Scheme 1 outlines the preparation of modified epoxy resin from neat epoxy.

Preparation of the samples

The curing agent (D-230) was mixed thoroughly with the modified epoxy resins and evacuated care-

fully to remove the air bubbles. The stoichiometric ratio of epoxy/amine, $[E]_{\text{modified EP}}/[H]_{\text{D-230}} = 1$, was used in this experiment. After evacuation, the mixture was casted into an open silicon mold. The blends were cured at 80°C for 4 h. After curing, the blends were allowed to cool naturally to room temperature. The weight ratio of neat epoxy to D-230 was varied from 100 to 30.

Characterization

Impact testing

Charpy impact testing was carried out on the HIT25P impact test machine (Zwick/Roell, Germany) at room temperature and at 77 K according to ASTM D-256. Specimens were immersed in liquid nitrogen (77 K) for at least 10 min and impact testing was performed immediately upon their removal from liquid nitrogen. The temperature of the specimen was monitored by a VarioCAM Infrared camera (Infratec GmbH, Germany). At least five species were tested for each sample.

FT-IR spectroscopy

Samples were dissolved in acetone and dropped onto KBr pellets. Fourier-transform infrared (FT-IR) spectrometry (Jasco, 4100E) was performed at 25°C over the wavenumber range of 4000–500 cm^{-1} with 4 cm^{-1} resolution for 64 scans.

DSC measurement

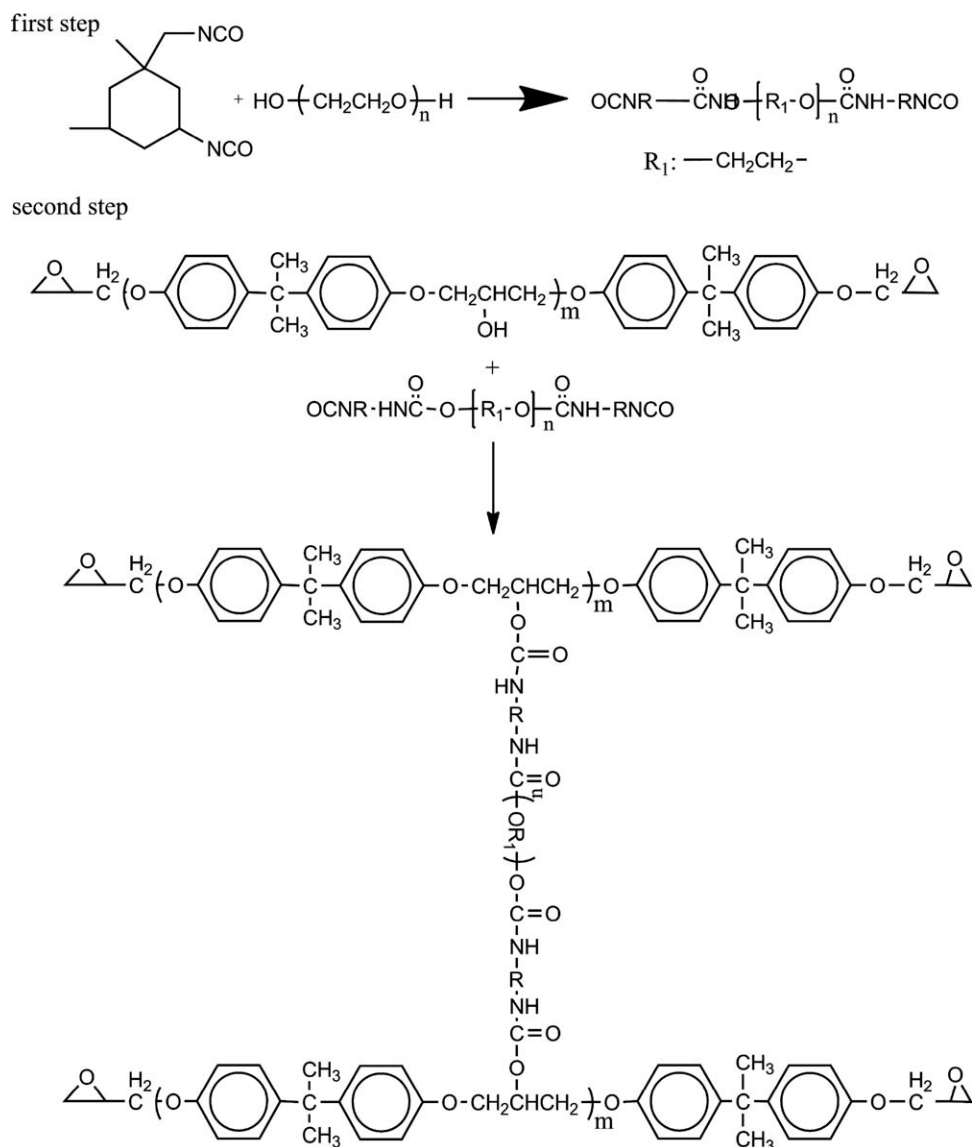
Curing thermal data were obtained by differential scanning calorimetry (TA Instruments, Q20), in the temperature range of 30–260°C at different heating rates (5, 10, and 15°C min^{-1}) under nitrogen. Small quantities of the samples (9–12 mg) were used for the DSC measurement in an aluminum cell. A similar empty cell was used as a reference. Heat flow data were obtained as a function of temperature and time using the area under the exothermic peak and processed further to obtain the degree of conversion and rate of reaction.

DMA measurement

Dynamic mechanical properties of the samples were measured using a TA Instruments (DMA Q 800) from –150 to 120°C at a heating rate of 3°C/min.

Kinetic analysis

The basic assumption for the application of DSC to the curing of thermoset polymers is that the rate of the kinetic process ($d\alpha/dt$) is proportional to the measured heat flow.^{24–26}



Scheme 1 The modification of epoxy resin with reactive PEO.

$$\frac{d\alpha}{dt} = \frac{dQ/dt}{Q_{\text{total}}} = k(T)f(\alpha) \quad (1)$$

where $d\alpha/dt$ is the curing rate, dQ/dt is the heat flow, Q_{total} is the total heat released when an uncured material is completely cured, α is the extent of the reaction (degree of conversion), $k(T)$ is the rate constant, and T is the absolute temperature. The reaction model function, $f(\alpha)$, is a function of the degree of conversion and can be described by various empirical kinetic models. The most commonly applied models to study the curing reactions are the reaction order model²⁷:

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

and the two-parameter autocatalytic model (Šesták-Berggren equation), which for a reaction with zero initial rate is

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (3)$$

where m and n are the reaction orders.

Explicit temperature dependence of the rate constant can be introduced by replacing with it the Arrhenius equation.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad (4)$$

where A is the pre-exponential factor and E_a is the apparent activation energy.

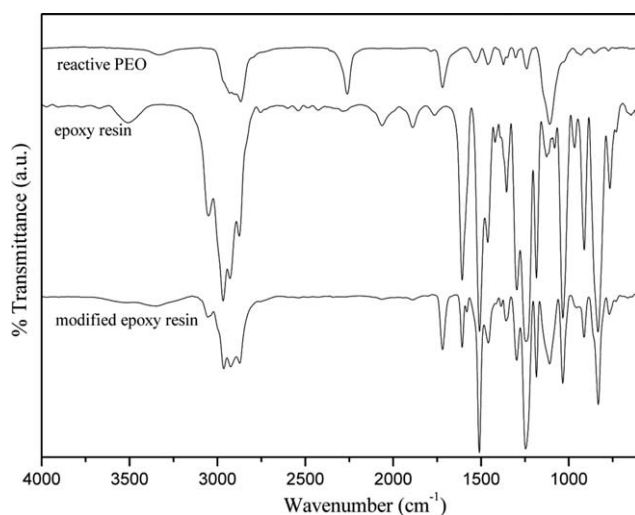


Figure 1 FT-IR spectra of reactive PEO, epoxy resin, and modified epoxy resin.

Under nonisothermal conditions, when the temperature varies with time ($\beta = dT/dt$), eq. (4) can become

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (5)$$

According to the method reported by Málek,^{24,28} it is possible to calculate all the kinetic parameters from a single nonisothermal DSC curve if E_a is known. The most suitable kinetic model can be evaluated by the special functions $y(\alpha)$ and $z(\alpha)$:

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) e^x \quad (6)$$

$$z(\alpha) = \pi(x) \left(\frac{d\alpha}{dt}\right) \frac{T}{\beta} \quad (7)$$

where x is the reduced activation energy (E_a/RT), β is the heating rate (K min^{-1}), and T is the absolute temperature (K). The expression of the temperature integral, $\pi(x)$, can be approximated using the fourth rational expression^{25,26}:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (8)$$

RESULTS AND DISCUSSION

FTIR analysis

Figure 1 shows the FTIR spectra of the reactive PEO, the epoxy resin, and the modified epoxy resin. The neat epoxy resin showed a broad peak at ca. 3500 cm^{-1} , assigned to stretching vibrations of hydroxyl ($-\text{OH}$) groups.²⁹ A peak characteristic of the epoxy group in DGEBA appeared at 912 cm^{-1} .³⁰ The peak at 2265 cm^{-1}

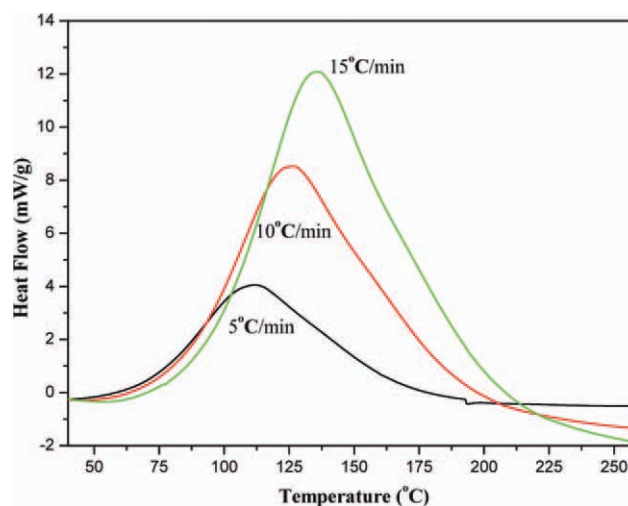


Figure 2 DSC curves for epoxy resin blend containing 10 wt % PEO measured at three different heating rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in the PEO spectrum was attributable to its NCO. The peaks at 2265 cm^{-1} and 3500 cm^{-1} were not observed in the spectrum of the modified epoxy resin. However, the peak located at 912 cm^{-1} was unchanged in the modified epoxy resin. This confirms that the reaction between the $-\text{NCO}$ groups of reactive PEO and the pendent $-\text{OH}$ groups of the epoxy resin was completed, whereas the oxirane groups remain unaffected.

Effect of PEO content on E_a

The curing reaction of PEO-modified epoxy resins with D-230 was examined by DSC at three different heating rates. Figure 2 shows the DSC curves for the modified epoxy resin with 10 wt % PEO at different heating rates. The DSC curves suggest that the peak

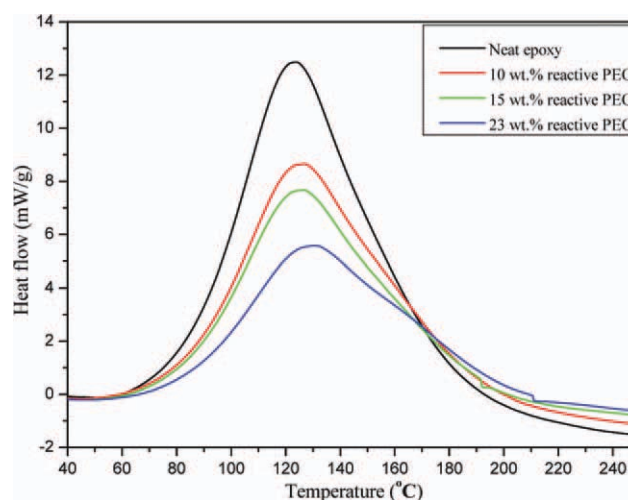


Figure 3 DSC curves for epoxy resin blends with different PEO contents measured at $10^\circ\text{C min}^{-1}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
The Kinetic Parameters Evaluated for the Curing of the Test Epoxy Resins

Sample	Heating rate	E_a	$\ln A$	Mean	m	Mean	n	Mean
0 % PEO	5	55.28	16.30	16.30	0.341	0.348	1.874	1.913
	10		16.31		0.346		1.946	
	15		16.30		0.357		1.920	
10 % PEO	5	51.89	15.03	15.07	0.316	0.341	1.856	1.918
	10		15.03		0.317		1.933	
	15		15.14		0.389		1.964	
15 % PEO	5	55.22	15.92	15.92	0.313	0.303	2.018	1.995
	10		15.97		0.289		1.990	
	15		15.88		0.307		1.978	
23% PEO	5	52.08	14.78	14.83	0.264	0.29	1.898	1.925
	10		14.78		0.264		1.913	
	15		14.92		0.342		1.965	

temperature increases with increasing heating rate. Figure 3 shows DSC curves for the modified epoxy resins with different PEO contents at a heating rate of 10°C/min. The peak temperature increased with increasing PEO content with a concomitant decrease in heat flow, suggesting that the curing rate

decreased with increasing PEO content mainly due to the unavailability of curing agent.

Apparent activation energy, E_a , was determined from the DSC scans at different heating rates by the Kissinger method.³¹ E_a was evaluated from plots of $\ln(\beta_i/T_p^2)$ versus $1/T_{p,i}$, where β_i is the heating rate, and $T_{p,i}$ is the maximum heating rate. Table I lists E_a values obtained by the Kissinger method, E_a did not change significantly with PEO content (51.89–55.28 kJ mol⁻¹).

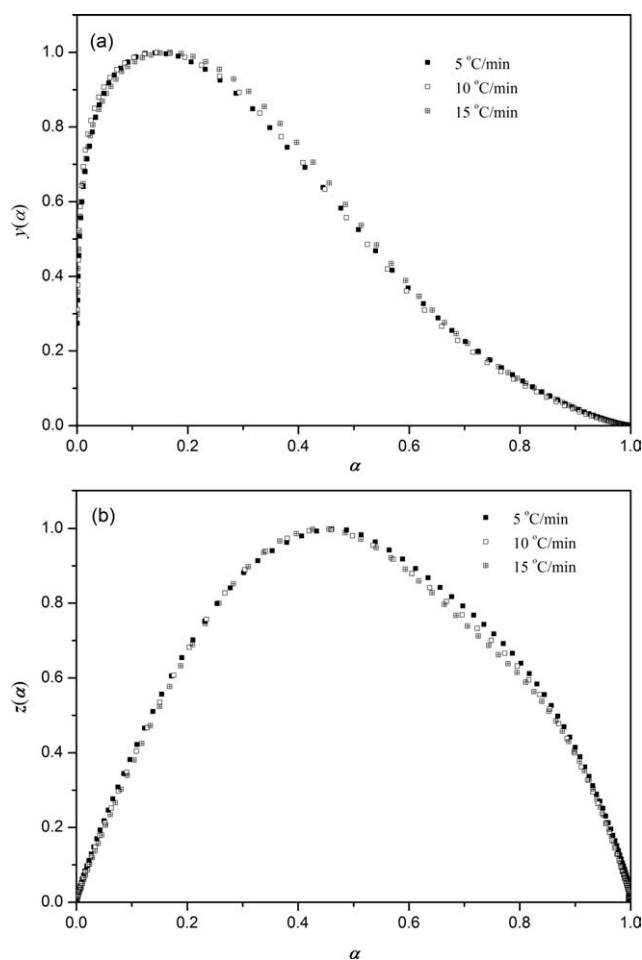


Figure 4 Changes in (a) $y(\alpha)$ and (b) $z(\alpha)$ versus conversion for the epoxy resin blend system containing 10 wt % PEO.

Curing kinetics analysis

Málek's method^{23,27} was used to examine the curing kinetics. For this, $y(\alpha)$ and $z(\alpha)$ were calculated using eqs. (6) and (7), respectively. Figure 4 shows how $y(\alpha)$ and $z(\alpha)$ vary with the degree of conversion (α) for the modified epoxy resins with 10 wt % reactive PEO. Both functions were normalized within the (0, 1) interval at the various heating rates and exhibited maxima at α_M and α_p^∞ , respectively. Both α_M and α_p^∞ aid the identification of the appropriate kinetic model. Table II lists the values of both maxima for all samples along with $\alpha_{p,r}$, the maximum of the DSC peak.

TABLE II
The Values of $\alpha_{p,r}$, α_M , and α_p^∞ Obtained from DSC Data for the Curing System

Sample	Heating rate	α_p	α_M	α_p^∞
0% PEO	5	0.449	0.154	0.469
	10	0.432	0.151	0.445
	15	0.434	0.157	0.451
10% PEO	5	0.439	0.145	0.465
	10	0.429	0.141	0.444
	15	0.424	0.165	0.441
15% PEO	5	0.427	0.125	0.447
	10	0.431	0.123	0.447
	15	0.422	0.134	0.442
23% PEO	5	0.425	0.122	0.454
	10	0.428	0.121	0.450
	15	0.421	0.148	0.436

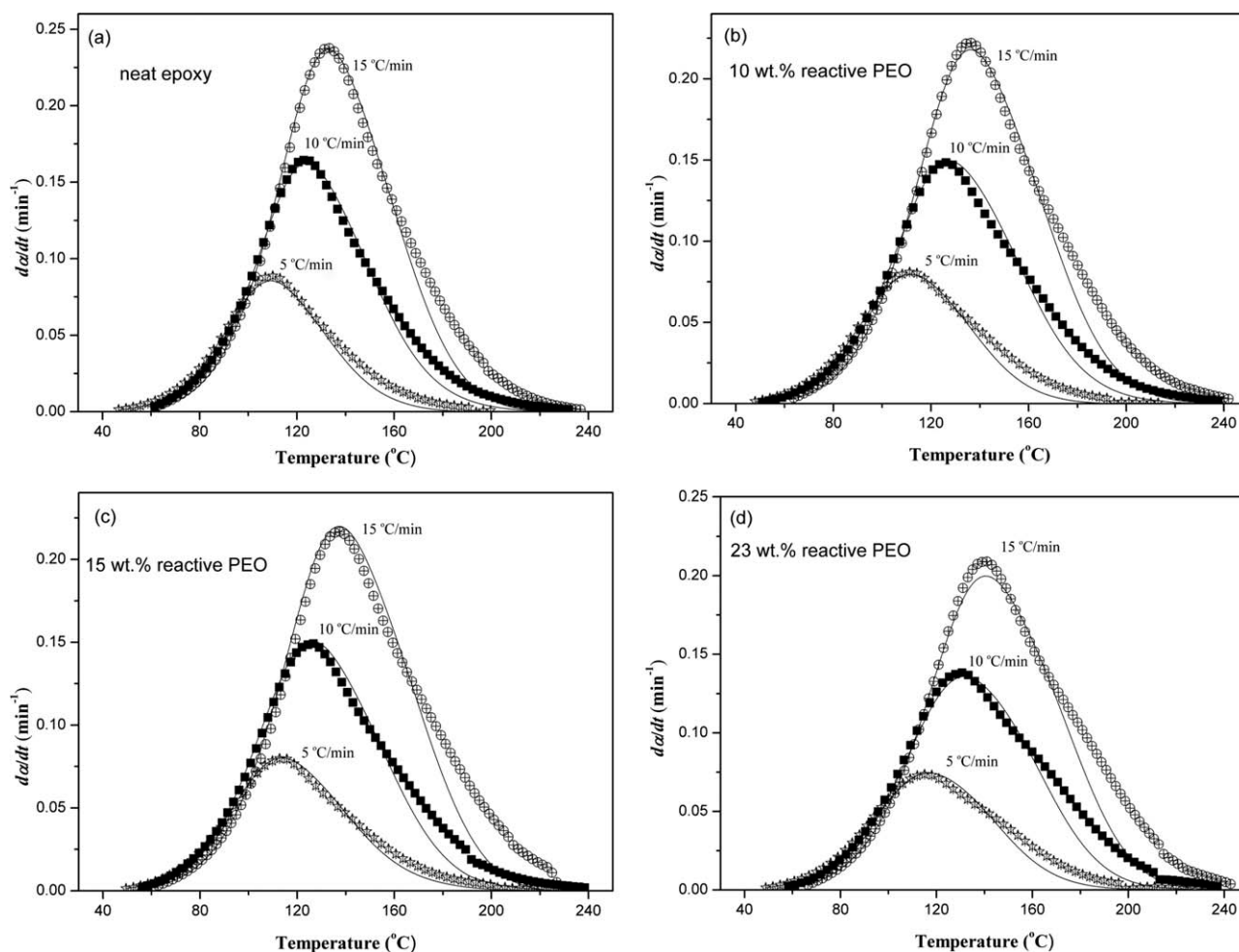


Figure 5 Experimental (dotted lines) and calculated (continuous lines) DSC curves for curing systems of (a) neat epoxy resin and modified epoxy resin with (b) 10, (c) 15, and (d) 23 wt % PEO content.

The values of α_p , α_M , and α_p^∞ were independent of heating rate. The values of α_M were located in the interval $0.05 < \alpha_M < \alpha_p$, and $\alpha_p^\infty < 0.632$, suggesting that this curing process can be described by the two-parameter autocatalytic kinetic model using the Šesták-Berggren equation (eq. (9))^{24,26,27}:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot \alpha^m \cdot (1 - \alpha)^n \quad (9)$$

The kinetic parameter, n , and $\ln A$ were obtained from the slope and intercept of the linear depend-

ence $\ln[(d\alpha/dt)e^x]$ versus $\ln[(1 - \alpha)\alpha^p]$ according to eq. (10) with α ranging from 0.2 to 0.8,^{25,26} where $m = pn$ and $p = \alpha_M/(1 - \alpha_M)$.

$$\ln[(d\alpha/dt) \cdot e^x] = \ln A - n \ln[\alpha^p \cdot (1 - \alpha)] \quad (10)$$

Table I lists the kinetic parameters (m , n , $\ln A$, and E_a) experimentally obtained from the proposed Šesták-Berggren kinetic model. The values of m , n , and $\ln A$ changed slightly with PEO content.

Theoretical curves ($d\alpha/dt$ versus temperature, continuous lines, Fig. 5) were calculated using the kinetic

TABLE III
The Maximum Values of $d\alpha/dt$ Determined from Experimental and Theoretical Curves

Sample	Experimental $d\alpha/dt$ (min^{-1}) (maxima) at different scan rates			Theoretical $d\alpha/dt$ (min^{-1}) (maxima) at different scan rates		
	5°C/min	10°C/min	15°C/min	5°C/min	10°C/min	15°C/min
Neat epoxy	0.0887	0.1647	0.2372	0.0856	0.1626	0.2362
Modified epoxy (10 wt % reactive PEO)	0.0811	0.1484	0.2221	0.0791	0.1493	0.2173
Modified epoxy (15 wt % reactive PEO)	0.0791	0.1490	0.2168	0.0791	0.1499	0.2197
Modified epoxy (23 wt % reactive PEO)	0.0737	0.1383	0.2093	0.0737	0.1353	0.1991

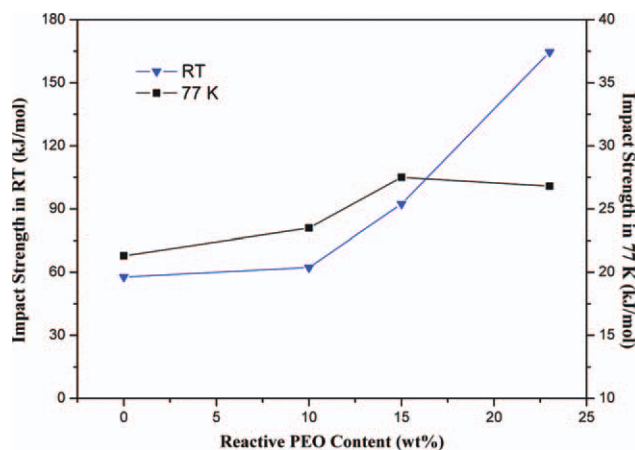


Figure 6 Impact strength versus reactive PEO content showing that impact strength increased with increasing reactive PEO content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

parameters for each heating rate. They agreed well with the experimental curves (dotted lines, Fig. 5), showing that the two-parameter Šesták-Berggren kinetic model gives a good description of the curing process. The maximum values of $d\alpha/dt$ determined from experimental and theoretical curves are shown in Table III. However, there was large deviation between the theoretical and experimental data during the final stages of the curing reaction and at higher PEO contents. This was possibly due to increases of viscosity and side reactions at higher temperatures.³² The viscosity of the epoxy system increased at higher conversion, which decreased the mobility of the reactive groups. In this situation, the reaction rate was controlled by diffusion rather than by kinetic factors. In addition, the concentration of hydroxyl groups increased during the curing reaction. Side reactions and etherification increased with increasing curing temperature and hydroxyl concentration.

Impact properties and DMA analysis

Figure 6 shows the dependence of impact strength on PEO content at RT and at CT. All the modified networks exhibited higher impact strength than the unmodified epoxy. Impact strength increased 184.8% as reactive PEO content increased from 0 to 23 wt % at RT (57.8–164.6 kJ/m²). This was due to the internal plasticization of the PEO chains to the epoxy network.^{33,34} The mobility of chain segments in the epoxy network increased with increasing PEO content. This can be confirmed by the change in glass transition temperatures (T_g) of the epoxy networks (Fig. 7). The improvement in impact strength was similar at both CT and RT but was higher at CT with up to 15 wt % PEO loading. This may be because chemical bonds and molecular segments shrank at CT,

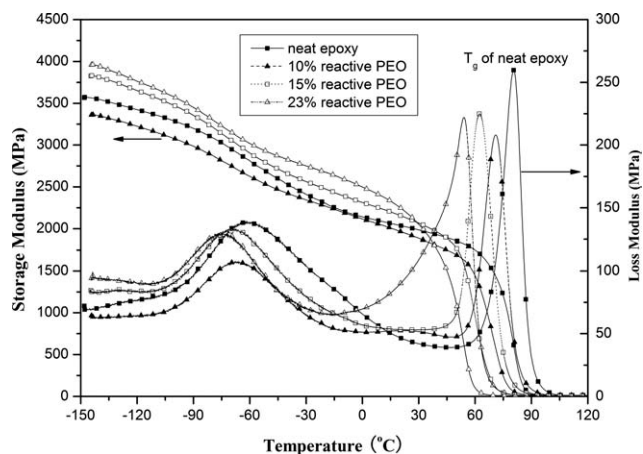


Figure 7 DMA curves of various modified epoxy resins show that glass transition temperature decreased with increasing reactive PEO content.

increasing the binding forces between the molecular segments.⁹ The mobility of the epoxy chain was restricted at the lower temperature, increasing thereby the impact strength. However, at 23 wt % PEO content, the impact strength did not change greatly with temperature. This indicates that the optimum content of PEO for impact strength at CT was 15 wt %. At lower temperatures, β -relaxation of the modified epoxy networks decreased with increasing reactive PEO content due to the plasticization effect of the PEO. The storage modulus of the modified epoxy resin increased with increasing PEO content. The change in T_g and storage modulus values in the modified epoxy resin have been summarized in Table IV. This may be due to the increased alignment of epoxy chains facilitated by the presence of flexible PEO molecules. These results show that the epoxy resins at CT can be toughened by introducing flexible PEO to the network.

The fracture surface morphologies of neat and modified epoxy resin shown in the SEM images (Fig. 8) were in line with the impact strength analysis. There was no obvious phase separation observed between the PEO and epoxy resin in the fracture surfaces. The adhesion between the polar reactive functional groups of the PEO and the epoxy molecules formed flexible chains that became homogeneous, toughened epoxy resin. The fractured surface of

TABLE IV
The Change in T_g and Storage Modulus Determined by DMA

	T_g (°C)	Storage modulus at 25°C (MPa)
Neat epoxy	80.2	2012
10% reactive PEO	71.2	1921
15% reactive PEO	62.5	2118
23% reactive PEO	54.2	2164

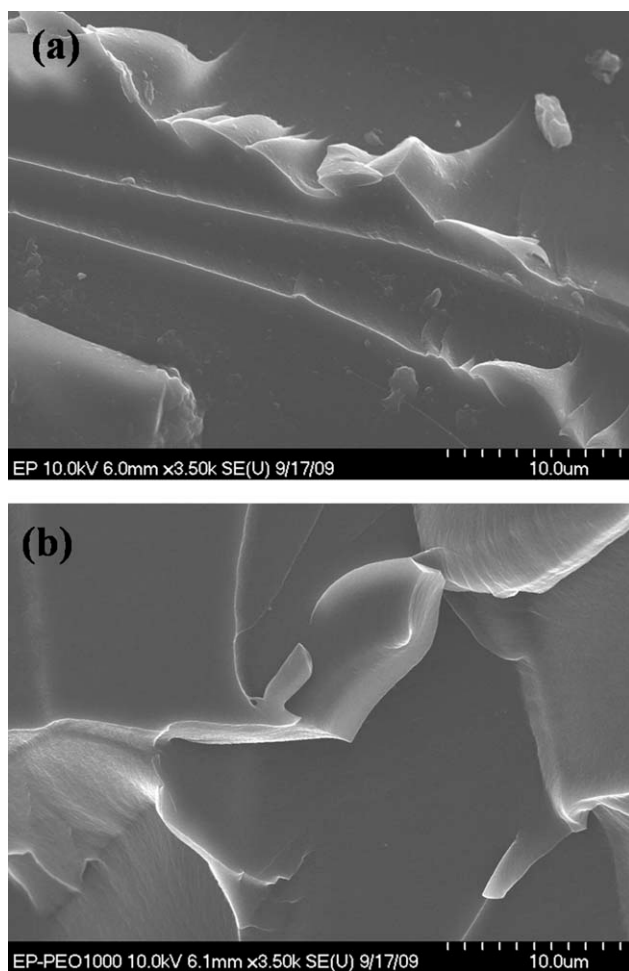


Figure 8 SEM images of impact fracture surfaces of (a) unmodified and (b) epoxy containing 15 wt % reactive PEO.

neat epoxy [Fig. 8(a)] was smooth while the modified epoxy [Fig. 8(b)] exhibited a slightly rougher fracture surface. Similar results were obtained by Martinez et al.³⁵ for polysulfone-modified DGEBA epoxy resins.

CONCLUSIONS

The curing kinetics of epoxy resins modified with reactive PEO in the presence of D-230 curing agent were examined using nonisothermal DSC. E_a varied slightly (51.89–56.30 kJ/mol) with the addition of PEO. The curing reaction followed a two-parameter autocatalytic model (Šesták-Berggren equation), with theoretical DSC curves calculated using the kinetic parameters agreeing well with experimentally determined curves. Impact strength was enhanced by introducing reactive PEO into the epoxy resins networks. DMA analysis showed that the flexible PEO chains increased the mobility of the molecular seg-

ments of the epoxy network and decreased the glass transition temperature.

References

1. Yang, S. E.; Bae, D. K.; Yong, K. Y.; Yoon, Y. S.; Ko, T. K.; Kim, S. H. *Cryogenics* 2006, 46, 338.
2. Turn, E. D. *Physica C* 2001, 354, 136.
3. Hara, M.; Okubo, H. *Cryogenics* 1998, 38, 1083.
4. Anashkin, O. P.; Keilin, V. E.; Patrikeev, V. M. *Cryogenics* 1999, 39, 795.
5. Garcia, S. J.; Serra, A.; Suay, J. *J Polym Sci Part A Polym Chem* 2007, 45, 2316.
6. Nobelen, M.; Hayes, B. S.; Seferis, J. C. *J Appl Polym Sci* 2003, 90, 2268.
7. Zhang, Z.; Evans, D. *Polym Eng Sci* 2003, 43, 1071.
8. Bittner-Rohrhofer, K.; Humer, K.; Weber, H. W. *Cryogenics* 2002, 42, 265.
9. Yang, G.; Zhang, B.; Yang, J. P.; Xu, G. S.; Fu, S. Y. *J Polym Sci Part A Polym Chem* 2008, 46, 612.
10. Yang, J. P.; Chen, Z. K.; Yang, G.; Fu, S. Y.; Ye, L. *Polymer* 2008, 49, 3168.
11. Chen, Z. K.; Yang, G.; Yang, J. P.; Fu, S. Y.; Ye, L.; Huang, Y. G. *Polymer* 2009, 50, 1316.
12. Huang, C. J.; Fu, S. Y.; Zhang, Y. H.; Lauke, B.; Li, L. F.; Ye, L. *Cryogenics* 2005, 45, 450.
13. Kim, M. G.; Hong, J. S.; Kang, S. G.; Kim, C. G. *Compos A Appl Sci* 2008, 39, 647.
14. Kim, B. C.; Park, S. W.; Lee, D. G. *Compos Struct* 2008, 86, 69.
15. Gosnell, R. B.; Levine, H. H. *J Macromol Sci Part A* 1969, 3, 1381.
16. Timmerman, J. F.; Tillman, M. S.; Hayes, B. S.; Seferis, J. C. *Compos Part A Appl Sci* 2002, 33, 323.
17. Thomas, R.; Ding, Y. M.; He, Y. L.; Yang, L.; Paula, M.; Yang, W. M. *Polymer* 2008, 49, 278.
18. Tripathi, G.; Srivastava, D. *Mater Sci Eng A* 2007, 443, 262.
19. Nobelen, M.; Hayes, B. S.; Seferis, J. C. *Polym Compos* 2003, 24, 723.
20. Ueki, T.; Nishijima, S.; Izumi, Y. *Cryogenics* 2005, 45, 141.
21. Kuila, T.; Acharya, H.; Srivastava, S. K.; Samantaray, B. K.; Kureti, S. *Mater Sci Eng B* 2007, 137, 217.
22. Timmerman, J. F.; Hayes, B. S.; Seferis, J. C. *Polym Compos* 2003, 24, 132.
23. Rosu, D.; Mustata, F.; Cascaval, C. N. *Thermochim Acta* 2001, 370, 105.
24. Málek, J. *Thermochim Acta* 2000, 355, 239.
25. Roșu, D.; Cașcaval, C. N.; Mustătă, F.; Ciobanu, C. *Thermochim Acta* 2002, 119, 383.
26. Tripathi, G.; Srivastava, D. *J Appl Polym Sci* 2009, 112, 3119.
27. Montserrat, S.; Andrew, G.; Cortes, P. *J Appl Polym Sci* 1996, 61, 1663.
28. Málek, J. *Thermochim Acta* 1992, 200, 257.
29. Liu, F.; Wang, Z.; Liu, D.; Li, J. *Polym Int* 2009, 58, 912.
30. Han, J. L.; Yu, C. H.; Lin, Y. H.; Hsieh, K. H. *J Appl Polym Sci* 2008, 107, 3891.
31. Vyszovkin, S.; Shirrazuoli, N. *Macromolecules* 1996, 29, 1867.
32. Sbirrazzuoli, N.; Mititelu-Mija, A.; Vincent, L.; Alzina, C. *Thermochim Acta* 2006, 447, 167.
33. Murali, M.; Ratna, D.; Samui, A. B.; Chakraborty, B. C. *J Appl Polym Sci* 2007, 103, 1723.
34. Ratna, D.; Samui, A. B.; Chakraborty, B. C. *Polym Int* 2004, 53, 1882.
35. Martinez, I.; Martin, M. D.; Eceiza, A.; Oyanguren, P.; Mondragon, I. *Polymer* 2000, 41, 1027.