A Novel Imidazole Derivative Curing Agent for Epoxy Resin: Synthesis, Characterization, and Cure Kinetic

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ABSTRACT: A novel imidazole derivative (named as EMI-*g*-BGE) was synthesized through the reaction of 2-ethyl-4-methyl imidazole (EMI) and butyl glycidyl ether (BGE) and characterized by elemental analysis, FTIR spectroscopy, and ^{1}H NMR spectroscopy. The curing kinetic of diglycidyl ether of bisphenol A (DGEBA) epoxy resin with EMI-*g*-BGE as curing agent was studied by nonisothermal DSC technique at different heating rates. Dynamic DSC scans indicated that EMI-*g*-BGE was an effective curing agent of epoxy resin. The apparent activation energy E_a was 71.8 kJ mol^{-1} calculated through Kissinger method, and the kinetic parameters were determined by Málek method for the kinetic analysis of the thermal treatment obtained by DSC measurement. A two-parameter (*m*, *n*) autocatalytic model (Šesták-Berggren equation) was found to be the most adequate selected kinetic model. In addition, the predicted curves from the kinetic model fit well with the nonisothermal DSC thermogram. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 223–227, 2008

Key words: resin; synthesis; DSC; curing kinetics; FTIR

INTRODUCTION

Epoxy resin is one of the most important thermosetting polymers, widely used in adhesives, coatings, electronics, high-performance composite materials, and aerospace industries due to the excellent mechanical and chemical properties, such as high tensile and compressive strength, good chemical resistance, and high heat distortion temperature.[1–3] Curing of a resin system is the critical and productivity-controlling step in the fabrication of thermosetting-matrix composites. 2-Ethyl-4-methyl imidazole (EMI) is a highly effective, fast-curing agent widely used at lower curing temperatures, and also as a catalyst for the reaction of different functional groups such as acid, phenolic, and amidic with epoxy resins.[4–6] However, EMI has low stability and short-useful life when mixed with epoxies, making them unsuitable as one-pot compositions. Varying the substituent on the imidazole ring or varying the material used to adduct the imidazole can change the specific chemical and physical properties, which can be used in various occasions after curing the epoxy resins.

In this work, we describe the preparation of a novel imidazole derivative by an epoxide ring opening from the second-type ring nitrogen of EMI. The graft of the large molecule of butyl glycidyl ether (BGE) to EMI, EMI-*g*-BGE, can be an effective latent-curing agent of epoxy resin and reduce the hydrophilicity of the products. Elemental analysis, FTIR spectroscopy, and ^{1}H NMR spectroscopy have been used to characterize EMI-*g*-BGE.

Curing reaction of epoxy resin involves the liberation of heat and the amount of heat liberated is proportional to the extent of curing. DSC both in dynamic and isothermal modes has been the most commonly used experimental technique to study the curing reaction through monitoring changes involving the absorption or liberation of heat. In this study, we have used nonisothermal DSC method to determine the curing reaction kinetic of DGEBA and EMI-*g*-BGE system (named as DGEBA/EMI-*g*-BGE). With the presumption that the heat flow as measured by DSC, dH/dt, is proportional to the rate of reaction $d\alpha/dt$, it is possible to determine the extent of fractional conversion, α, directly from the experimental curve by partial integration:[7,8]

$$\alpha = \frac{1}{\Delta H_T} \int_0^t \frac{dH}{dt} dt \qquad (1)$$

where ΔH_T stands for the total heat of reaction as determined by dynamic DSC scans and it was assumed to be specific to each heating rate and that the total heat was chosen such that conversion was 100%.
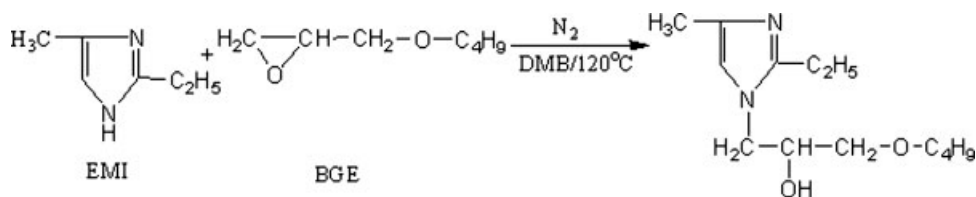
Scheme 1

EXPERIMENTAL

Raw materials

Diglycidyl ether of bisphenol A (DGEBA, the epoxy equivalent was 196 g/eqiv) was obtained from Blue Star New Chemical Materials, China. Commercially available BGE and EMI were distilled under reduced pressure. Dimethylbenzene (DMB) was purchased from Shanghai Reagent, China, and distilled in vacuum prior to use.

Synthesis of EMI-*g*-BGE

The synthesis route to chemically modified EMI grafted with BGE is shown in Scheme 1. EMI (11.0 g, 0.1 mol) dissolved in 20-mL dimethylbenzene was introduced into a flask equipped with a reflux condenser and a stir bar, and the mixture was stirred under nitrogen at 110°C. After 30 min, BGE (13.65 g, 0.105 mol) was added continuously at a constant rate in 1 h. The reaction mixture was heated to 120°C for 2 h under nitrogen atmosphere. Removing the dimethylbenzene by distillation and then the crude product was poured into water containing 50% petrol ether to extracted imidazole and BGE, respectively. After 12 h, the product was collected and the extracted process stated earlier was repeated again, and the final product EMI-*g*-BGE was dried in vacuum at 50°C for 24 h.

Characterization

FTIR spectra were generated on Bruker Vector-22 Fourier transfer infrared spectrometer (KBr pellets). ^{1}H NMR spectra were obtained using a Bruker DRX-500 spectrometer with CDCl$_3$ as solvent. Elemental analyses were performed with a CHN-O-Rapid Heraeue elemental analyzer.

Thermal analyses were obtained by means of a TA instruments DSC 10 Differential Scanning Calorimeter. Data were recorded with different heating rates (2, 5, 10, 15, and 20 K min^{-1}) from 50 to 200°C, and the sample mass was typically 10 mg using EMI-*g*-DGB as the curing agent at a concentration of 10%.

The basic assumption for the application of DSC technique to the cure of the polymers is that the rate of conversion $d\alpha/dt$ is proportional to the measured heat flow ϕ.[9]

$$\frac{d\alpha}{dt} = \frac{\phi}{\Delta H} \tag{2}$$

ΔH can be considered as a constant over the whole cure reaction.

The rate of the kinetic process in kinetic analysis can be described as:[10]

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = k(T)f(\alpha) \tag{3}$$

where $k(T)$ is a temperature-dependent reaction rate constant, $f(\alpha)$ is the differential conversion function, which is associated with a reaction mechanism, and $\beta = dT/dt$ is a constant heating rate. The rate constant, $k(T)$, is temperature-dependent according to Arrhenius law shown in eq. (4).[11]

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where A is the pre-exponential factor, T is the absolute temperature, and E_a is the apparent activation energy, which can be determined by isoconversional method without assuming the kinetic model function.[12,13] Kissinger method is based on a linear relationship between the logarithm of β/T_P^2 with the inverse of the peak temperature of the exothermic curing reaction through the following expression:[14]

$$\ln\left(\frac{\beta_i}{T_{pi}^2}\right) = \ln\frac{AR}{E_a} + \ln\left[\frac{-df(\alpha)}{d\alpha}\right]_{\alpha_p} - \frac{E_a}{R}\frac{1}{T_{pi}},$$
$$i = 1, 2 \dots 5 \tag{5}$$

The graphic representation of eq. (5) allows us to examine the activation energy E_a of curing kinetics without assuming any model of kinetic parameters. The values of E_a can be used to determine the special functions $y(\alpha)$ and $z(\alpha)$ from Málek method.[15,16] On the basis of the Málek method, the function that best describes the mechanism can be chosen from the shape of the plot of the standardized curves $y(\alpha)$ and $z(\alpha)$.

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)\exp(x) \tag{6}$$

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

where x is the reduced activation energy (E_a/RT); β is the heating rate (K/min); T is the absolute temper-

TABLE I
Elemental Analysis of EMI-g-BGE

Elements	C	H	O	N
Calculated value (%)	65.00	10.00	13.33	11.67
Analyzed value (%)	63.88	9.37	15.43	11.32

ature (K) and $\pi(x)$ is the expression of temperature integral. As was pointed out,[17] $\pi(x)$ can be described using a fourth rational expression of Senum and Yang as[18]

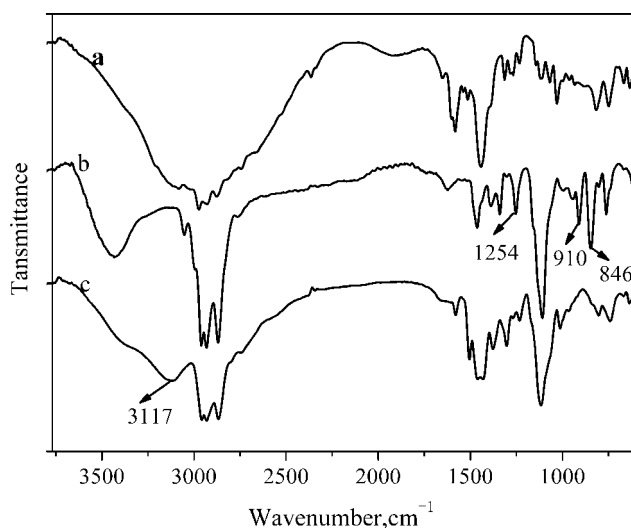$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (8)$$

The functions $y(\alpha)$ and $z(\alpha)$ exhibit maxima at α_M and α_p^∞, respectively. Both α_M and α_p^∞ help to decide the choice of the kinetic model.[19]

RESULTS AND DISCUSSION

Synthesis of EMI-g-BGE

The reaction between EMI and BGE is a convenient method of epoxide ring opening reaction with hydrogen of imidazole according to Scheme 1. The chemical structure of EMI-g-BGE was confirmed by elemental analysis, and the results are shown in Table I. It was found that the elemental analysis of the product prepared was basically in agreement with the calculated values.

FTIR spectrums of EMI, BGE, and EMI-g-BGE are shown in Figure 1. The epoxide ring opening reaction with imidazole nucleophiles results in the appearance of characteristic absorption at 3117 cm^{-1} of —OH, and characteristic absorption at 1116 cm^{-1} of

C—O; while the disappearance of intrinsic absorption at 1252, 910, and 846 cm^{-1} to the ternary epoxide group in BGE, intrinsic absorption at 3000–3300, 1539, and 1068 cm^{-1} to secondary amine in imidazole. The peak of C—N is usually observed at 1000–1300 cm^{-1}, but the peak is hardly seen because of its overlap with the other peaks. ^{1}H NMR is further confirmed the chemical structure of EMI-g-BGE: δ 6.48–6.57 (1H, =CH—N); δ 3.91–3.95 (2H, CH$_2$); δ 3.76–3.77 (1H, CH); 3.62 (1H, OH); δ 3.53, 3.38 (2H, CH$_2$); δ 3.42–3.46 (2H, CH$_2$); δ 2.60–2.63 (2H, CH$_2$); δ 2.10–2.15 (3H, CH$_3$); δ 1.54–1.57 (2H, CH$_2$); δ 1.34–1.38 (2H, CH$_2$); δ 1.21–1.23 (3H, CH$_3$); δ 0.89–0.93 (3H, CH$_3$).

Curing kinetic analysis

The curing reaction of DGEBA/EMI-g-BGE was investigated by nonisothermal DSC at five different heating rates. The heat flows of the resin from 70 to 180°C are shown in Figure 2, while the variation of the fractional conversion [calculated according to eq. (1)] as a function of temperature is shown in Figure 3. From the curves, information about the nature of the curing reaction such as initial curing temperature (T_i), peak temperature (T_p), and the curing range of the resin at different scan rates could be derived. It can be observed that the exothermic peak shifts to a higher temperature with higher heating rate.

As the multiple heating rate methods for nonisothermal analysis proposed by Kissinger can be used as an alternative way of calculating the activation energy, the logarithm plots of heating rate versus the reciprocal of the absolute peak temperature are given in Figure 4. The average activation energy values can be calculated from the slope of the plot.
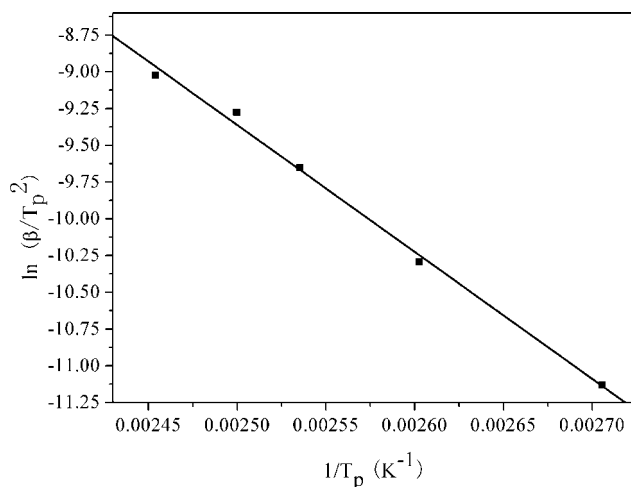

Figure 1 FTIR spectra of (a) EMI, (b) BGE, and (c) EMI-g-BGE.
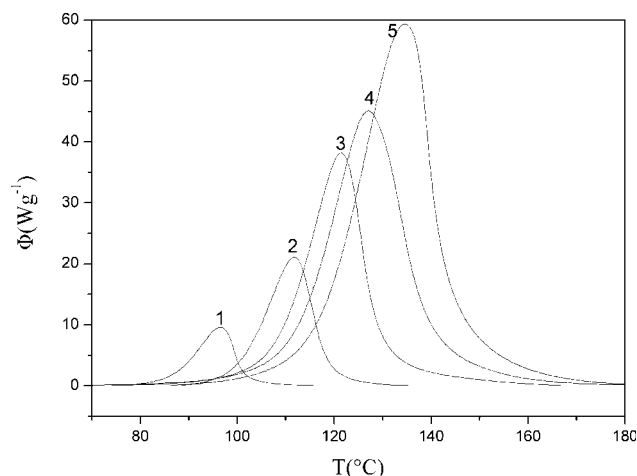
Figure 2 Typical DSC curves recorded for DGEBA/EMI-g-BGE system at different heating rates: (1) 2; (2) 5; (3) 10; (4) 15; (5) 20°C min^{-1}.
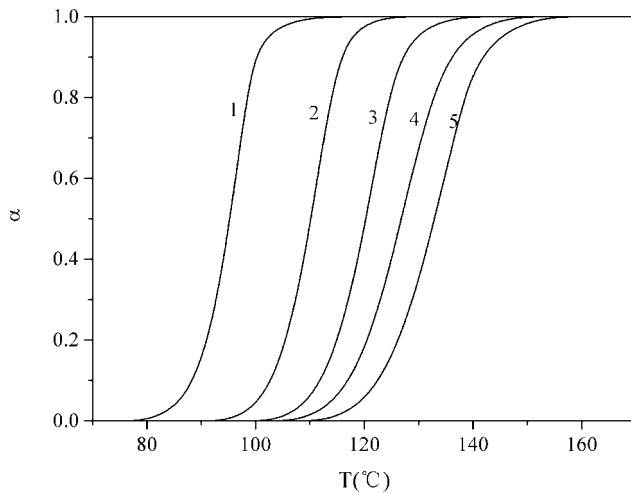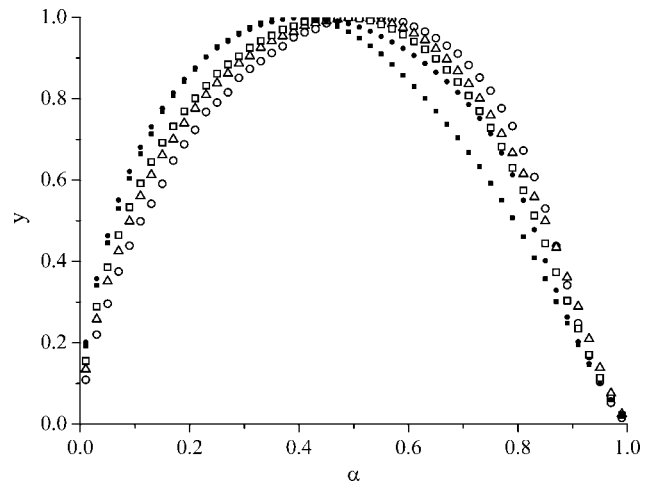
Figure 3 Fractional conversion as a function of temperatures for DGEBA/EMI-*g*-BGE system: (1) 2; (2) 5; (3) 10; (4) 15; (5) 20°C min^{-1}.

Figure 5 Variation of *y*(α) function versus conversion for DGEBA/EMI-*g*-BGE system: (○) 2°C min^{-1}; (Δ) 5°C min^{-1}; (□) 10°C min^{-1}; (■) 15°C min^{-1}; (●) 20°C min^{-1}.

The value of E_a determined from DSC data was used to calculate both $y(\alpha)$ and $z(\alpha)$ functions using eqs. (6) and (7), respectively. Figures 5 and 6 show the variation of $y(\alpha)$ and $z(\alpha)$ values with conversion. The values of both $y(\alpha)$ and $z(\alpha)$ were normalized within the (0,1) interval of DGEBA/EMI-*g*-BGE system for various heating rates. Table II lists the values of maxima α_M and α_p^∞ corresponding to functions $y(\alpha)$ and $z(\alpha)$ for the resin system, together with α_p taken as the maximum of the DSC peak.

As was noted, data in Figures 5 and 6, respective in Table II, show that α_p, α_M, and α_p^∞ values are independent of the heating rate. Simultaneously, the values of α_M are higher than zero and lower against α_p^∞, while α_p^∞ exhibits values unequal to 0.633. These remarks indicate that the studied curing process can be described using the two-parameter autocatalytic

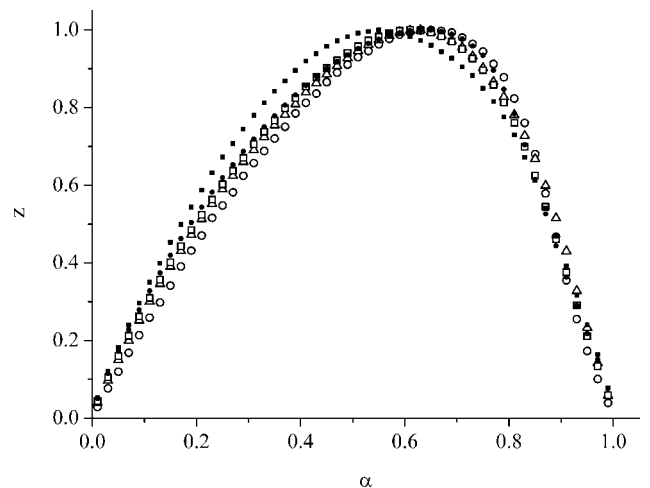kinetic model Šesták-Berggren in the following eq. (9).[19]

$$f(\alpha) = \alpha^m(1 - \alpha)^n \qquad (9)$$

where *m* and *n* are the kinetic exponents.[17]

From eqs. (3), (4), and (9), the following eq. (10) can be obtained:[20]

$$\ln\left[\left(\frac{d\alpha}{dt}\right)e^x\right] = \ln A + n\ln\left[\alpha^S(1 - \alpha)\right] \qquad (10)$$

The kinetic parameter *n* and the pre-exponential factor *A* can be obtained by the slope of the linear dependence $\ln[(d\alpha/dt)e^x]$ versus $\ln[\alpha^S(1 - \alpha)]$, and $m = S_n$, where $S = \alpha_M/(1 - \alpha_M)$. Table III lists some kinetic parameters evaluated for the proposed

Figure 4 Kissinger method plot for apparent activation energy determination of DGEBA/EMI-*g*-BGE system.

Figure 6 Variation of *z*(α) function versus conversion for DGEBA/EMI-*g*-BGE system: (○) 2°C min^{-1}; (Δ) 5°C min^{-1}; (□) 10°C min^{-1}; (■) 15°C min^{-1}; (●) 20°C min^{-1}.

TABLE II
The Values of α_p, α_M and α_p^∞ obtained from DSC Thermograms Analysis

Heating rate ($^\circ$C min^{-1})	α_p	α_M	α_p^∞
2	0.6297	0.51	0.65
5	0.5899	0.5	0.60
10	0.5859	0.47	0.6
15	0.5159	0.41	0.55
20	0.5917	0.41	0.63

Šesták-Berggren kinetic model. As it is shown in Table III, the values of the kinetic parameter A, m, and n of all heating rates can be obtained using the average activation energy from Kissinger method.

The solution of the direct kinetic problem is the best way to test the accuracy of the kinetic parameters. For this purpose, numerical modeling of the reaction of DGEBA with EMI-g-BGE at different heating rates (experimental curves) was verified by plotting $d\alpha/dt$ versus temperature, using the Šesták-Berggren equation. The experimental results and the calculated curves are shown in Figure 7, from which we can see that the calculated data from the model are in good agreement with the experimental results.

CONCLUSIONS

A novel imidazole derivative, EMI-g-BGE, was successfully synthesized by the reaction of EMI and BGE. Dynamic DSC scans indicated that the EMI-g-BGE was an effective curing agent of epoxy resin. Curing properties of DGEBA/EMI-g-BGE system was studied by nonisothermal DSC with different heating rates, and the curing kinetics can be successfully described with the two-parameter autocatalytic model (Šesták-Berggren equation). The kinetic parameters, which were experimentally determined, were used to calculate the theoretically DSC curves. The results are in good agreement with the nonisothermal DSC data. The apparent activation energy E_a was 71.8 kJ mol^{-1}, while the apparent activation energy of unmodified EMI was 49.03 kJ mol^{-1} reported by Zhou.[21] This indicated that the new curing agent EMI-g-BGE exhibited greater levels of la-

TABLE III
The Kinetic Parameters Evaluated for the DGEBA/EMI-g-BGE System

Heating rate ($^\circ$C min^{-1})	E (kJ mol^{-1})	ln A	Mean	n	Mean	m	Mean
2	71.8	23.18	22.90	0.99	1.02	1.03	0.87
5		22.89		0.90		0.90	
10		22.96		1.02		0.90	
15		22.75		1.11		0.77	
20		22.70		1.10		0.77	
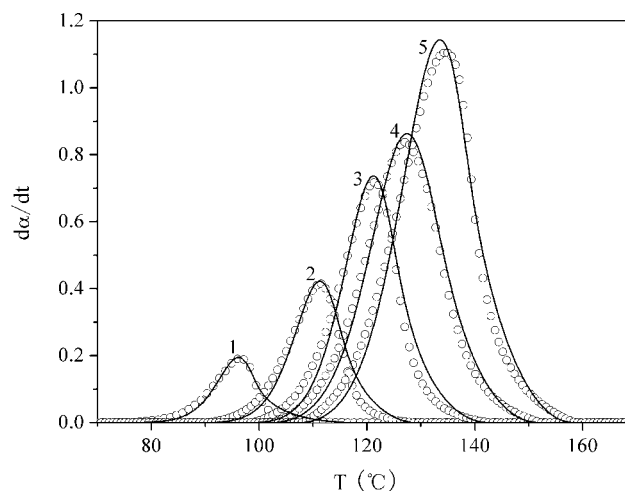
Figure 7 Comparison of experimental (hollow lines) and calculate (solid lines) DSC curves for DGEBA/EMI-g-BGE system: (1) 2; (2) 5; (3) 10; (4) 15; (5) 20°C min^{-1}.

tency during cure or increased the pot life of epoxy resin.

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