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Nonisothermal reaction kinetics of DGEBA with four-armed starlike polyamine with benzene core (MXBDP) as novel curing agent

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ABSTRACT

A four-armed starlike polyamine with a benzene nucleus (MXBDP) was prepared, characterized, and employed as the novel curing agent for epoxy resin of bisphenol A (DGEBA). Nonisothermal reaction kinetics of DGEBA/MXBDP was systematically investigated using a differential scanning calorimeter (DSC) in terms of a model-fitting Málek approach and a model-free advanced isoconversional method of Vyazovkin (AICM). A two-parameter autocatalytic model of Šesták–Berggren (SB(m, n) model) was substantiated to be able to well describe the nonisothermal reaction rate of DGEBA/MXBDP. In addition, the correlation between effective activation energy E_α upon fractional conversion α was determined with the AICM. The result showed E_α dropped quickly at the initial stage of the reaction up to $\alpha \approx 10\%$, then showed a relative constant value of ≈57 kJ/mol for $\alpha \approx 10$–35%, and finally decreased again from ≈57 to ≈45 kJ/mol until the completion, which implicates quite complex mechanisms of the reaction.

1. Introduction

Epoxy resins have excellent all-round properties such as good mechanical strength, outstanding chemical resistance, strong adhesion to many substrates, superior dimensional stability, and wide formulation diversity. Due to these good properties, epoxy resins have found wide applications in protective coatings, adhesives, high-performance composites, insulating materials, and modeling compounds for more than half a century [1–5]. Because of their extreme significance, tremendous scientific studies have devoted to epoxy resins in the past decades, covering their characterizations, reaction thermodynamics and kinetics, network formation, mechanical properties, modification and toughening, ageing and thermal decomposition, composites, and so on [6–15].

To achieve desired end-use properties, epoxy resins must transform into infusible and insoluble hard plastics in the presence of curing agents such as polyamines, anhydrides, BF_3-amine complexes, organometallic compounds, and so forth [16]. Curing processes of epoxy resins involve transformation of linear or branched epoxy monomers or oligomers to a crosslinked three-dimensional network macromolecule with an infinite molecular weight via a variety of thermosetting reactions [17]. In particular, curing agents play a very crucial role in determining reaction mechanisms, curing conditions, processability, network structures, final properties, and applicability of epoxy resins. Nevertheless, amine-based epoxy curing agents hold the largest market share in all commercial products, because of their easy access, wide applicability, relatively low cost, and excellent overall properties.

Numerous efforts have been directed to epoxy-amine systems over the past decades [18], among which epoxy systems with linear diamines or polyamines as the curing agents are the focus of the extensive studies. Using nonlinear (i.e., branched, starlike, and dendritic) polyamines to cure epoxy resins, however, is still sparsely addressed in open literature until now [19–25]. On the other hand, multifunctional epoxy resins (i.e., tetraglycidyl-4,4-diaminodiphenylmethane (TGDDM) and *p*-aminophenol triglycidyl ether (TGAP)) with the nonlinear molecular architecture can impart the resultant epoxy resins with improved thermal, mechanical performances, and favorable processability compared with their conventional bisphenol an epoxy counterparts of similar molecular weights, accounting for their paramount positions in high-performance epoxy composites [26–29]. Likewise, in principal amine curing agents of nonlinear molecular architectures have advantages of extraordinary high functionality per molecule, low bulk viscosity, reduced tendency to crystallize, and inherent junction points over their linear analogues of comparable molecular weights. Hence, introducing nonlinear structures into the amine curing agents without alternating their basic element compositions is likely a feasible way to improve specific properties of epoxy resins, as the nonlinear epoxy resins can do.

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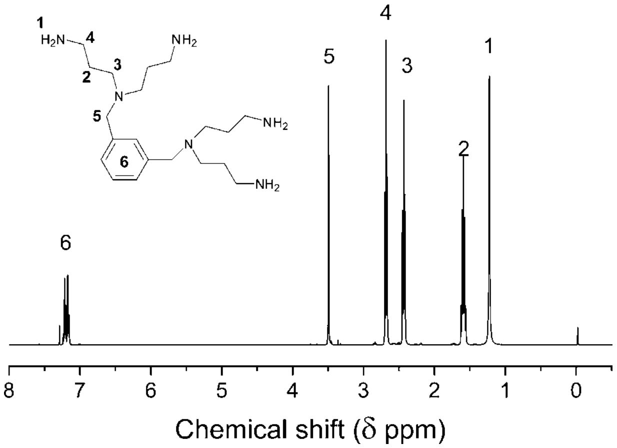


Fig. 1. ^{1}H NMR spectrum of MXBDP in $CDCl_3$.

In addition, although ultimate properties of epoxy materials are primarily determined by their chemistry and formulations, they are also strongly affected by curing conditions and processing techniques. For a given epoxy formulation, the proper selection of curing cycles becomes very crucial in tailoring and optimizing ultimate properties of epoxy materials. For these reasons, a fundamental knowledge of reaction kinetics is of great value, from which such parameters as conversion, time, temperature, and reaction rate can be well related to predict a real epoxy curing process [30]. Moreover, it can also serve as an instructive guideline to manufacture and quality control of epoxy materials [31,32], particularly for newly emerging epoxy formulations.

In this context, we prepared a nonlinear polyamine (MXBDP) with the starlike molecular architecture and the benzene core. MXDBP possesses such superiorities over conventional amine curing agents (e.g., linear ethylenediamine, hexamethylendiamine, and diethylenetriamine) [33,34] as very low vapor pressure, reduced skin irritation, no crystallization, decreased carbonation rate in air, improved compatibility with epoxy resins, enlarged mix ratios, and rapid cure. These good properties of MXDBP result from its extraordinary high primary amine functionalities, much increased molecular weight, benzene core, highly symmetrical starlike molecular structure, extended flexible chain length, inherent crosslink junctions, and tertiary amine functionalities. These merits are also particularly preferred for room-temperature epoxy coatings, adhesives, sealants with improved specific properties such as curing speed, compatibility, flexibility, and surface brightness. In this paper, we report an original, systematic study on conventional model-fitting kinetics and model-free isoconversional kinetics of the nonisothermal reaction of bisphenol A epoxy resin (DGEBA) with stoichiometric MXBDP.

2. Experimental

2.1. Materials

DGEBA, diglycidylether of bisphenol A (EEW = 196 g/mol, number of repeating unit equals 0.18), see Scheme 1, was obtained from Heli Resin Co., China, and desiccated in vacuum at 100 °C for 2 h before use. MXBDP (Scheme 1), 1,3-bis[bis(3-aminopropyl)aminomethyl]benzene (CAS No. 66128-37-8) [35], was synthesized in our laboratory via the exhaustive Michael-addition of acrylonitrile to 1,3-metaxylenediamine, followed by a catalytic reduction sequence [36,37]. FTIR, ^{1}H NMR, and ESI-MS data of MXBDP are given below, and they are in alignment with the predications from its molecular structure. To be clearer, ^{1}H NMR of MXBDP is shown in Fig. 1, where assignments of chemical shifts for different kinds of protons are indicated by numbers.

MXBDP: FTIR (ν_{max}, cm^{-1}) 3354, 3284 (NH_2), 2936, 2861, 2800, 1578 (NH_2), 1464, 1383, 1308, 1149, 1083, 900, 821, 746, 701. ^{1}H NMR (400 MHz, in $CDCl_3$) δ ppm 1.22, s (broad), 8H, $N\boldsymbol{H}_2$; 1.59, m (5), 8H, $NH_2CH_2C\boldsymbol{H}_2$; 2.43, t, $NH_2CH_2CH_2C\boldsymbol{H}_2$; 2.68, t, 8H, $NH_2C\boldsymbol{H}_2$, 8H; 3.49, s, $PhC\boldsymbol{H}_2$; 7.14–7.23, m, 4H, $\boldsymbol{H}$(Ph). ESI-MS: $[M+1]^+ = 365.1$.

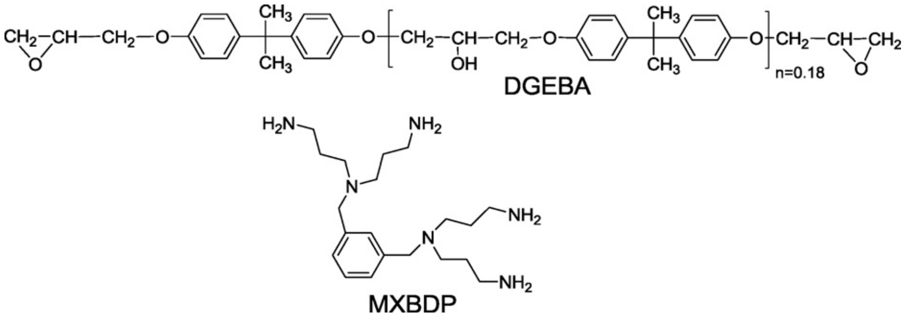
2.2. DSC measurement

A Perkin Elmer differential scanning calorimeter (DSC-7) was used to monitor the curing reactions of DGEBA/MXBDP under non-isothermal conditions. The instrument power and temperature were calibrated previously with high-purity indium for each of heating rates applied, and the instrumental baseline was subtracted for each the temperature run. Stoichiometric DGEBA and MXBDP were mixed quickly under vigorous agitation at room-temperature to yield homogenous reaction mixture. Then, the approximately 10 mg fresh reaction mixture was enclosed an aluminum DSC crucible, and subjected to a temperature scan with an identical crucible as the reference. The heat flow as a function of temperature and time was registered on the DSC thermographs with a computer data acquisition system; the original thermal files (*.dsd) were processed with the compatible TA Universal Analysis 2000® for Windows 2000 and XP (Version 4.2E) Software. Heating rates were 5, 10, 15 and 20 °C/min, temperature ranged from 25 to 250 °C, and protection gas was a dynamic dry N_2 flow (20 ml/min).

3. Results and discussion

3.1. Basic theory of model-fitting kinetic approach

Curing reactions of epoxy resins involve opening of epoxy rings with release of a large amount of heat; in this instance, DSC is very suitable for studying reaction kinetics of epoxy polymerizations. In DSC kinetics, reaction exotherms are assumed to be directly proportional to extent of reaction or fractional conversion α [38]. Thus,



Scheme 1. Molecular structures of DGEBA epoxy resin and MXBDP.

when an epoxy reaction carries out at a constant heating rate, then one can obtain basic rate equation [12,39] as expressed by Eq. (1).

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = \frac{dH/dt}{\Delta H_o} = k(T)f(\alpha) \tag{1}$$

In Eq. (1), T is the temperature (K), t is the reaction time β, dT/dt is the heating rate, H is the reaction exotherm, ΔH_o is the total reaction exotherm, $f(\alpha)$ is the function of conversion associated with a reaction model, and $k(T)$ is the temperature-dependent reaction rate constant, which universally obeys the Arrhenius law:

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where A denotes the pre-exponential factor or frequency factor, E_a denotes the activation energy, and R denotes the universal gas constant.

A large number of reaction models have been developed to model epoxy polymerizations [40], among which the nth order reaction model and the autocatalytic reaction model [40–42] are most frequently cited. In thermal practices, however, using different kinetic models and computing methods even for the same thermal process always gives rise to undesired uncertainties in values of calculated kinetic parameters, especially in activation energy, largely stemming from the mutual compensation among kinetic triplets, E_a, A, and $f(\alpha)$ [43–45]. Málek [46] has proposed an approach to settling this obstacle by which one can probably determine an appropriate model and estimate a complete set of meaningful kinetic parameters to describe a nonisothermal process. Nevertheless, the Málek method has been used to study nonisothermal reactions of epoxy resins with considerable successes achieved [39,47–49]. In this context, we have applied the Málek method to analysis of the nonisothermal reaction of DGEBA/MXBDP.

When applying the Málek method, a prerequisite is to know apparent activation energy, and the Kissinger method (ASTM E 698-79) [48,50–53] have been frequently cited to calculate values of apparent activation energies for nonisothermal reaction of epoxy resins. The Kissinger method is written by Eq. (3):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \text{Const.} - \frac{E_a}{RT_p} \tag{3}$$

where T_p is the exothermal peak temperature, β is the constant heating rate, E_a is the apparent activation energy, and R is the universal gas constant (8.314 J K^{-1} mol^{-1}). Subsequently, two special functions, $y(\alpha)$ and $z(\alpha)$ (Eqs. (4) and (5)), can be constructed as the criteria for kinetic model determination and parameter estimation.

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)\exp(x) \tag{4}$$

$$z(\alpha) = \pi(x)\left(\frac{d\alpha}{dt}\right)\frac{T}{\beta} \tag{5}$$

In Eqs. (3) and (4), x is the reduced activation energy which equals E_a/RT, $d\alpha/dt$ is the conversion rate (reaction rate), and $\pi(x)$ is the function of temperature integrals [46] whose value can be approximated with sufficient accuracy using a fourth-order rational expression of Senum and Yang (Eq. (6)) [54].

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{6}$$

Finally, judging from the shape and the peak conversions (α_M, α_p^∞) of the normalized $y(\alpha)$ and $z(\alpha)$, associated with α_p for the maximum reaction rate, one will find out an appropriate reaction model, and then can calculate the involved model parameters to describe a nonisothermal process of interest [39,46].

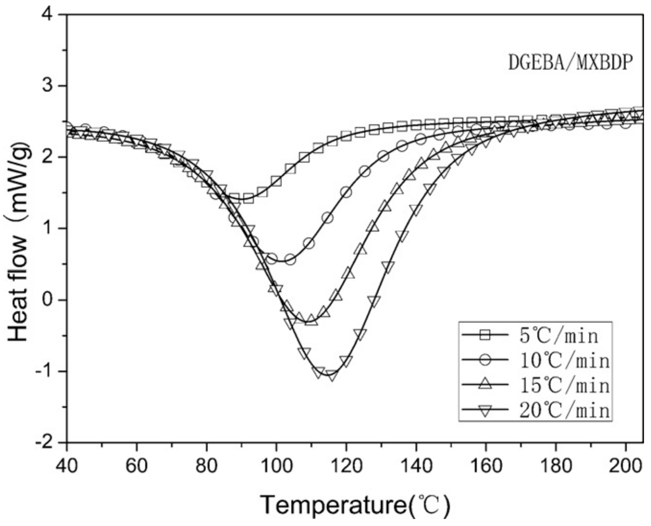


Fig. 2. DSC thermographs of DGEBA/MXBDP reaction for heating rates of 5, 10, 15 and 20 °C/min.

3.2. Nonisothermal reaction of DGEBA/MXBDP

Presented in Fig. 2 is the heat flow of DGEBA/MXBDP as a function of temperature for the heating rates of 5, 10, 15 and 20 °C/min. All the curves show a single, fairly symmetric exothermic peak without any shoulders detected, which likely suggests that the amine functionalities (NH) including the primary amines inherent from MXBDP and the secondary amines generated during the reaction can react with the epoxy groups simultaneously. Therefore, the difference in reactivity of the amine functionalities towards DGEBA is insignificant, and thus the nonisothermal reaction of DGEBA/MXBDP can be considered as a single process from a macroscopic perspective [55]. Integration of the exothermic peak with respect to the linear baseline gives rise to the values of reaction enthalpy ΔH_R, onset cure temperature T_{onset}, and peak temperature T_p for the different heating runs, as seen in Table 1. Clearly, increasing the heating rates leads to the systematically increased the peak areas, T_{onset}, and T_p, but little affects ΔH_R within experimental errors. These findings suggest that the reaction rate is very sensitive to the reaction temperature, but the basic chemical reaction involved remains unchanged, and the final extent of cure is essentially the same. Furthermore, ΔH_R for the different heating rates are in a rather narrow range of 114–119 kJ/mol epoxide, which is consistent with the typical value range (98–122 kJ/mol epoxide) collected from a considerable number of epoxy-amine reactions [6,12,56–59]. This agreement also implicates that MXBDP can cure epoxy resins as effectively as other conventional amine curing agents under a proper reaction condition to a fully acceptable extent of reaction, from a practical application point of view.

3.3. Model-fitting kinetic analysis

In the previous subsection, we have demonstrated a series of the nonisothermal measurements at the different heating rates

Table 1
Onset and peak cure temperatures, T_{onset} and T_p, and exotherms, ΔH_R, of DGEBA/MXBDP at heating rates of 5, 10, 15 and 20 °C/min.

β (°C/min)	T_{onset} (°C)	T_p (°C)	ΔH_R (J/g)	ΔH_R (kJ/mol)
5	59.6	90.2	472.8	114.2
10	68.5	101.5	488.6	118.0
15	75.2	109.0	487.4	117.7
20	80.4	114.7	493.4	119.2

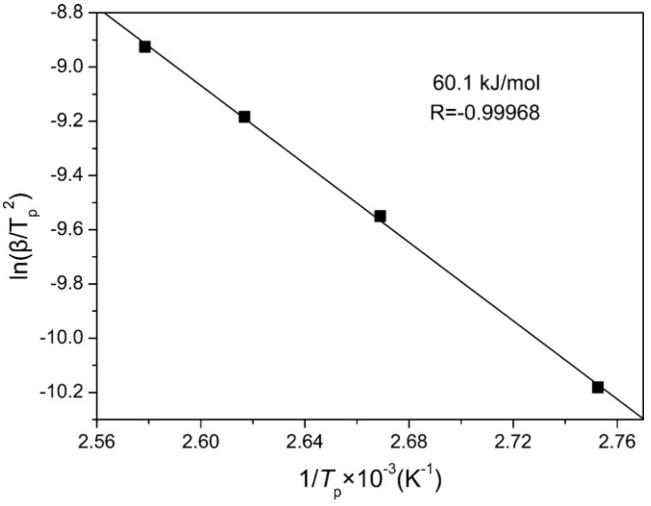


Fig. 3. Kissinger plots of $\ln(\beta/T_p^2)$ vs. T_p^{-1} for DGEBA/MXBDP.

to relate T_p with β, as seen in Fig. 2 and Table 1. Now, according to the Kissinger method a plot of $\ln(\beta/T_p^2)$ against T_p^{-1} for DGEBA/MXBDP are constructed in Fig. 3, wherein an excellent linear correlation ($R = -0.99968$) is found. Consequently, the slope of the fitted straight line has been use to calculate E_a, and its value is 60.1 kJ/mol locating within the typical range (about 50–70 kJ/mol) for a number of epoxy-amine polymerizations [3,12,56,60].

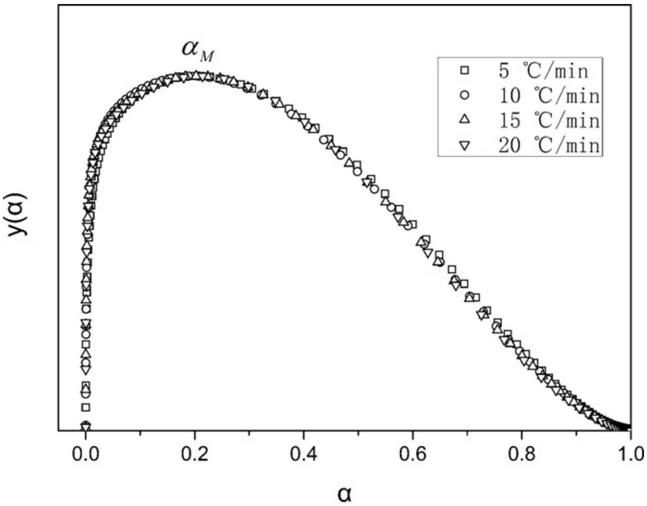


Fig. 4. Plots of normalized $y(\alpha)$ function vs. α for heating rates of 5, 10, 15 and 20 °C/min.

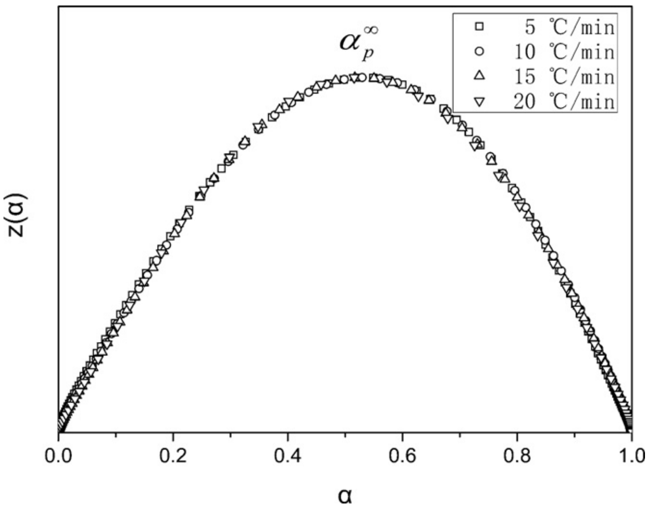


Fig. 5. Plots of normalized $z(\alpha)$ function against α for heating rates of 5, 10, 15 and 20 °C/min.

Table 2
Values of α_p, α_M and α_p^∞ for heating rates of 5, 10, 15 and 20 °C/min.

β (°C/min)	α_p	α_M	α_p^∞
5	0.514	0.201	0.542
10	0.510	0.199	0.533
15	0.503	0.204	0.520
20	0.493	0.208	0.523

Substitution of the calculated values of E_a, $d\alpha/dt$, β and R into Eqs. (4)–(6) yields curves of the normalized $y(\alpha)$ and $z(\alpha)$ functions, as indicated by Figs. 4 and 5. Evidently, $y(\alpha)$ exhibits a sigmoidal contour with the peak conversion $\alpha_M \approx 0.20$ little dependent on the heating rates; $z(\alpha)$ shows the relative constant peak conversion $\alpha_p^\infty \approx 0.52$. Moreover, each the experimental conversion rate $d\alpha/dt$ manifests a convex outline with the constant peak conversion $\alpha_p \approx 0.50$, as presented in Fig. 6. The values of α_M, α_p^∞ and α_p for the different heating rates are summarized in Table 2. Obviously, they simultaneously satisfy $\alpha_p^\infty \neq 0.623$ and $\alpha_M < \alpha_p < \alpha_p^\infty$ for each the heating run, which implies a two-parameter autocatalytic reaction model of Šesták–Berggren (SB(m, n) model) [61] is probably the best candidate to describe the nonisothermal reaction of DGEBA/MXBDP. The SB(m, n) model can be expressed by

$$\frac{d\alpha}{dt} = A\ \exp\left(-\frac{E_a}{RT}\right)\alpha^m(1-\alpha)^n \tag{7}$$

where m and n are the reaction orders, and other parameters have the same meanings as in Eqs. (1) and (2).

In Eq. (7), the ratio of the reaction orders p can be replaced by [46]

$$p = \frac{m}{n} = \frac{\alpha_M}{(1-\alpha_M)} \tag{8}$$

where α_M is the peak conversion for $y(x)$ (Eq. (3)), whose values are listed in Table 2.

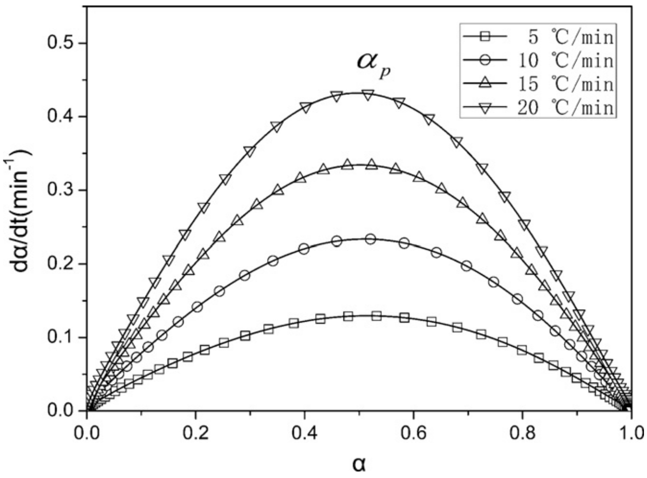


Fig. 6. Dependence of reaction rate $d\alpha/dt$ on conversion α for heating rates of 5, 10, 15 and 20 °C/min.

Table 3
Estimated parameters m, n and $\ln A$ for SB(m, n) model.

β (°C/min)	m	n	$\ln A$ (min^{-1})	R
5	0.360	1.430	19.105	0.9994
10	0.368	1.482	19.131	0.99971
15	0.393	1.537	19.149	0.99979
20	0.416	1.590	19.166	0.99979
Mean	0.384	1.510	19.138	–

Replacement of the reaction order m in Eq. (7) by pn, followed by rearrangement produces Eq. (9).

$$\ln\left[\frac{d\alpha}{dt}\exp(x)\right] = \ln A + n\ln[\alpha^{p}(1-\alpha)] \tag{9}$$

From Eq. (9), the reaction order n and A can be estimated from the slope and the intercept of the fitted straight line of $\ln[(d\alpha/dt)\exp(x)]$ vs. $\ln[\alpha^{p}(1-\alpha)]$, respectively, and then m can be readily determined with Eq. (8). Herein, we use Eq. (9) to treat the nonisothermal data of DGEBA/MXBDP for $\alpha \in [0.1, 0.9]$ with excellent linear correlation achieved ($R > 0.999$). As a result, m, n and $\ln A$ are readily obtained, and their values with R are listed together in Table 3.

From Table 3, with increasing the heating rates, the values of m, n and $\ln A$ change very slightly with the heating rate, with no variation exceeding 10% of their averaged values. The stable values of these SB(m, n) model parameters substantiate the Málek method can provide us with a unique rate equation to model the nonisothermal reaction of DGEBA/MXBDP. Direct substitution of the averaged values of these parameters and E_a into the SB(m, n) model yields the final rate equation:

$$\frac{d\alpha}{dt} = 2.05\times 10^{8}\ \exp\left(\frac{-60,115}{RT}\right)\alpha^{0.384}(1-\alpha)^{1.51}\quad \alpha \in [0, 1] \tag{10}$$

Finally, the experimental curing rates (dot) and the predicated (full line) with Eq. (10) are compared straightforwardly in Fig. 7. Evidently, these data agree well with each other over the entire temperature and heating rate range inspected. Thus, we can generalize that Eq. (10) is adequate to model the nonisothermal reaction rate of DGEBA/MXBDP; the model-fitting kinetic analysis achieves satisfactory results.

3.4. Model-free kinetic analysis

It is known to us curing reactions of epoxy resins are extremely complicate processes in which a great number of elementary reactions, intricate mass transportation phenomena, and multiple state or phase transitions are involved [10,41,62,63]. As discussed in Section 3.3, we have obtained a simple kinetic rate equation to well model the nonisothermal reaction rate of DGEBA/MXDBP, certainly, which is great helpful in forecasting reaction rates on a phenomenological level, but still insufficient to account for the complexity involved in the reaction. To understand mechanisms of the nonisothermal reaction of DGEBA/MXBDP in more depth, it is necessary to use other methods independent upon any specific kinetic models to derive some more straightforward information that can clearly reveal the microscopic reaction mechanisms. Applying model-free isoconversional methods [42,64,65] to analyzing reaction kinetics of epoxy resins may be a good choice.

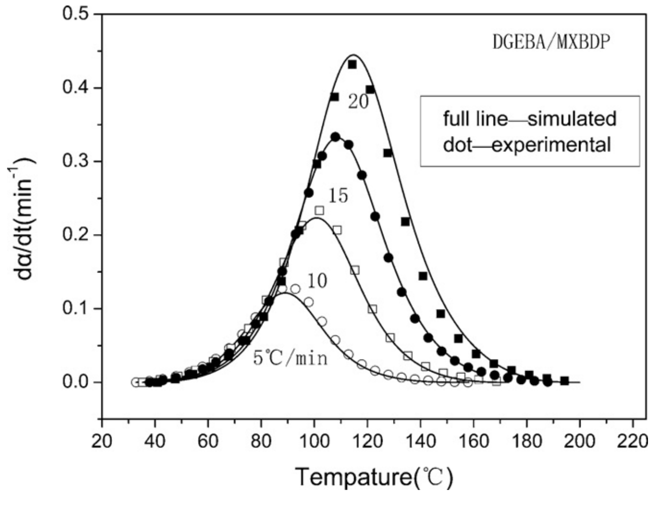


Fig. 7. Comparison of rates predicated with SB(m, n) model and experimental values.

Model-free isoconversional methods [42,64,65], taking assumption that the reaction rate at fixed conversion is merely a function of the temperature, can partially overcome the limitation of conventionally used model-fitting methods. With these methods, one can readily obtain a dependence of effective activation energies E_α on conversion α for a thermal process with no necessity of assigning any specific kinetic models. Furthermore, if the variation of E_α with α is associated with the change of mechanisms, this correlation will be of great value in untangling complex mechanisms of epoxy polymerizations [42]. Herein, we adopt the advanced isothermal conversional method (AICM) to analysis of the reaction mechanisms of DGEBA/MXBDP. Note here that another frequently cited isoconversional method, namely the FWO method [66,67], could also be employed for this propose, but significant relative errors result even reaching 20–30% or greater [68–70], due largely to introduction of the Doyle approximation [71], thus almost unavoidably concealing much valuable kinetic information. In contrast, the AICM can eliminate these errors easily [70] owing to its advanced computing method; additionally, an increasing number of scholars [42,72–80] have justified its applicability to thermal analyses of epoxy reactions, with unprecedented successes achieved and significant findings revealed. For clarity, a brief introduction to the AICM is given below.

In the light of the AICM, one should undertake a series of thermal experiments under different temperature programs. More specially, for nonisothermal epoxy reactions heating rates β is always kept constant during thermal measurements; therefore, the AICM can be expressed as the following equations:

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_\alpha, T_{\alpha,i})\beta_i^{-1}}{I(E_\alpha, T_{\alpha,j})\beta_j^{-1}} = \min \tag{11}$$

$$I(E_\alpha, T_{\alpha,i}) = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha}\exp\left[\frac{-E_\alpha}{RT_\alpha}\right]dT \tag{12}$$

where subscripts, i and j, are the different thermal measurements; $\Delta\alpha$ is the small increment in α, which is usually fixed at 0.02; $I(E_\alpha, T_{a,i})$ in Eq. (12), the temperature integral, can be numerically approached with a trapezoid rule with great accuracy [68]. Then, one can minimizes Eq. (11) by finding an appropriate value of E_α, and repeating this minimization procedure for each α will eventually result in a dependence of E_α on α.

The nonisothermal data of DGEBA/MXBDP were converted into the relationship between conversion α and temperature T for each the heating rate, as shown in Fig. 8. Clearly, the conversional curves shift toward a systematically increased and broadened temperature area as the heating rates increases, which means the reaction rate is an increasing function of temperature. Then, in the light of the AICM, insert these $T-\alpha$ data into Eqs. (11) and (12), then start the minimization procedure for each of α values using a home-made program based upon the Matlab® (R2007b) Software interface, and eventually a dependence of E_α on α results, as presented in Fig. 9. Clearly, E_α depends heavily on α, which indicates that the non-

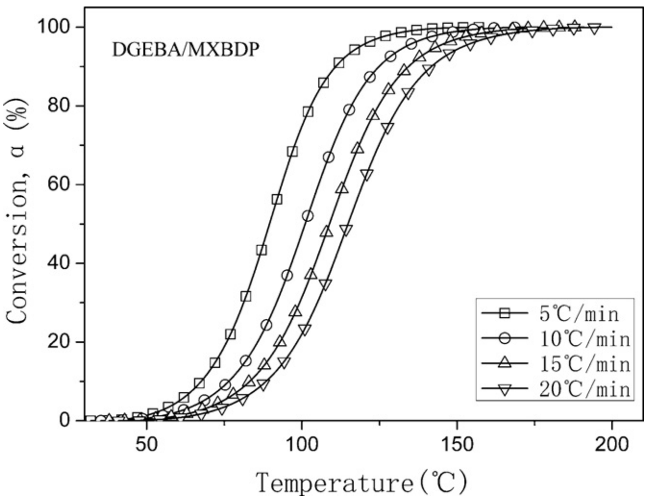


Fig. 8. Dependence of conversion α on temperature T for varied heating rates.

isothermal reaction of DGEBA/MXBDP involves multiple kinetic processes, as specified below.

As seen in Fig. 9, at the initial stage of the reaction E_α decreases from >60 to ≈57 kJ/mol up to $\alpha \approx 10\%$, which could be elucidated as follows. Evidently, secondary –OH species generated from epoxy-ring opening can markedly catalyze the epoxy-amine reaction via an activated epoxy-amine-hydroxyl trimolecular transition state [6,41,81] whereby the energetic barrier for the epoxy-amine reaction lowers. Meanwhile, the dramatic drop in the viscosity of the reaction mixture with increasing temperature decreases the energetic barrier for the diffusion of reactive species [82]. Consequently, superposition of the above effects leads to the decrease of the overall effective activation energy. As α continues increasing, a plateau appears for $\alpha \approx 10$–35% with relatively constant $E_\alpha \approx 57$ kJ/mol. This finding could be interpreted as the dynamic compensating balance among the steadily elevated temperature, the rapidly increased molecular weight, and the gradually reinforced autocatalysis, which may have respective contributions to the effective activation energy, positive or negative.

When the conversion increases beyond ≈35%, E_α monotonously decreases from ≈57 to ≈45 kJ/mol until the completion of the reaction. This observation is also somewhat similar to the previous findings for the nonisothermal reaction of another epoxy-amine system proceeding in different conversion range [64]. Thus, here the decrease in E_α could be considered as a sign of the onset of diffusion-complicated reaction kinetics, probably triggered by the gelation of the reaction mixture [80] and gradually strengthen by the increases in junction points in the epoxy network with increasing conversion, as detailed below.

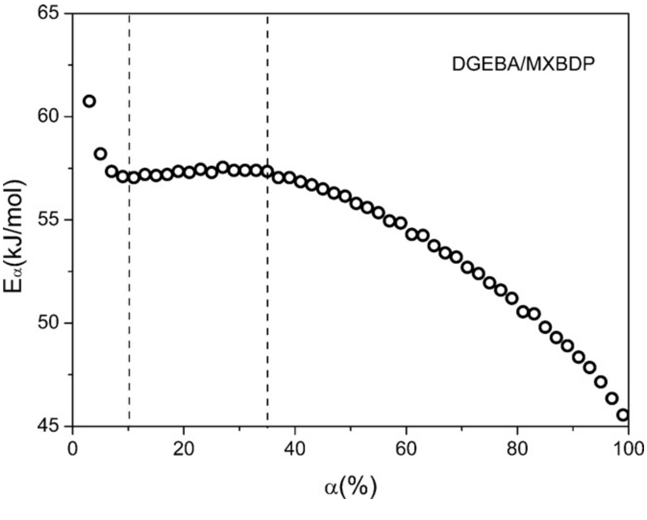


Fig. 9. Variation of effective activation energy E_α with conversion α identified with AICM.

Theoretically, for a thermosetting resin reaction, critical conversion of gelation depends on both functionality of reactants and their stoichiometry, irrespective of reaction temperatures. To be more specific, for a stoichiometric epoxy-amine system one can use Eq. (13) [83] to predict gelation conversion:

$$\alpha_{\text{gel}} = \left[\frac{1}{(f_A - 1)(f_E - 1)}\right]^{1/2} = \left[\frac{1}{(8-1)(2-1)}\right]^{1/2} \approx 0.378 \qquad (13)$$

where f_A is the averaged functionality of an amine curing agent, f_E is the averaged functionality of an epoxy resin, and α_{gel} is the gelation conversion. As regards the stoichiometric DGEBA/MXBDP system, f_A and f_E equal 8 and 2, respectively; then, we get $\alpha_{\text{gel}} \approx 0.378$ with Eq. (13). Obviously, the predicated α_{gel} is fairly close to the observed threshold conversion $\alpha \approx 0.35$ in Fig. 9. Sbirrazzuoli and Vyazovkin firstly revealed the similar finding for the DGEBA/1,3-phenylenediamine system, that the decrease of E_α occurred near the gelation conversion during its nonisothermal reaction process due to diffusion-controlled reaction kinetics [80]. This resemblance suggests the onset of the gelation greatly decelerate the diffusion of the reactive species into the tangible distance for the epoxy-amine reactions taking place, since the further reactions must invoke a huge number successive jumps along molecular chains, in particular, after the gelation. Furthermore, after that the crosslink density of the network steadily increases with conversion, which may make the diffusion of the reactive species more and more restricted. Consequently, the effect of the diffusion on the reaction kinetics becomes increasingly significant after the gelation. In short, the decrease of E_α at the late stage of the reaction is owing to the gradually being enhanced diffusion-complicated reaction kinetics.

4. Conclusions

We have successfully studied the nonisothermal reaction kinetics of DGEBA/MXBDP. Increasing the heating rates could accelerate the reaction rate, but little influenced the nonisothermal reaction exotherm (114–119 kJ/mol epoxide). The apparent reaction activation energy was 60.1 kJ/mol determined, and the SB(m, n) model was justified to able to well describe the nonisothermal reaction of DGEBA/MXBDP. The dependence of the effective activation energy E_α on conversion α suggested that the overall reaction kinetics was very complex, which was affected to different extents by the viscosity of the reaction mixture, autocatalysis, reaction temperature, gelation, crosslink density, and conversion. In summary, MXBDP can well cure epoxy resin to an acceptable reaction extent, and may find a promising usage in practical epoxy formulations such as room-temperature coatings, adhesives, and sealants. Our further investigation will focus upon the isothermal reaction of MXBDP/DGEBA and the mechanical properties of the cured epoxy network.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.06.021.

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