Curing kinetics of Benzoxazine–epoxy copolymer investigated by non–isothermal differential scanning calorimetry

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ABSTRACT

The reaction of epoxy novolac resin cured with benzoxazine resin (BA-a) was investigated under non-isothermal DSC at different heating rates. The kinetic parameters and the kinetic models of the curing processes of the benzoxazine-epoxy novolac mixtures were examined utilizing isoconversional methods, Flynn-Wall-Ozawa and Friedman methods. The benzoxazine-epoxy novolac mixture exhibits two dominant curing processes. The reaction 1 at lower temperature is attributed to the reaction among the benzoxazine monomers, while the reaction 2 corresponds to the formation of an etherification between hydroxyl group of polybenzoxazine and epoxide group or homopolymerization reaction of epoxide group at high temperature. The average activation energies of the reaction 1 and reaction 2 were determined to be 81 kJ mol^{-1} and 118 kJ mol^{-1}, respectively. The autocatalytic kinetic model was found to be the best description of the investigated curing reactions. In addition, the predicted curves from our kinetic models fit well with the non-isothermal DSC thermogram.

1. Introduction

Polybenzoxazine has been developed as a new class of thermosetting polymers based on the ring opening polymerization of benzoxazine precursors only by thermally cure without generating byproduct or volatiles. The polymer has been reported to render high glass-transition temperature (T_g) and high modulus [1–8]. Some properties of polybenzoxazine exceed many epoxy resin, as well as conventional phenolics. Recently, several US patents have been issued on the applications of the benzoxazine compound or resin that has utility especially for use within semiconductor fabrication industry [9–14]. Moreover, the use of the resin as a matrix for highly filled composites has been achieved [15,16]. Furthermore, the ability of benzoxazine resin to alloy with other polymers [2,6,17–22], provides the resin with even broader range of applications.

In the past decades, epoxy resins have been widely used in those applications required thermosetting characteristics. However, the hardeners used for the epoxy resins including amines and anhydrides, have some drawbacks such as high toxicity or low storage stability [23]. In a number of recent works, alloying between benzoxazine resin and epoxy has been reported to be a potentially effective measure for thermal and mechanical property enhancement of the resulting copolymer because both polymers have been shown to compatibly undergo hybrid network formation as reported [9,19,24]. In addition, Rimdusit and Ishida [25] recently reported the characteristic of the curing reaction of the benzoxazine-epoxy systems. The curing reaction of the benzoxazine-epoxy resins shows two exothermic peaks, and the two peaks will be more distinguishable with an increasing amount of epoxy resin. However, the kinetic aspects of the curing of these resins were not discussed. In order to understand the nature of curing process of the benzoxazine-epoxy resins, the curing kinetic of the system is investigated in this work.

The cure kinetics of a thermosetting polymer is conveniently monitored by differential scanning calorimetry (DSC). The heat flow measured in DSC is proportional to both overall heat release and cure rate [26]:

$$\frac{dQ}{dt} = Q_{cure}\frac{d\alpha}{dt} = Q_{cure}k(T)f(\alpha) \tag{1}$$

where dQ/dt is the heat flow, t is the time, Q_{cure} is the total heat released when an uncured samples is brought to complete cure, $d\alpha/dt$ is the cure rate, α is the extent of a monomer conversion to a crosslinked network, $k(T)$ is the Arrhenius rate constant, and $f(\alpha)$ is the differential conversion function depending on the reaction

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mechanism. The rate constant, k, is dependent on temperature according to Arrhenius equation shown in Eq. (2).

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

where A is the pre-exponential factor and E is the activation energy which are Arrhenius parameters and R is the gas constant (8.314 J mol^{-1} K^{-1}).

The explicit temperature dependence of the rate constant, k, is introduced by replacing $k(T)$ with the Arrhenius equation, which gives

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{3}$$

Kinetic analysis of non-isothermal resin-cured system in which a sample is heated at a constant rate, is eliminated through the trivial transformation.

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{4}$$

Where $\beta = dT/dt$ is a constant heating rate.

1.1. Kinetic analysis

Kinetic analysis of non-isothermal resin-cured system can be performed by the multiple heating rates [27–31]. A multiple heating rates method, which is isoconversional method, provides a good example to produce reliable kinetic parameters as well as to accomplish agreement with isothermal conditions. Two different isoconversional methods are as follows.

1.1.1. Flynn-Wall-Ozawa method

The isoconversional integral method was also proposed independently by Flynn, Wall and Ozawa [27,28] using Doyle's approximation of the temperature integral. This method is based on Eq. (5) and (6).

$$\ln\beta = \ln\left(\frac{AE_a}{R}\right) - \ln g(\alpha) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \tag{5}$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{6}$$

where $g(\alpha)$ is the integral conversion function.

This method has been used in present computations of the activation energy at different values of conversion. Thus, for a constant α, the plot of $(\ln \beta)$ vs. $(1/T)$ obtained from DSC thermograms using various heating rates, should render a straight line where the slope allows the determination of the apparent activation energy. The experimentally evaluated values of the activation energy were used to determine the appropriate kinetic model which best describes the conversion function of the process studied.

1.1.2. Friedman method [30]

The Friedman method is also used to determine a kinetic model of the curing process. The method is based on Eq. (7):

$$\ln\frac{d\alpha}{dt} = \ln\beta\frac{d\alpha}{dT} = \ln[Af(\alpha)] - \frac{E_\alpha}{RT} \tag{7}$$

In case of the nth – order reaction : $f(\alpha) = (1 - \alpha)$ (8)

$f(\alpha)$ in Eq. (7) is substituted by Eq. (8)

$$\ln[Af(\alpha)] = \ln\left[\frac{d\alpha}{dt}\right] + \frac{E_\alpha}{RT} = \ln A + n\ln(1 - \alpha) \tag{9}$$

The value of $\ln[Af(\alpha)]$ can be obtained from the known values of $\ln[d\alpha/dt]$ and E_α/RT. Therefore, the plot of $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ yields a straight line where the slope corresponds to the reaction order (n). The intercept is the natural logarithm of the frequency factor if the reaction mechanism of the nth-order kinetics. Otherwise, for autocatalytic process, the Friedman plot would reveal a maximum of $\ln(1-\alpha)$ approximately around -0.51 to -0.22 which is equivalent to degree of curing (α) of about $0.2-0.4$.

As aforementioned, the advantage of two kinetics methods under non-isothermal condition is that they do not require prior knowledge of the reaction mechanism in order to quantify kinetic parameters [32]. In the past, the curing kinetic of benzoxazine resin (BA-a) with and without catalysts by using both isothermal and non-isothermal differential scanning calorimetry was determined [3,33]. The authors reported that the curing of benzoxazine precursors was an autocatalysed reaction prior to diffusion control stage. The apparent activation energy calculated by Ozawa and Kissinger method of the curing process in uncatalysed system was found to be 107 kJ mol^{-1} and 116 kJ mol^{-1}, respectively, with an overall reaction order $(m + n)$ of about 2. Recently, the kinetic analysis of other systems of benzoxazine resins such as random copolybenzoxazine of bifunctional benzoxazine (BA-a) type and monofunctional benzoxazine (P-a) type with low viscosity at room temperature has also been reported [34]. Under the dynamic DSC experiments, the curing process of the copolybenzoxazine precursor involves an autocatalytic-type curing mechanism and the activation energy was found to be 72 kJ mol^{-1} based on the Kissinger method and 84 kJ mol^{-1} using the Flynn-Wall-Ozawa method.

Meanwhile, numerous studies on curing kinetics of epoxy resin have been reported in the past decade [35]. The literature values of the activation energies and the kinetic equation for epoxy-anhydride cure under isothermal and non-isothermal conditions. The activation energy values were reported to be in a range of 28–158 kJ mol^{-1} and the kinetic analysis of epoxy resins preformed by several kinetic methods showed the autocatalytic cure [36,37]. Moreover, the curing kinetics of various epoxy resin systems utilizing the isoconverional method was investigated [26,28,36,38].

The present paper reports the cure kinetics of benzoxazine-epoxy novolac resin mixtures. The cure kinetics of the studied system was examined by non-isothermal differential scanning calorimetry (DSC) at different heating rates in order to understand the reaction kinetics of the benzoxazine-epoxy systems for achieving optimal processing.

2. Experimental

2.1. Materials

The BA-a type benzoxazine based on bisphenol-A, formaldehyde, and aniline was synthesized by patented solventless technology [4]. Bisphenol-A and paraformaldehyde were obtained from Thai Polycarbonate Co., Ltd. and Merck Company, respectively. An aromatic amines, i.e. aniline (99%), was purchased from Fluka Chemika. The o-cresol novolac epoxy (EPON164, epoxy equivalent weight 200–240 g/equiv., value for $n = 3.5$) was obtained form Shell Chemicals and was used as-received without further purification. The resin is light yellow solid at room temperature.

2.2. Processing method

Each resin was first measured at the desirable mass fraction. The benzoxazine-epoxy novolac resin mixtures to be investigated are BE55. In the nomenclature of the samples, B stands for the bifunctional BA-a resin whereas E is an epoxy novolac resin. The numbers after letters are the mass ratio of the two monomers in the respective order. The mixture was then heated to about 80 °C in an aluminum pan and was mixed by hand for a few minutes until the homogeneous mixture was obtained.

2.3. Differential scanning calorimetry (DSC)

The polymerization behavior of benzoxazine-epoxy novolac resins was examined using differential scanning calorimetry (DSC) model 2910 from TA Instruments. The reaction mixture was cured in DSC under non-isothermal conditions at heating rates of 0.5, 0.75, 1, 1.5, and 2 °C min^{-1} which was heated from 30 up to 300 °C in a constant flow of nitrogen of 50 ml min^{-1}.

A small quantity of the mixture (10 mg) was used for the DSC studies in an aluminum cell. An identical empty cell was taken as reference. The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exotherm. They were processed further to obtain a fractional conversion (α) and the rate of the reaction $d\alpha/dt$.

3. Results and discussion

3.1. Curing reaction of BE resin mixtures

Determination of the average activation energy based on Flynn-Wall-Ozawa method of the curing reaction of BE55 resin which is a ratio that shows the highest glass-transition temperature of 205 °C compared to that of polybenzoxazine (160 °C) was investigated. Non-isothermal DSC scans at five different heating rates recorded at 0.5, 0.75, 1, 1.5 and 2 °C min^{-1}, which are a slower curing rate that renders a better peak resolution were performed and the responses are shown in Fig. 1. From this figure, information about the nature of the curing reaction such as initial curing temperature, peak temperature, and the finishing temperature of

the BE55 resin, could be obtained. In Fig. 1, we can see that the curing reaction at slower heating rate of the BE55 resin shows two exothermic peaks. Therefore, the curing reaction of the BE55 resin is expected that the exothermic peak of the BE55 resin has at least two cure stages as similarly investigated to the alloy systems based on BA-a and EPON825 [25] or maleimide-functionalized benzoxazine/epoxy systems [39] for curing behavior. In addition, the exothermic heat of reaction of the BE55 resin estimated from the area under the exothermic peak of each heating rate is about the same and the average value was calculated to be $228 \pm 8.5 \, J \, g^{-1}$.

The kinetics analysis of the DSC curves for BE55 resin mixture at the heating rates shown in Fig. 1 was carried out by separating of the two overlapping exothermic peaks using Pearson VII distribution equation from PeakFit v4.12 program and analyzing the distinct characteristic of each exothermic peak. As an exemplification, the DSC thermogram for the curing reaction of the BE55 resin at a heating rate of 2 °C min^{-1} (solid line) as well as the calculated data from Peakfit v4.12 (dash line) with two resolved peaks of reaction 1 and reaction 2 (peak 1-filled circles and peak 2-unfilled circles) were illustrated in Fig. 2.

3.2. Kinetic model

To study the kinetic models of both reactions occurred in BE55 resin, a more complete assessment of the apparent activation energy of the BE resin system throughout the entire conversion range may be acquired using the isoconversional method i.e. the Flynn-Wall-Ozawa method. If the data fall into a straight line, the slope should then correspond to E_α/R at the particular conversion. The variation of E_α of the BE55 resin at different conversion for the two reactions is shown in Fig. 3. For both reactions, it can be seen that the activation energy values tend to increase with the degree of conversion. An interpretation of this behavior is an apparent decrease in molecular mobility and the polymer gels or due to a kinetic compensation effect has been reported [40]. To eliminate these effects, the mean of the activation energy value determined at the degree of cure (α) in ranges of 0.1–0.5, was found to be 81 kJ mol^{-1} for reaction 1 and 118 kJ mol^{-1} for reaction 2. We can observe that the average activation energy value of reaction 1 for the BE55 resin is almost the same as the activation energy of BA-a resin reported by other workers [3,33,34,41]. This implies that the
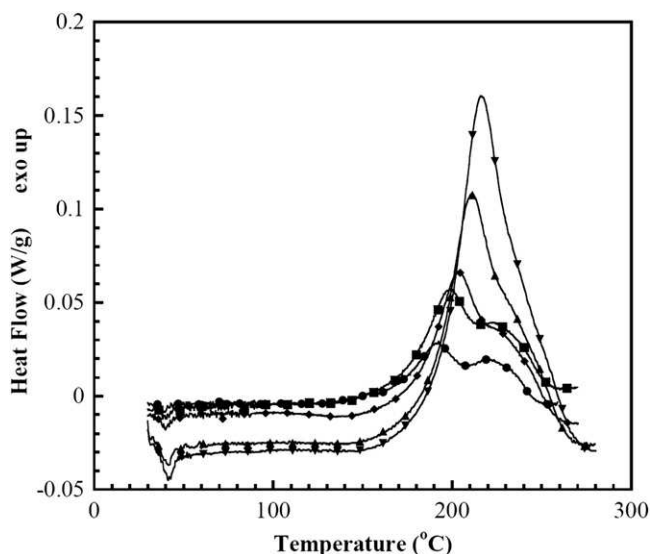

Fig. 1. DSC thermograms of BE55 resin at different heating rates: (●) 0.5 °C min^{-1}, (■) 0.75 °C min^{-1}, (◆) 1 °C min^{-1}, (▲) 1.5 °C min^{-1}, (▼) 2 °C min^{-1}.
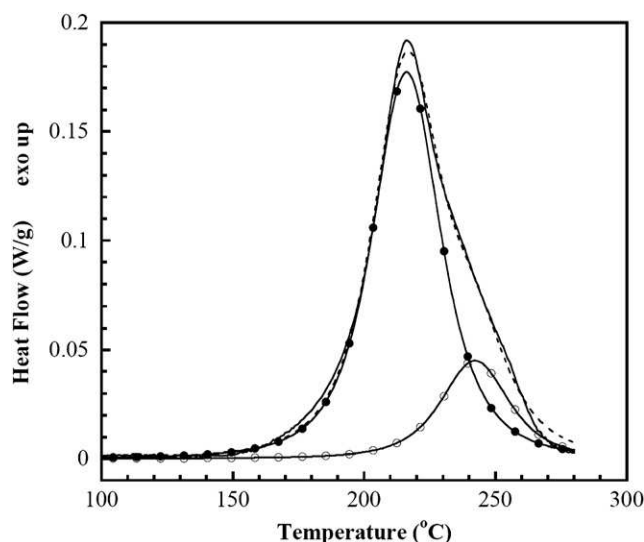

Fig. 2. DSC thermograms of BE55 resin recorded at 2 °C min^{-1}: the DSC thermogram (solid line), calculated the DSC thermogram (dash line), (●) reaction 1, (○) reaction 2.
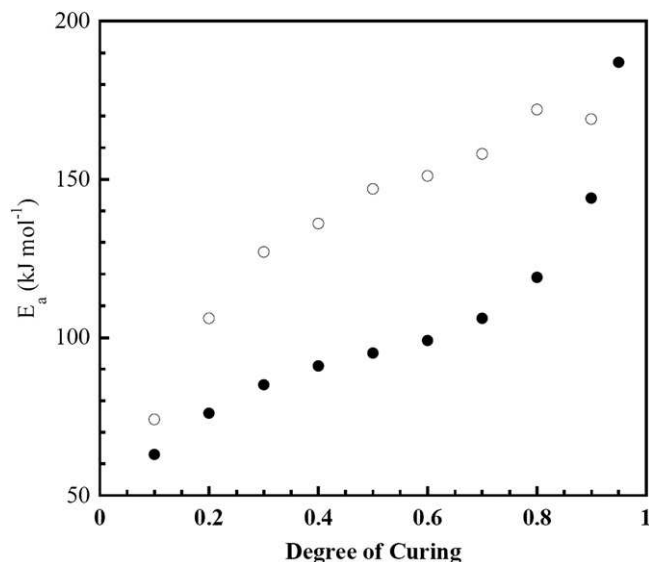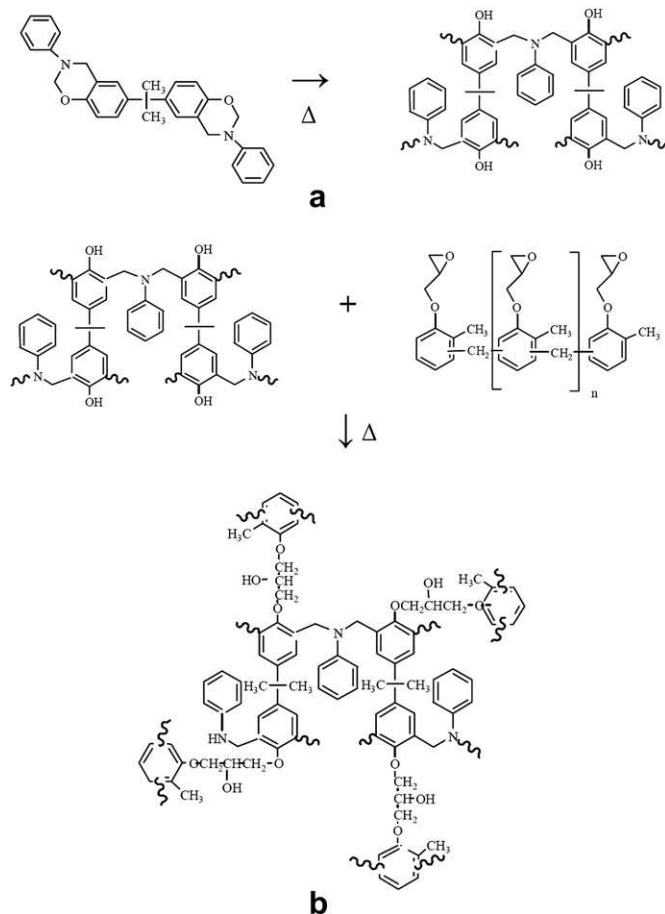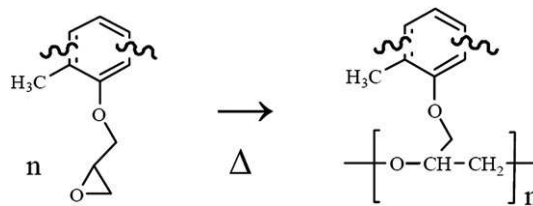
Fig. 3. Values of the apparent activation energy of BE55 resin obtained from Flynn-Wall-Ozawa method: (●) reaction 1, (○) reaction 2.

Scheme 2. Curing reaction of epoxy novolac resin at high temperature.

nature of reaction 1 of BE55 curing is related to the reaction among the BA-a monomers. The mechanism is attributed to the heterocyclic ring opening polymerization of benzoxazine precursors since the oxazine ring is the reactive site for curing of the benzoxazine

resin as shown in Scheme 1(a). The phenolic moieties generated by thermal cure of the benzoxazine resin were reported to function as a hardener for epoxy polymerization [18,25]. Therefore, the second exothermic peak of the BE55 was speculated that the possible reaction corresponded to the side reaction such as etherification reaction between a hydroxyl group of polymerized benzoxazine resin and an epoxide to form ether link and a new hydroxyl group as chemical reaction investigated in Scheme 1(b). Another expected reaction is the homopolymerization that epoxide group polymerized at high temperature, reaction that also produces an ether link as shown in Scheme 2. The reaction 2 in BE resin was found to exhibit activation energy with the value substantially higher than that of reaction 1. In summary, during the processing of this BE resin, the predominant reaction that tends to occur at early stage should be the reaction among the benzoxazine monomers due to its lower processing temperature as seen in DSC thermogram and its lower activation energy shown in the above calculation. For the reaction 2, the activation energy is in excellent agreement with those reported for etherification and homopolymerization by Cole et al. (101.4 kJ mol^{-1}) [42] and Sbirrazzuoli et al. (104, 170 kJ mol^{-1}) [43].

To examine the kinetic model, the kinetic method requires the previously known activation energy value. In our case, the average activation energy value obtained from Flynn-Wall-Ozawa method was used for the determination of the reaction order of the BE55 system. In general, the mechanisms of thermoset curing are classified into two major kinetic reactions, a nth-order and an autocatalytic reactions [44]. In this work, the method used to find kinetic model is Friedman method. For nth-order reaction,
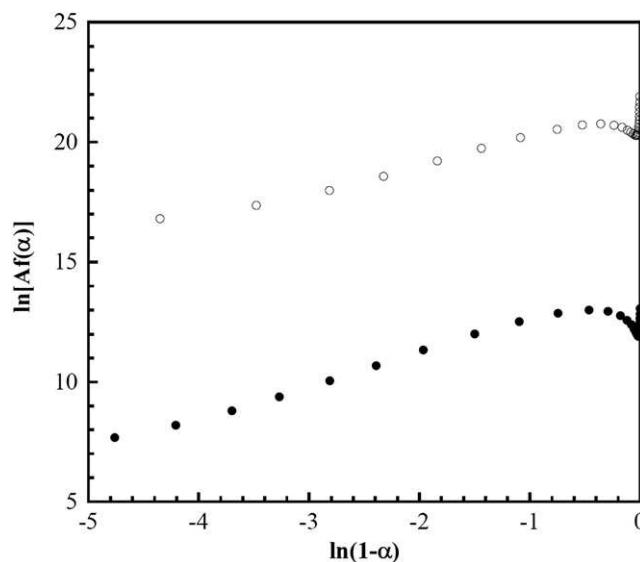

Scheme 1. Curing reaction: (a) benzoxazine resin, (b) epoxy novolac resin with a pendant hydroxyl group.

Fig. 4. Plots of ln[$Af(\alpha)$], vs ln($1-\alpha$) of BE46 resin using the heating rate of 10 °C min^{-1} and using the average activation energy from Flynn-Wall-Ozawa method: (●) reaction 1, (○) reaction 2.

Table 1
The kinetic parameters evaluated for the curing of benzoxazine-epoxy resin(BE55) reaction 1.

Heating rate (°C min⁻¹)	E (kJ mol⁻¹)	lnA(s⁻¹)	n	m
0.5	81	14.26	1.7	0.9
0.75		14.56	1.8	1.0
1		14.45	1.7	0.9
1.5		14.31	1.4	0.7
2		14.58	1.6	0.8

* For benzoxazine resin [40]: lnA (s⁻¹) = 15.60, m = 0.8, n = 1.7 and E (kJ mol⁻¹) = 81.

the average activation energy from Flynn-Wall-Ozawa method is taken as a constant, Eq. (9) may be written as:

$$\ln[A f(\alpha)] = \ln A + n\ln(1 - \alpha) \qquad (10)$$

Friedman suggested that the relationship between $\ln[Af(\alpha)]$ against $\ln(1-\alpha)$ should yield a straight line of which the slope corresponds to the order of n of the reaction. Otherwise, for auto-catalytic process, the Friedman plot would show a maximum of ln $(1-\alpha)$ approximately around -0.51 to -0.22 which is equivalent to α of about 0.2–0.4. This is due to the autocatalytic nature that shows the maximum reaction rate at 20–40% conversion. The results are in good agreement with several works reported [31,45].

Fig. 4 depicts Friedman plots as an exemplification of the reactions 1 and 2 of BE55 resin at a heating rate of 2 °C min⁻¹. For both reactions, since $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ are not linearly related and evidently show a maximum in the range of the degree of conversion mentioned above, this suggests that both curing reactions are autocatalytic in nature. The autocatalytic nature of benzoxazine resin can be explained by the generation of free phenol groups while the benzoxazine ring starts to open. These groups can actually accelerate further ring opening reaction of the monomers [3,33]. Similar phenomenon is expected to occur and to make benzoxazine monomers more reactive towards the epoxy resin in reaction 2. As previously mentioned, the curing reaction 2 is also the autocatalytic process which is consistent with the literature report [46] that o-cresol novolac epoxy resin cured with phenol novolac as hardener proceeds through an autocatalytic kinetic mechanism while nth-order kinetic reaction is observed in o-cresol novolac epoxy resin using phenol resin hardener such as Xylok and DCPDP. In our work, the autocatalytic process occurred in the reaction 2 can be explained that a secondary hydroxyl group produced by a reaction between epoxy resin and polybenzoxazine would participate in cure reaction as investigation in epoxy resin systems with phenol novolac hardener.

$$f(\alpha) = (1 - \alpha)^n \alpha^m \qquad (11)$$

For the autocatalytic model, the term $f(\alpha)$ in Eq. (3) may have the form

Substituting Eq. (11) into Eq. (3) Thus, the following expression can be written:

Table 2
The kinetic parameters evaluated for the curing of benzoxazine-epoxy resin(BE55) reaction 2.

Heating rate (°C min⁻¹)	E (kJ mol⁻¹)	lnA(s⁻¹)	n	m
0.5	118	21.68	1.5	0.7
0.75		21.77	1.5	0.7
1		21.98	1.6	0.8
1.5		21.87	1.3	0.6
2		21.97	1.4	0.6

* For epoxy resin (EPON HPT1071) using hyperbranched polymer (HBP(Bz)) as hardener [45]: m = 0.45, n = 1.13 and E (kJ mol⁻¹) = 103.
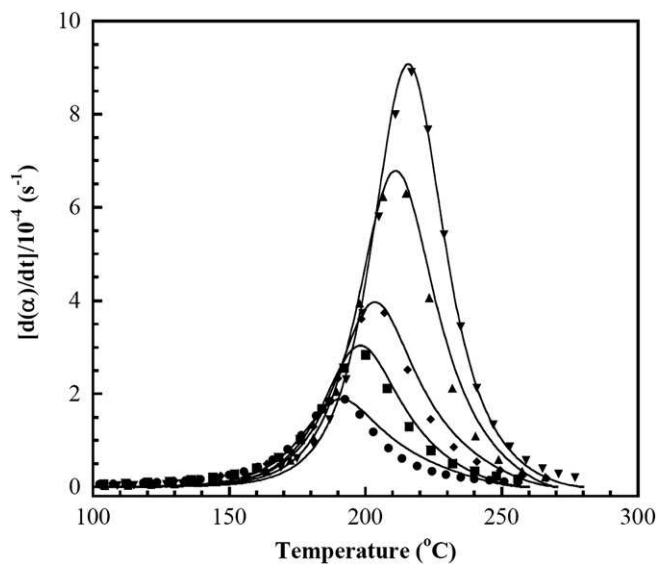

Fig. 5. Experimental (symbols) and calculated (solid lines) DSC peaks corresponding to the curing process of BE55 resin of reaction 1: (●) 0.5 °C min⁻¹, (■) 0.75 °C min⁻¹, (◆) 1 °C min⁻¹, (▲) 1.5 °C min⁻¹, (▼) 2 °C min⁻¹.

$$\frac{d\alpha}{dt} = A\exp(-Ea/RT)(1 - \alpha)^n \alpha^m \qquad (12)$$

Theoretically, Eq. (12) could be solved by multiple nonlinear regressions because the curing rate is an exponential function of the reciprocal of the absolute temperature. By taking the logarithm of Eq. (12), a linear expression for the logarithm of curing rate can be obtained.

$$\ln\left(\beta\frac{d\alpha}{dT}\right) = \ln A - \left(\frac{E_a}{RT}\right) + n\ln(1 - \alpha) + m\ln(\alpha) \qquad (13)$$

Eq. (13) can be solved by multiple linear regression, in which the dependent variable is $\ln(d\alpha/dt)$, and the independent variables are $\ln\alpha$, $\ln(1-\alpha)$, and $1/T$. Therefore, the values of A, m, and n can be
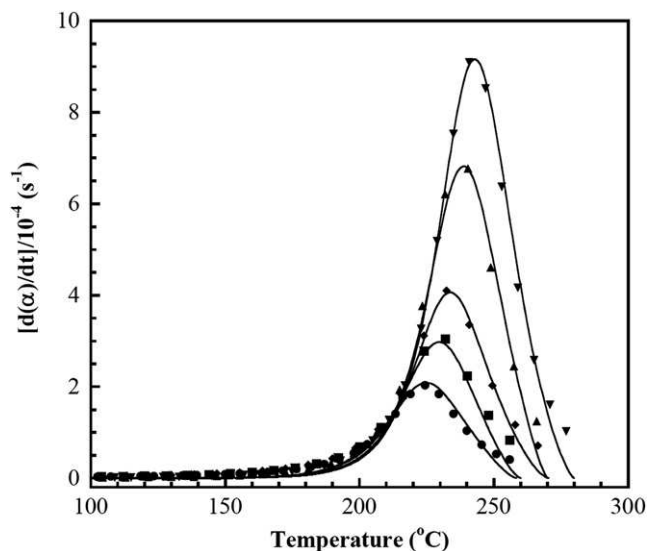

Fig. 6. Experimental (symbols) and calculated (solid lines) DSC peaks corresponding to the curing process of BE55 resin of reaction 2: (●) 0.5 °C min⁻¹, (■) 0.75 °C min⁻¹, (◆) 1 °C min⁻¹, (▲) 1.5 °C min⁻¹, (▼) 2 °C min⁻¹.
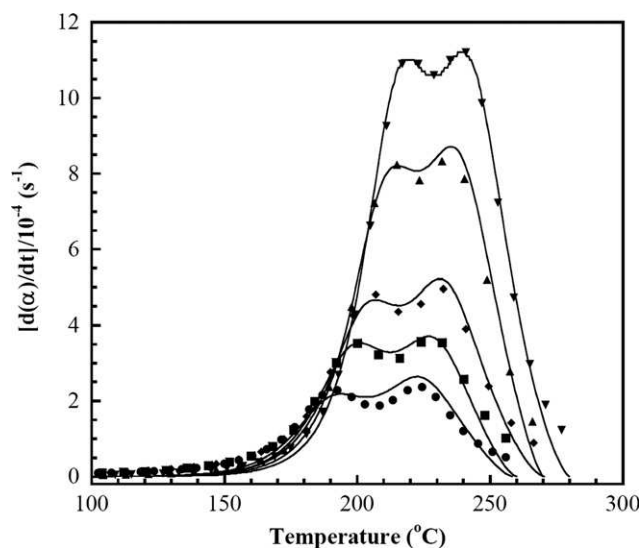
Fig. 7. Experimental (symbols) and calculated (solid lines) DSC peaks corresponding to the curing process of BE55 resin of total curing reaction: (●) 0.5 °C min^{-1}, (■) 0.75 °C min^{-1}, (◆) 1 °C min^{-1}, (▲) 1.5 °C min^{-1}, (▼) 2 °C min^{-1}.

obtained using the average activation energy from Flynn-Wall-Ozawa method. The degree of curing is chosen between the beginning of the reaction and the maximum peak of degree of curing ($\alpha = 0.1–0.5$). The results of the multiple linear regressions analysis for all heating rates used of benzoxazine-epoxy novolac system (reaction 1 and 2) are listed in Table 1, and Table 2, respectively. It can be seen that the variation of A, m, and n with the heating rate for both BA-a system is in the same range as those reported by Jubsilp et al. [41] whereas those values for reaction 2 are closer to the literature values of epoxy resin using hyper-branched polymeranhydride as hardener [47].

The experimental curves and predicted curves based on the determined kinetic parameters of curing reaction for peak 1 at different heating rates are shown in Fig. 5 and those of curing reaction for peak 2 are exhibited in Fig. 6. It is clearly seen that the calculated data from the model are in good agreement with the experimental results. Furthermore, the curing rates, $d\alpha_1/dt$, of reaction 1 and, $d\alpha_2/dt$, of reaction 2 are a function of a total curing conversion, α, which equals to the sum of the curing conversion of reaction 1, α_1, and the curing conversion of reaction 2, α_2. The correlations of those conversions are shown in Eq. (14).

$$\frac{d\alpha}{dt} = \frac{d\alpha_1}{dt} + \frac{d\alpha_2}{dt} \tag{14}$$

The plots of the total curing conversion, α, with respect to temperature can be obtained from Eq. (14) and the results are plotted in Fig. 7. From this figure, the calculated DSC curve fits relatively well with the experimental data using the obtained models.

4. Conclusions

The curing reaction of epoxy novolac resin by bisphenol A-based benzoxazine resin was studied. The curing of BE resin mixture was consisted of two dominant reactions (reaction 1 and 2), as evidenced by the presence of a double peak on the DSC thermograms. The activation energy value of the reaction 1 of the BE curing is similar to the activation energy of the neat benzoxazine resin curing. Therefore, reaction 1 was confirmed to be the reaction among the benzoxazine monomers while the activation energy

value of reaction 2 is substantially higher than that of reaction 1 and is closer to that of epoxy curing. Thus we speculate that reaction 2 is attributed to side reactions such as etherification reaction of the glycidyl ether by a hydroxyl group of polymerized benzoxazine resin or homopolymerization. The autocatalytic models proposed were found to adequately describe the curing kinetics of both reactions of the BE resins. Evidently, the kinetic models of the curing reaction of the BE resin are in good agreement with non-isothermal DSC results.

Acknowledgments

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