Curing kinetics of arylamine-based polyfunctional benzoxazine resins by dynamic differential scanning calorimetry

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Abstract

In this study, the curing kinetics of polyfunctional benzoxazine resins based on arylamine, i.e. aniline and 3,5-xylidine, designated as BA-a and BA-35x, respectively, were investigated. Non-isothermal differential scanning calorimetry (DSC) at different heating rates is used to determine the kinetic parameters and the kinetic models of the curing processes of the arylamine-based polyfunctional benzoxazine resins were proposed. Kissinger, Ozawa, Friedman, and Flynn–Wall–Ozawa methods were utilized to determine the kinetic parameters of the curing reaction. BA-a resin shows only one dominant autocatalytic curing process with the average activation energy of 81–85 kJ mol^{-1}, whereas BA-35x exhibits two dominant curing processes signified by the clear split of the curing exotherms. The average activation energies of low-temperature curing (reaction (1)) and high-temperature curing (reaction (2)) were found to be 81–87 and 111–113 kJ mol^{-1}, respectively. The reaction (1) is found to be autocatalytic in nature, while the reaction (2) exhibits nth-order curing kinetics. In addition, the predicted curves from our kinetic models fit well with the non-isothermal DSC thermogram.
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1. Introduction

Polyfunctional benzoxazine resins which can be modified by changing the amine group on the ring structure were reported to provide self-polymerizable crosslink-system with high thermal and mechanical integrity [1–3]. The polymers undergo ring-polymerization upon heating without the aid of a curing agent (strong acid and alkaline); therefore, no condensation by-products are released during a fabrication process as well as no corrosion of processing equipments. Moreover, polybenzoxazines possess several outstanding properties such as near-zero shrinkage after curing, low water absorption, and relatively high glass transition temperature even though it has relatively low cross-linking density [1,4]. In recent years, Ishida and Sanders [5–7] disclosed improving thermal and mechanical properties of polybenzoxazines based on alkyl-substituted aromatic amines (e.g. BA-35x type benzoxazine). A series of benzoxazine resins

have been synthesized that, upon polymerization, produced a varying amount of phenolic Mannich bridges, arylamine Mannich bridges, and methylene linkages. For the 3,5-xylidine-based benzoxazine, its thermal degradation temperature at 5% weight loss was reported to be 350 °C which is higher than that of BA-a type benzoxazine, i.e. about 315 °C. In theory, polybenzoxazines with additional amounts of arylamine Mannich bridges, and methylene linkages showed improved mechanical and thermal properties as a result of greater crosslink densities. Correlations between the observed mechanical properties and network structures of polybenzoxazines were reported [8]. Consequently, the polybenzoxazine and its alloys were investigated as a high performance matrix of composite materials such as in electronic packaging applications [9–14]. In order to make on optimum use of the benzoxazine resins, it is important to understand the nature of their curing process, the structure of the cured material, and how its kinetic parameters can be influenced by temperature, etc. The curing reaction is a very complex process because many reactive processes sometimes occur simultaneously. The final properties of the crosslinked benzoxazine resins depend significantly on the kinetics of the curing reaction concerned

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with extent of curing, the curing conditions, etc. [2,15]. Therefore, the study of the curing kinetics contributes to both a better knowledge of process development and an improvement of the quality of final products related to the structures of the polymer network [16,17]. In addition, the availability of reliable methods for cure monitoring also plays a crucial role in process control and optimization of the polymer network processing [18].

There are several techniques previously used to examine the kinetics of the polybenzoxazine curing, for instance, differential scanning calorimetry (DSC) [2,16,19,20–28], Fourier Transform Infrared Spectroscopy (FTIR) [29], and rheokinetic measurements [20]. Among these, differential scanning calorimetry has been the most utilized technique for the determination of kinetic parameters and the corresponding rate equation of the polybenzoxazine curing [2,15,19,21–27]. In general, the kinetic parameters estimated from DSC dynamic experiments were reported to agree relatively well with those estimated by other methods [30]. The basic assumption for the application of DSC is that the measured of heat flow, dH/dt, is proportional to the reaction rate, $d\alpha/dt$. Without knowing the exact reaction mechanism, it is reasonable to assume that the reaction rate at a given time is only a function of the conversion fraction particularly in the isothermal method [18].

1.1. Kinetic analysis

Kinetic analysis of non-isothermal resin-cured system is based on the rate equation [22]

$$\frac{d\alpha}{dt} \equiv \beta \frac{d\alpha}{dT} = k(T)f(\alpha) \tag{1}$$

where $k(T)$ is a temperature-dependent reaction rate constant, $f(\alpha)$ the differential conversion function depending on the 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. (2)

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

where A is the pre-exponential factor, E_a is the activation energy, and T is the absolute temperature.

Non-isothermal method, a more precise measure to evaluate the curing kinetic parameters, is carried out at different heating rates. This method is very attractive because the kinetic data can be obtained in a relatively short period of time. Nevertheless, there are some complications in the mathematical analysis of the temperature integral which are inherent to the non-isothermal approach. In addition, the isothermal method renders the destabilization of the DSC heat flow at the beginning of the measurement which leads to experimental errors. The two methods also cover different temperature domains as discussed by Sbirrazzuoli et al. [23]. Moreover, considering the shape of curing peak, the number of peaks and/or shoulders in the isothermal and non-isothermal DSC thermograms may be different. Although there is only a single peak in the isothermal DSC thermogram, a peak and a shoulder may appear in the non-isothermal DSC thermogram. Consequently, the kinetic parameters obtained from an

isothermal cure study may not be good in predicting the non-isothermal curing behaviors [31]. The non-isothermal method which involves single or multiple dynamic temperature scans has been applied extensively in the study of the curing reactions of thermosetting polymers [16,17,32]. Four kinetic methods widely used to study dynamic kinetics of thermosetting polymers are Kissinger, Ozawa, Friedman, and Flynn–Wall–Ozawa methods.

1.1.1. The Kissinger method

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 [25,33]:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{Q_p A R}{E_a}\right) - \frac{E_a}{RT_p} \tag{3}$$

where $Q_p = -[d f(\alpha)/d\alpha]_{\alpha=\alpha_p}$.

The graphic representation of Eq. (3) allows us to examine both the activation energy and the pre-exponential factor of curing kinetics.

1.1.2. The Ozawa method

A similar method to Kissinger method is Ozawa method, which relates the logarithm of the heating rate and the inverse of the exothermic peak temperature. Therefore, the curing activation energy can be determined from the resultant slope [34].

$$\ln\beta = \ln\left(\frac{A E_a}{R}\right) - \ln F(\alpha) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \tag{4}$$

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{5}$$

where $F(\alpha)$ is a constant function.

1.2. Isoconversional method

The isoconversional method assumes that both of the activation energy and pre-exponential factor are the functions of the degree of curing. In addition, the isoconversional approach can be used to evaluate both simple and complex chemical reactions. The significance of this technique is that no kinetic rate expression is assumed for the data evaluation [35]. Two different isoconversional methods are as follows.

1.2.1. Friedman method

The Friedman method, differential isoconversional method, is used to determine a kinetic model of the curing process. The method is based on Eqs. (1) and (2) that leads to:

$$\ln\frac{d\alpha}{dt} = \ln\beta\frac{d\alpha}{dT} = \ln[Af(\alpha)] - \frac{E_a}{RT} \tag{6}$$

In case of the nth-order reaction:

$$f(\alpha) = (1-\alpha)^n \tag{7}$$

From (1), (2), and (7)

$$\ln[Af(\alpha)] = \ln\left[\frac{d\alpha}{dt}\right] + \frac{E_a}{RT} = \ln A + n\,\ln(1-\alpha) \quad (8)$$

The value of $\ln[Af(\alpha)]$ can be obtained from the known values of $\ln[d\alpha/dt]$ and E_a/RT. Therefore, the plot of $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ yields a straight line which the slope providing the reaction order. The intercept is the natural logarithm of the frequency factor if the reaction mechanism is of the *n*th-order kinetics. The rate, $d\alpha/dt$, at each temperature can be determined from

$$\frac{d\alpha}{dt} = \frac{\varphi}{\Delta H} \quad (9)$$

where ΔH is the enthalpy of the curing reaction and φ is the measured heat flow normalized with the sample mass.

1.2.2. Flynn–Wall–Ozawa method

The isoconversional integral method was also proposed independently by Flynn, Wall, and Ozawa [25] using Doyle's approximation of the temperature integral. This method is based on Eqs. (10) and (11).

$$\ln\beta = \ln\left(\frac{AE_a}{R}\right) - \ln g(\alpha) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \quad (10)$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (11)$$

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

Thus, for a constant α, the plot of $(\ln\beta)$ versus $(1/T)$ 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 apparent activation energy received from the Flynn–Wall–Ozawa analysis is reported to be more reliable than that from the Friedman analysis. Moreover, the Flynn–Wall–Ozawa method, owing to its integrating character, exhibits less sensitivity to noise than the Friedman method. The latter, however, provides a better visual separation of more reaction steps as well as information concerning the existence of an autocatalytically activated process [36].

The advantage of these four kinetics methods over other non-isothermal methods is that they do not require prior knowledge of the reaction mechanism in order to quantify kinetic parameters [18]. Some of these methods had been used to determine the kinetic parameters of benzoxazine resins. Recent work by Ishida and Rodriguez [2,15] examined the curing kinetic of benzoxazine resin (BA-a) with and without catalysts by using both isothermal and non-isothermal differential scanning calorimetry. They reported that the curing of benzoxazine precursors was an autocatalysed reaction prior to diffusion control stage. The apparent activation energy by Kissinger and Ozawa method of the curing process was found to be about 102–116 kJ mol^{-1} in an uncatalysed system and 99–107 kJ mol^{-1} in a catalysed system, with an overall order of reaction of about 2. The phenol moiety of the ring-opened benzoxazine monomers was reported to have a catalytic effect on the curing reaction, i.e. reducing a reaction induction time and increasing reaction rate. Weak acids such

as adipic acid and sebacic acid can also be effectively used as catalysts for benzoxazine resin. The kinetic analysis of other systems of benzoxazine resins such as random co-polybenzoxazine of BA-a type and P-a type benzoxazines has also been reported [19]. The isothermal curing process of the co-polybenzoxazine precursor involves an autocatalytic-type curing mechanism. In the dynamic DSC experiments, 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. Furthermore, in the isothermal experiments, the activation energy was reported to be 50 kJ mol^{-1} based on the Kamal method, whereas the total order of reaction is between 2.66 and 3.03, depending on the isothermal curing temperature. Moreover, comparison of the activation energy of polybenzoxazine to that of an epoxy resin-based underfill material used in electronic packaging as reported by He [18] indicates nearly the activation energy values of the epoxy system to be 87 kJ mol^{-1} based on the Kissinger method. Sbirrazzuoli et al. [22–26] and Vyazovkin et al. [21,27] also investigated the curing kinetics of various epoxy resin systems utilizing the isoconversional analysis. The authors observed a dependence of the effective activation energy on the extent of cure with the value approaching 70 kJ mol^{-1} when the extent of cure reached 0.8, i.e. the system of DGEBA + HHMPA + DMBA [22].

To our best knowledge, the effect of alkyl-substituted arylamines in the curing kinetics of the polyfunctional benzoxazine resins has not been explored. It is, therefore, of interest to investigate that of the polyfunctional benzoxazine resins based on arylamine, i.e. aniline and 3,5-xylidine. The curing kinetics of the systems were examined by non-isothermal differential scanning calorimetry at different heating rates in order to understand the reaction kinetics of both systems and be the way of achieving successful processing.

2. Experimental

2.1. Materials

The BA-a type benzoxazine based on bisphenol-A, formaldehyde, and aniline, and the BA-35x type based on bisphenol-A, formaldehyde, and 3,5-xylydine were synthesized by patented solventless technology [37]. Bisphenol-A and paraformaldehyde were received from Thai Polycarbonate Co. Ltd. and Merck Company, respectively. A series of aromatic amines, i.e. aniline (99%) and 3,5-xylidine (98%), purchased from Fluka Chemika were used as received. A series of benzoxazine resin based upon alkyl-substituted arylamines were investigated [5,6] as shown in Scheme 1.

2.2. GPC measurements

Gel permeation chromatography (GPC) analysis was performed at 40 °C on a Waters 600 using three Waters Styragel® HT columns (Styragel® HT 0.5, Styragel® HT 1, and Styragel® HT 4). Molecular weights are relative to monodisperse polystyrene standards. Samples were prepared by dissolving the benzoxazine resins in tetrahydrofuran (THF) mobile phase at
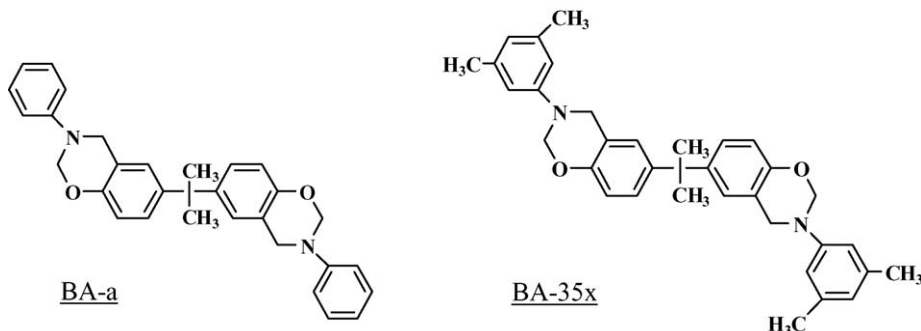
Scheme 1. Arylamine-based benzoxazine monomers.

30 °C in order to reach the final concentration of 0.25% (w/v). The detector was Waters 2414 refractive index (RID).

2.3. DSC measurements

A differential scanning calorimeter model 2910 from TA Instruments was employed to study the exothermic curing reactions. The samples were scanned by non-isothermal method from 30 to 290 °C at five different heating rates of 1, 2, 5, 10, and 20 °C/min under a constant flow of nitrogen at 50 ml/min.

3. Results and discussion

3.1. Curing reaction

The heat flows of BA-a and BA-35x from the conventional DSC mode are shown in Figs. 1 and 2, respectively. From these figures, information about the nature of the curing reaction such as initial curing temperature, peak temperature, and the curing range of the both resins at different scan rates could be derived. It can be observed that the exothermic peak shifts to a higher temperature with higher heating rate. In our systems, the heating rates show no effect on the total exothermic reaction heat

estimated from the area under the exothermic peak of BA-a and BA-35x. The average total exothermic reaction heat of BA-a and BA-35x is 341 and 299 J g^{-1}, respectively. It is noticed that the curing reaction of BA-a has more amount of heat released than that of BA-35x. This suggests that BA-a would be more sensitive to accelerate the curing than BA-35x. Moreover, the step changes of the thermograms of both resins at the temperature range of 45–60 °C are the glass transition temperature of the benzoxazine monomers or $T_{g,o}$. From Fig. 3, one can observe that BA-a benzoxazine shows only one exothermic peak of the non-isothermal DSC traces while BA-35x type benzoxazine shows overlapped exothermic peaks or a small shoulder beside the main peak. Thus, it is suggested that the curing reaction of BA-35x type benzoxazine has at least two cure stages; the curing reaction at lower temperature was caused by reaction (1) and the one occurring at higher temperature was caused by reaction (2). The individual reaction may be calculated by a combination of programmed and isothermal techniques. To verify the two curing reactions of BA-35x, further experiments on isothermal curing of partially cured samples (5–120 min) at 160 °C are depicted in Fig. 4. It can be noticed that the thermogram of partially cured BA-35x resin at 5 min shows no significant change of the exothermal peak temperature (200 °C) and still indicates the
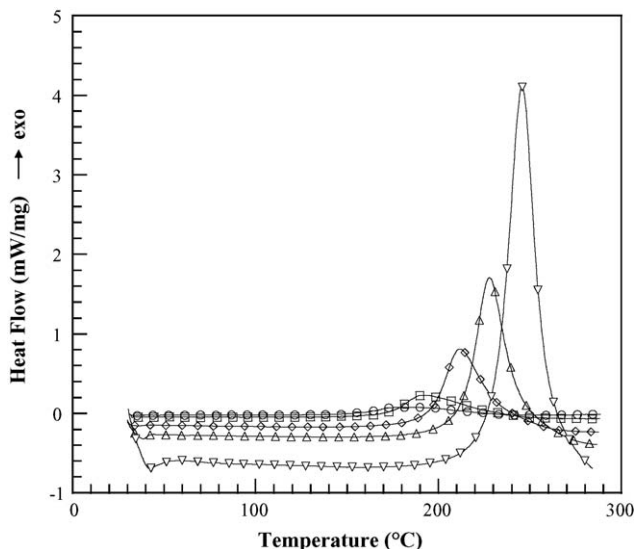

Fig. 1. DSC thermograms of BA-a resin at different heating rates: (◯) 1 °C/min, (□) 2 °C/min, (◇) 5 °C/min, (△) 10 °C/min, and (▽) 20 °C/min.
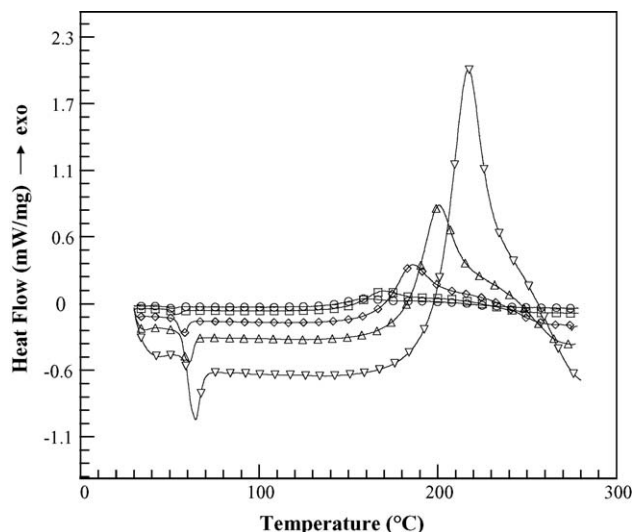

Fig. 2. DSC thermograms of BA-35x resin at different heating rates: (◯) 1 °C/min, (□) 2 °C/min, (◇) 5 °C/min, (△) 10 °C/min, and (▽) 20 °C/min.
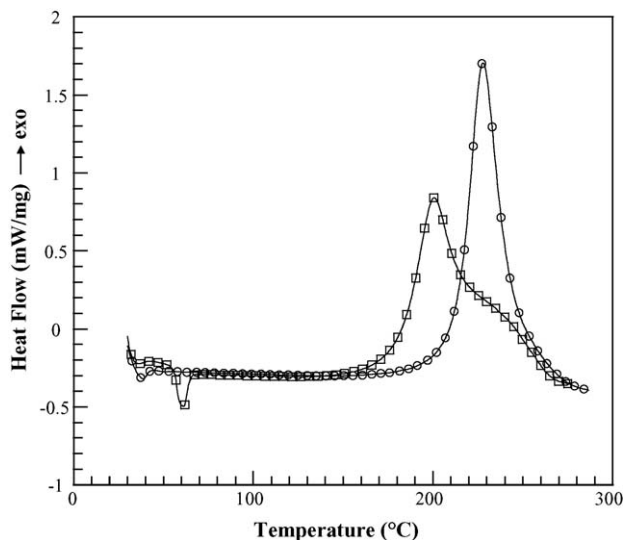
Fig. 3. DSC thermograms of two types of benzoxazine resins at 10 °C/min: (○) BA-a resin and (□) BA-35x resin.

overlapped exothermic peaks, i.e. the effect of the second reaction to the first peak is small. However, when the sample is cured to 10 min, the peak temperature is shifted to 210 °C, revealing stronger effect of the second reaction on the first peak. When the sample is cured to 15 min, the first peak almost disappears as the second peak is obviously observed. The partially cured BA-35x resin to 120 min clearly shows only one exothermic peak at higher temperature, implying that the effect of the first reaction to the second peak temperature could be neglected. The results in Fig. 4 ensure that there are two reaction phases in the hypothetical product.

The kinetics of the DSC curves for BA-35x at the heating rates of 1–20 °C/min were analysed using PeakFit v4.12. In order to separate two exothermic peaks, and to analyse the distinct characterization of each, Pearson VII distribution was used as
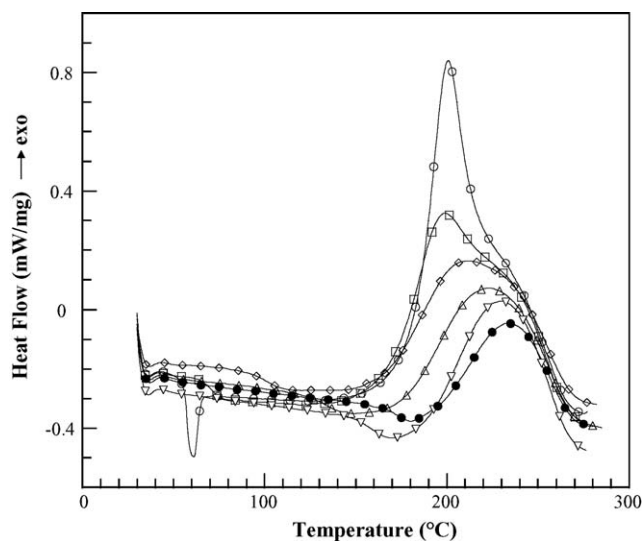

Fig. 4. DSC thermograms of BA-35x resin by using 10 °C/min heating rate after isothermal curing of 160 °C at different curing times in oven: (○) uncured BA-35x monomer, (□) 5 min, (◇) 10 min, (△) 15 min, (▽) 60 min, and (●) 120 min.
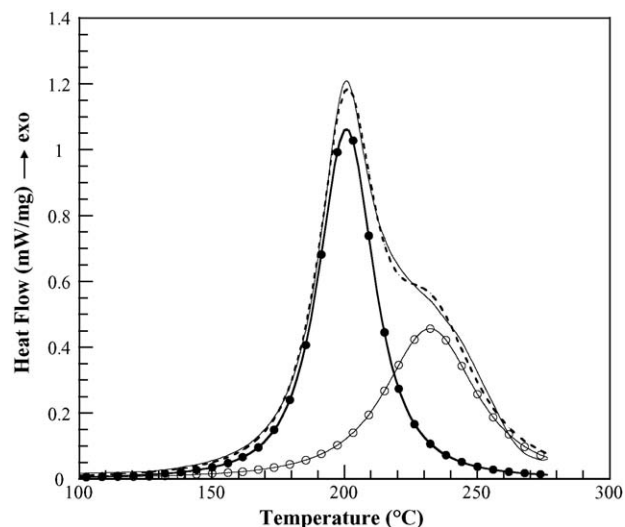

Fig. 5. DSC thermograms of BA-35x resin recorded at 10 °C/min: the DSC thermogram (solid line), the calculated DSC thermogram (dash line), (●) reaction (1), and (○) reaction (2).

shown in Fig. 5. The DSC thermograms were recorded for the curing reaction of the BA-35x sample at 10 °C/min (solid line) and calculated data from PeakFit v4.12 (dash line) with two distinct peaks (peak I—black circles and peak II—white circles).

3.2. Kinetic model

As the multiple heating rate methods for non-isothermal analysis proposed by Kissinger and Ozawa can be used as an alternative way of calculating the activation energy without assuming any model of kinetic parameters and without integrating the exothermic peak, the logarithm plots of heating rate versus the reciprocal of the absolute peak temperature of BA-a resin are given in Fig. 6. They are shown that a good linear relationship between the heating rate and the reversal of the exothermic peak temperature can be obtained. The average acti-
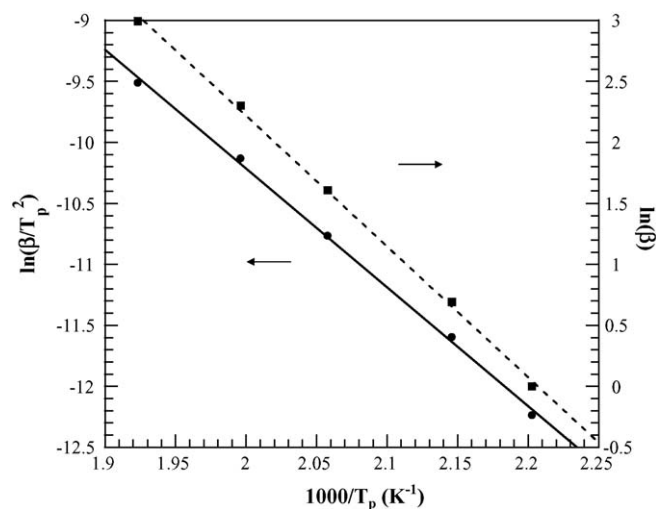

Fig. 6. (●) Kissinger method and (■) Ozawa method plots for averaged activation energy determination of the BA-a resin.

Table 1
Average activation energy of BA-a and BA-35x obtained by Kissinger and Ozawa methods

Method	Average activation energy (E_a, kJ mol^{-1})		
	BA-a resin	BA-35x resin	
		Reaction (1) (E_{a1})	Reaction (2) (E_{a2})
Kissinger	81	81	111
Ozawa	85	87	113

vation energy values of BA-a and BA-35x resins calculated from the slopes of the plots are listed in Table 1. BA-a resin shows only one dominant cueing kinetic process with the average activation energy of 81–85 kJ mol^{-1}, whereas BA-35x exhibits two major curing processes. The average activation energies of BA-35x for reactions (1) and (2) were 81–87 and 111–113 kJ mol^{-1}, respectively. In addition, the average activation energy values obtained from Kissinger and Ozawa methods are not significantly different. From the results, the calculated values of the activation energy values of BA-a and BA-35x are different from other reported works [2,15] because the molecular weight distribution of the benzoxazine precursor is different as indicated by GPC results. The precursor obtained is a mixture of monomers, dimers, and other oligomers formed in subsequent reactions during the synthesis, for instance, in case of BA-a, the molecular weight is 431, 498, and 807 g mol^{-1}, respectively, while those of BA-35x are 462, 562, and 964 g mol^{-1}, respectively. Typically, the molecular weight of purified BA-a and BA-35x type benzoxazine monomers is 463 and 527 g mol^{-1}, respectively [38]. Furthermore, considering the system of BA-35x, one can see that the activation energy of reaction (2) is much higher than that of reaction (1). As a result, reaction (1) is more sensitive to the temperature than reaction (2).

From the results, we can observe that the average activation energy value of reaction (1) for BA-35x resin is almost the same as the average activation energy of BA-a resin. This implies that the curing mechanism in the first stage of BA-35x resin is the same as that of BA-a resin. This mechanism is the heterocyclic ring opening polymerization of benzoxazine precursors since the oxazine ring is the reactive site for curing of the benzoxazine. The conformation of an oxazine ring containing benzoxazine is a distorted semichair structure, with the nitrogen and the carbon between the oxygen and nitrogen on the oxazine sitting, respectively, above and below the benzene ring plane. This resulting oxazine ring strain leads to the ring-opening polymerization to occur under certain conditions [39], whereas the second exothermic peak of the reaction (2), indicated by the high-temperature shoulder, corresponds to the side reactions which generate the bisphenolic methylene linkages and possible reaction to the *para* position of the arylamine ring called arylamine Mannich bridge and methylene linked structures. In addition, Ishida and Sanders [7] have reported different network structures of polybenzoxazine (BA-a and BA-35x types) investigated by FTIR. They found that the FTIR absorbed peak position of BA-35x after polymerization shows a large band centered at 847 cm^{-1} corresponding to the out-of-plane, in-phase hydrogen wagging mode
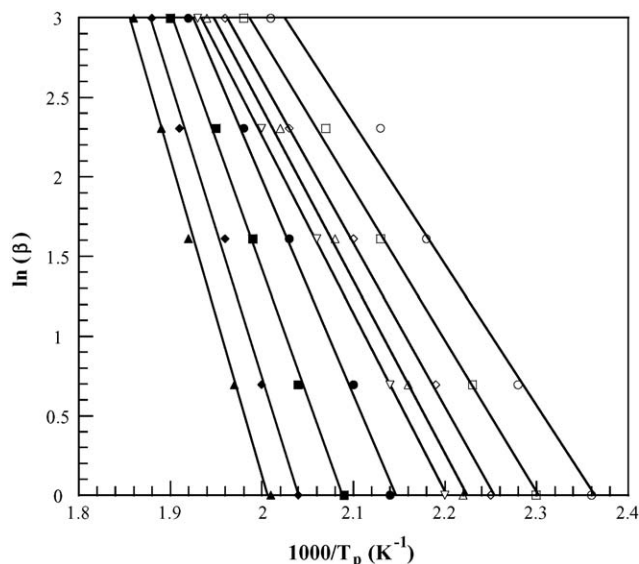

Fig. 7. Flynn–Wall–Ozawa plots at various degrees of curing of the BA-a resin: (○) $\alpha = 0.05$, (□) $\alpha = 0.10$, (◇) $\alpha = 0.20$, (△) $\alpha = 0.30$, (▽) $\alpha = 0.40$, (●) $\alpha = 0.60$, (■) $\alpha = 0.80$, (♦) $\alpha = 0.90$, and (▲) $\alpha = 0.95$.

of the 1,2,3,5-tetrasubstituted arylamine ring, but this peak cannot be observed for BA-a resin. However, the spectrum of both polybenzoxazine types centered at 878 cm^{-1}. This band agrees with the frequency predicted for the out-of-plane, out-of-phase hydrogen wagging node for the 1,2,3,5-tetrasubstituted aromatic ring.

Moreover, a more complete assessment of the apparent activation energy of benzoxazine resins throughout the entire conversion range may be obtained using the isoconversional methods that are the Flynn–Wall–Ozawa and Friedman methods. If the data fall into a straight line, the slope should then correspond to E_a/R at the particular conversion. For instance, Figs. 7 and 8 are Flynn–Wall–Ozawa and Friedman plots of
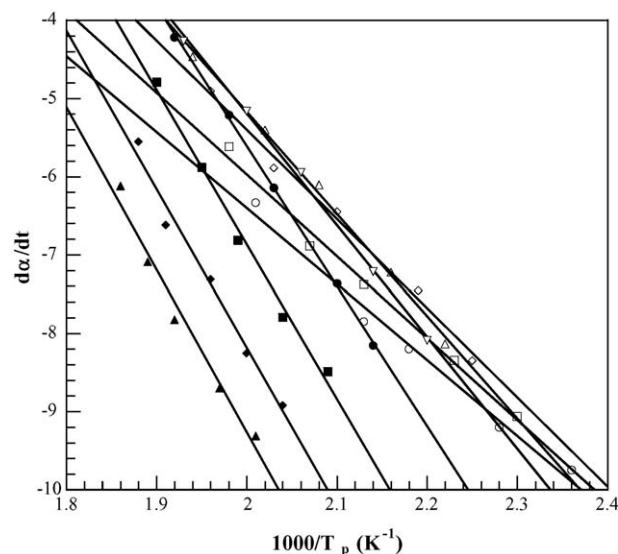

Fig. 8. Friedman plots at various degrees of curing of the BA-a resin: (○) $\alpha = 0.05$, (□) $\alpha = 0.10$, (◇) $\alpha = 0.20$, (△) $\alpha = 0.30$, (▽) $\alpha = 0.40$, (●) $\alpha = 0.60$, (■) $\alpha = 0.80$, (♦) $\alpha = 0.90$, and (▲) $\alpha = 0.95$.
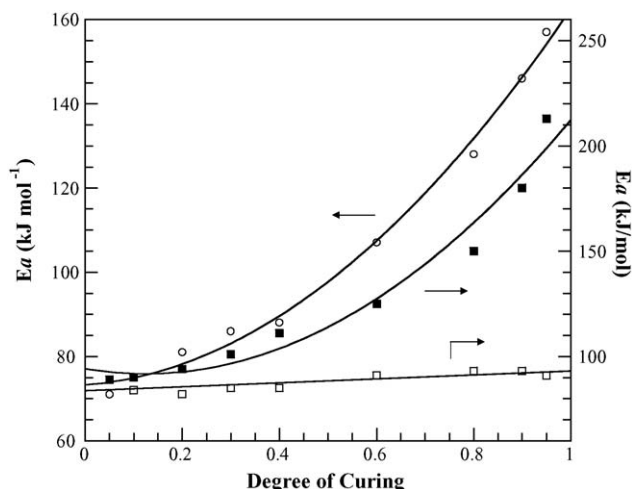
Fig. 9. Values of the apparent activation energy obtained from Flynn–Wall–Ozawa plots at different degrees of curing: (○) BA-a resin, (□) BA-35x (reaction (1)), and (■) BA-35x (reaction (2)).

BA-a resin system for $\alpha = 0.05$–0.95, respectively. A good linear relationship was observed from both Flynn–Wall–Ozawa and Friedman plots. Values of E_a of BA-a and BA-35x resins obtained in this manner at different degrees of curing are shown in Figs. 9 and 10. From the plots, the dependence of the apparent activation energies of both benzoxazine resins as a function of degree of curing was observed. The effect has been known in literatures as a kinetic compensation effect [40]. As there was no significant difference in the calculated activation energy values either using differential or integral kinetic methods, the activation energy obtained from Kissinger method was then selected for further determining the reaction order of our systems as recommended by Sbirrazzuoli et al. [25].

As previously mentioned, the mechanisms of the curing reaction of thermoset resins usually have two general kinetic reactions, an nth-order and an autocatalytic reaction [41]. In this work, the method used to find kinetic model is Friedman

method. For nth-order reaction, the average activation energy from Kissinger method is taken as a constant, Eq. (8) may be written as:

$$\ln[Af(\alpha)] = \ln A + n \ln(1 - \alpha) \qquad (12)$$

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 equiv-alent 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 [42–44].

Fig. 11 shows Friedman plots of reactions (1) and (2) of BA-35x resin, respectively. In case of reaction (1), since $\ln[Af(\alpha)]$ and $\ln(1 - \alpha)$ are not linearly related, this implies that the curing reaction is autocatalytic in nature. In contrast, the plot for reac-tion (2) shows linear relationship indicating nth-order kinetic behavior. Using the same analysis for BA-a (not shown here), only single peak reaction is obtained suggesting the behavior of autocatalytic reaction. According to other works reported, the autocatalytic nature of the reaction kinetics of this resin can be explained by the generation of free phenol groups while the ben-zoxazine ring starts to open. These groups can actually accelerate further ring opening [2,15].

For the nth-order model, it is assumed that the reaction obeys Eq. (13)

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right)(1 - \alpha)^n \qquad (13)$$
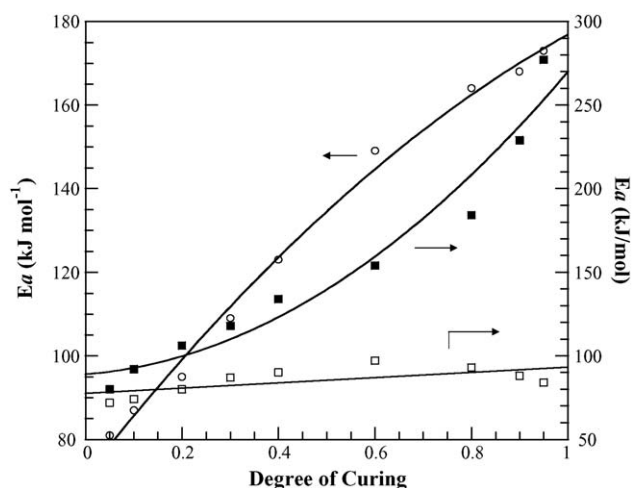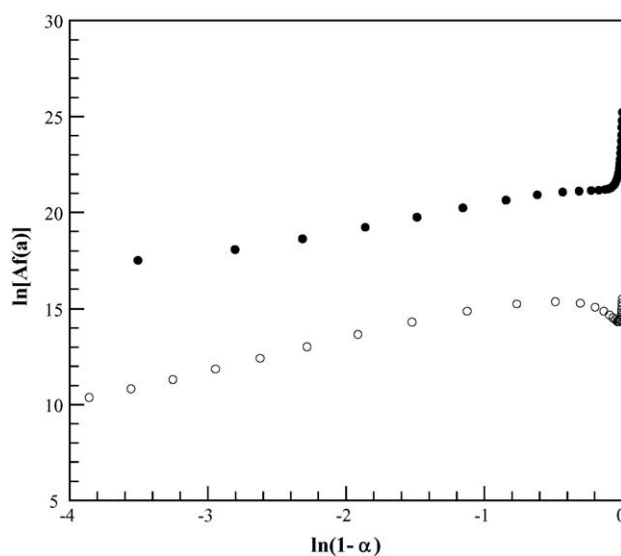

Fig. 10. Values of the apparent activation energy obtained from Friedman plots at different degrees of curing: (○) BA-a resin, (□) BA-35x (reaction (1)), and (■) BA-35x (reaction (2)).

Fig. 11. Plots of $\ln[Af(\alpha)]$ vs. $\ln(1 - \alpha)$ of BA-35x resin using the heating rate of 10 °C/min and using the average activation energy from Kissinger method: (○) reaction (1) and (●) reaction (2).

Table 2
The kinetic parameters evaluated for the curing of the BA-a system

Heating rate (°C/min)	E (kJ mol^{-1})	$\ln A$ (s^{-1})	Mean	n	Mean	m	Mean
1	81	14.57	15.60	1.7	1.7	0.4	0.8
2		14.99		1.9		0.4	
5		16.12		2.1		1.0	
10		16.28		1.6		1.2	
20		16.05		1.2		1.0	

Table 3
The kinetic parameters evaluated for the curing of the BA-35x system (reaction (1))

Heating rate (°C/min)	E (kJ mol^{-1})	$\ln A$ (s^{-1})	Mean	n	Mean	m	Mean
1	81	16.37	16.83	1.6	1.7	0.6	0.8
2		16.26		1.3		0.5	
5		17.00		1.8		0.9	
10		17.42		2.0		1.1	
20		17.08		1.7		1.1	

Conversely, the autocatalytic model considers independent reaction orders: m and n, as shown in Eq. (14)

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \alpha^m \qquad (14)$$

Theoretically, Eqs. (13) and (14) 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 Eqs. (13) and (14), a linear expression for the logarithm of curing rate can be obtained.

$$\ln\left(\beta\frac{d\alpha}{dt}\right) = \ln A - \left(\frac{E_a}{RT}\right) + n\ln(1-\alpha) \qquad (15)$$

$$\ln\left(\beta\frac{d\alpha}{dt}\right) = \ln A - \left(\frac{E_a}{RT}\right) + n\ln(1-\alpha) + m\ln(\alpha) \qquad (16)$$

Eqs. (15) and (16) 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 obtained using the average activation energy from Kissinger 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 BA-a and BA-35x

Table 4
The kinetic parameters evaluated for the curing of the BA-35x system (reaction (2))

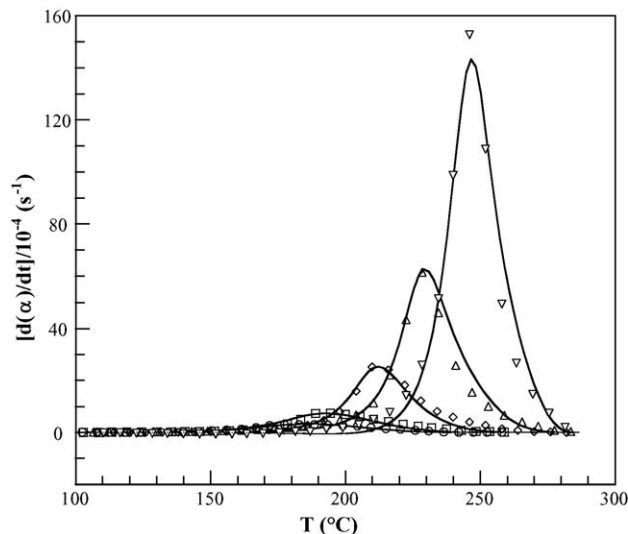| Heating rate (°C/min)	E (kJ mol^{-1})	$\ln A$ (s^{-1})	Mean	n	Mean
1	111	21.52	21.46	1.8	1.4
2		21.47		1.4	
5		21.39		1.3	
10		21.45		1.0	
20		–		–	

Fig. 12. Experimental (symbols) and calculated (solid lines) DSC peaks corresponding to the curing process of BA-a resin: (○) 1 °C/min, (□) 2 °C/min, (◇) 5 °C/min, (△) 10 °C/min, and (▽) 20 °C/min.

(reactions (1) and (2)) are listed in Tables 2–4, respectively. It can be seen that the variation of A, m, and n with the heating rate for both BA-a and BA-35x systems is in the same range as those reported by Ishida and Rodriquez [2,15]. Consequently, we obtain a mathematical model for autocatalytic kinetics of BA-a system as,

$$\frac{d\alpha}{dt} = (5.96 \times 10^6) \exp\left(\frac{-9743}{T}\right)(1-\alpha)^{1.7}\alpha^{0.8} \qquad (17)$$

Similarly mathematical models for autocatalytic kinetics of BA-35x (reaction (1)) and for nth-order kinetics of BA-35x (reaction (2)) are presented in Eqs. (18) and (19), respectively.

$$\frac{d\alpha}{dt} = (2.04 \times 10^7) \exp\left(\frac{-9743}{T}\right)(1-\alpha)^{1.7}\alpha^{0.8} \qquad (18)$$
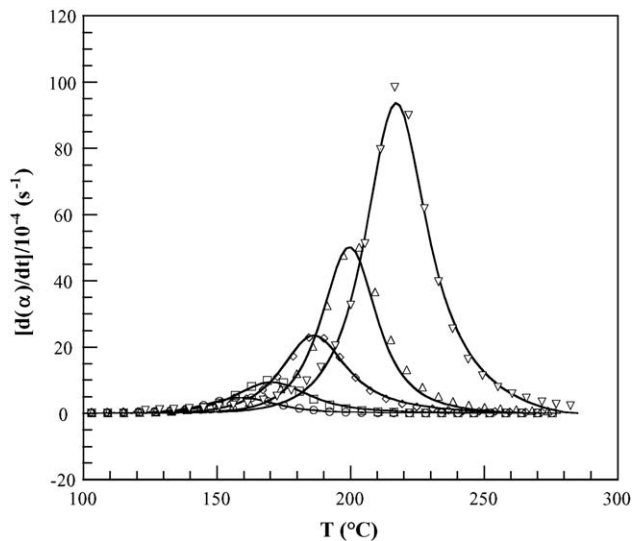

Fig. 13. Experimental (symbols) and calculated (solid lines) DSC peaks corresponding to the first curing process (reaction (1)) of BA-35x resin: (○) 1 °C/min, (□) 2 °C/min, (◇) 5 °C/min, (△) 10 °C/min, and (▽) 20 °C/min.
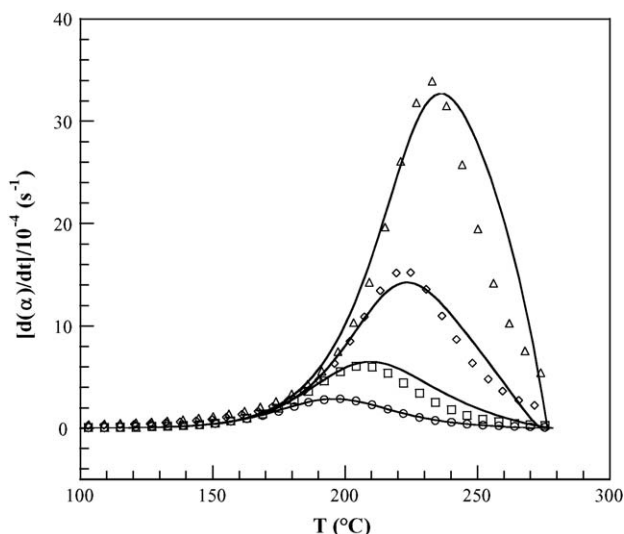
Fig. 14. Experimental (symbols) and calculated (solid lines) DSC peaks corresponding to the second curing process (reaction (2)) of BA-35x resin: (○) 1 °C/min, (□) 2 °C/min, (◇) 5 °C/min, and (△) 10 °C/min.

$$\frac{d\alpha}{dt} = (2.09 \times 10^9) \exp\left(\frac{-13,351}{T}\right) \alpha^{1.4} \qquad (19)$$

The experimental results are compared with those predicted from the models for both systems, as shown in Figs. 12–14. It is clearly seen that the calculated data from the model are in good agreement with the experimental results.

4. Conclusions

The curing reaction of polyfunctional benzoxazine resins based on two types of arylamine, aniline and 3,5-xylidine, was studied. It was found that the curing process of BA-a was a single curing reaction, while the curing reaction of BA-35x was composed of two processes (reactions (1) and (2)), as evidenced by the presence of a double peak on the DSC thermograms.

By using Kissinger, Ozawa, Flynn–Wall–Ozawa, and Friedman methods approach, the obtained activation energy values of both resins are almost invariable. In addition, the activation energy value of BA-a is close to that of BA-35x (reaction (1)). This indicates the same mechanism of the curing reaction of both exothermic peaks. In the case of BA-35x, the activation energy value at the reaction (1) is much smaller than that of the reaction (2). Therefore, reaction (1) is more sensitive to the temperature than reaction (2). The reaction orders of reactions (1) and (2) are also different. This leads to the fact that there are two different mechanisms involved in the curing reactions. The autocatalytic models are proposed to adequately describe the curing kinetics of the BA-a and BA-35x (reaction (1)) systems while the nth-order model is found to present the curing process of the BA-35x (reaction (2)). Evidently, the kinetic models of the curing reactions of the both resins are in good agreement with non-isothermal DSC results.

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