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Kinetic investigation of a complex curing of the guaiacol bio-based benzoxazine system

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Abstract: Curing kinetics of guaiacol based benzoxazine synthesized from guaiacol, furfurylamine and formaldehyde forming bio-based polybenzoxazine was investigated. The curing process showed complex polymerization behavior, as the exothermal signal consisted of several overlapped peaks. Differentiation and fitting of overlapped peaks was performed by Pearson VII distribution obtaining two separate exothermal signals further associated to stage 1 and stage 2. The apparent activation energies of both stages were determined to be 113.8 kJ mol^{-1} and 117.5 kJ mol^{-1}, respectively, according to Kissinger. The first could be explained by benzoxazine ring-opening and electrophilic substitution, whereas the second stage corresponds to the rearrangement and diffusion-controlled step. Kinetics of each stage was studied separately. As a result, the first stage was described by Šesták-Berggren autocatalytic model, whereas the second stage appeared to follow n^{th} order kinetics proved by the Friedman method. Application of both kinetic models demonstrated that the predicted curves fit well with the non-isothermal DSC thermograms and as such sufficiently describes the complex curing behavior of guaiacol based benzoxazine.

Keywords: bio-based polybenzoxazine; deconvolution; guaiacol; kinetic model; thermal polymerization.

1 Introduction

Polybenzoxazines are a relatively new class of thermosetting resins which, besides the adaptability of the benzoxazine monomer molecule, also possess excellent thermal, mechanical, electrical and other properties (1–3). Moreover, the ability of benzoxazine resin to blend with other polymers provides the material with an even broader range of applications (4, 5). Benzoxazine monomers are a class of heterocyclic compounds with typically one or two oxazine rings in their molecules and are synthesized from a formaldehyde, primary amine and phenolic derivative (1, 6). In general, polybenzoxazines are prepared from 1,3-benzoxazines in ring-opening polymerization reaction at elevated temperatures (7). Recently, due to the world-wide energy crisis and environmental concerns, much attention has been given to polymers from renewable resources. This is why it is not surprising that there is an increasing demand for the transition from fossil fuels towards the fully bio-based thermosetting materials (8–10).

There is much research dealing with synthesis and characteristics of fully or partially bio-based synthesis of benzoxazines based particularly on cardanol, guaiacol and eugenol as phenolic precursors. Cardanol is usually obtained from cashew nutshell liquid, guaiacol from biomass pyrolysis and eugenol from certain essential oils especially from clove oil, nutmeg and cinnamon. The polymerization of benzoxazine is normally carried out at temperatures above 180°C, which is unfavorable for the synthesis of fully bio-based polybenzoxazines due to the possible decomposition of bio-based raw materials at high temperatures. For that reason researches deals mainly on the synthesis of novel bio-based benzoxazines, their thermal stability during the curing process and in finding promoters to lower the polymerization temperature. However, although previous research described the bio-based benzoxazine resins characteristics in detail, less attention has been given to the kinetic aspects of the curing (8–14).

The cure kinetics of a thermosetting polymer is easily monitored by differential scanning calorimetry (DSC). The basic assumption when using DSC technique is that the rate kinetics process is proportional to the measured heat flow (Eq. [1]) (15).

$$\alpha = \frac{\Delta H(t)}{\Delta H_{tot}} \qquad [1]$$

where $\Delta H(t)$ is the partial area under the DSC curve up to the time t and ΔH_{tot} is the total heat released during the curing reaction. Furthermore, kinetic analysis of

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non-isothermal curing system is based on the rate equation (Eq. [2]) and can be performed only when curing at multiple heating rates is applied (15, 16).

$$\frac{d\alpha}{dt} \equiv \beta \frac{d\alpha}{dT} = k(T) f(\alpha) \quad [2]$$

where t is time, T is temperature in K, α is the extent of the reaction, $d\alpha/dt$ is the conversion rate in s^{-1}, β is the heating rate in K min^{-1}, and $f(\alpha)$ is the reaction model. Temperature dependence on rate constant is represented through the Arrhenius equation (Eq. [3]) (15):

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad [3]$$

where A is the pre-exponential factor in s^{-1}, E_a is the apparent activation energy in J mol^{-1}, R is the ideal gas constant in J mol^{-1} K^{-1}, and T is the absolute temperature in K. Evaluation of the Arrhenius kinetic parameters can be accurately done by the use of numerous model-free methods, which allow calculations without knowing the form of the reaction model. The basic approach in model-free kinetics is the use of the isoconversional principle which indicates that the reaction rate is only a function of the temperature. The most commonly used model-free methods are the Kissinger (17) and isoconversional Friedman (18) and Flynn-Wall-Ozawa methods (19). The Kissinger method is based on a linear relationship with the logarithm of β/T_p^2 with the inverse of the peak temperature (T_p) (Eq. [4]) whereas isoconversional method assumes that activation energy and pre-exponential factor are functions of the degree of curing.

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{Q_p A R}{E_a}\right) - \frac{E_a}{RT_p} \quad [4]$$

where Q_p is defined as $-[df(\alpha)/d\alpha]_{\alpha=\alpha p}$. Differential isoconversional method proposed by Friedman is based on Eq. [5]:

$$\ln\frac{d\alpha}{dt} = \ln\left[A f(\alpha)\right] - \frac{E_a}{RT} \quad [5]$$

The isoconversional integral method was also proposed independently by Flynn, Wall and Ozawa using Doyle's approximation of the temperature integral. It has to be noted that Doyle's approximation gives linear relationship of temperature integral and is as such less accurate as the non-linear approximation by Vyazovkin (16). The Flynn-Wall-Ozawa method is based on equations as follows:

$$\ln\beta = \ln\left(\frac{AE_\alpha}{R}\right) - \ln g(\alpha) - 5.331 - 1.052\left(\frac{E_\alpha}{RT}\right) \quad [6]$$

where

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad [7]$$

is the integral form of the reaction model (16).

In order to understand the nature of the curing process of guaiacol based benzoxazine its curing kinetic is investigated in this research. Curing processes of previously investigated benzoxazine samples in general consisted of a simple exothermic signal following autocatalytic reaction typical for benzoxazine curing process (6, 20–24), whereas in our case the curing process showed complex polymerization behavior, as the exothermal signal consisted of several overlapped peaks. We presumed that the above mentioned was the result of the benzoxazine structure with an attached furan side group, which caused such a polymerization behavior. There were also some benzoxazine research dealing with two overlapped peaks kinetics (25, 26), however, to our knowledge, none of them were describing furan-benzoxazine kinetics supported with mechanism explanation. Nevertheless, each overlapped peak was differentiated by peaks fitting and deconvolution using Pearson VII distribution. The latter suggested that the polymerization of benzoxazine has at least two polymerization stages: the polymerization at lower temperatures attributed to stage 1 and the polymerization at higher temperatures attributed to stage 2. The cure kinetics of the studied system was investigated by non-isothermal DSC at different heating rates.

2 Experimental

2.1 Materials

Furfurylamine, guaiacol and formaldehyde were obtained from Sigma Aldrich (Chemie GmbH, Steinheim, Germany) and used as received. Bio-based benzoxazine 3-furfuryl-8-methoxy-3,4-dihidro-2*H*-1,3-benzoxazine (guaiacol based benzoxazine) was synthesized as previously reported (11). Formed product was confirmed by ^{1}H NMR analysis ($CDCl_3$, Bruker Avance III 500 MHz NMR spectrometer, Billerica, USA).

2.2 Curing investigation by DSC

The thermal properties and curing of guaiacol based benzoxazine was measured by DSC. DSC measurements

were performed on a Mettler Toledo DSC 1 instrument with intra-cooler (Schwerzenbach, Switzerland) using STAR software. Nitrogen atmosphere and standard 40 µl alumina pans were used. Sample mass was about 10 mg. The alumina pan containing the sample was inserted on the DSC sensor at 20°C and heated to 350°C using heating rates of 5, 10, 15 and 20 K min^{-1} in order to investigate the curing kinetics and perform kinetic modeling under non-isothermal conditions.

3 Results and discussion

3.1 Curing reaction

Thermal properties and curing of guaiacol based benzoxazine were assessed by DSC analysis. Non-isothermal DSC scans were performed at four different heating rates (5, 10, 15, 20 K min^{-1}). The normalized responses are shown in Figure 1, indicating that an exothermal signal consisted of several overlapped peaks representing the complex mechanism of a curing process. The overlapping was evident even when high heating rates were applied. Nevertheless, the average exothermic heat of the reaction of guaiacol based benzoxazine was 210 J g^{-1}.

According to the literature the curing of guaiacol based benzoxazine has at least two curing stages (stage 1 and stage 2). The polymerization at lower temperatures could be associated with the autocatalytic nature of benzoxazine resin, when phenol groups are generated while the benzoxazine ring starts to open, and to electrophilic substitution attack which followed (stage 1). The intermediate product of ring opening transformation is zwitterionic species consisted of phenoxy and imine groups, which propagates polybenzoxazine chain growth. In theory, there are two possible attacks on imine species: one being the O-attack of oxygen incorporated in the benzoxazine ring attack (this transformation also facilitates another ring opening of benzoxazine) and other attack being the electrophilic aromatic substitution, which can happen at the aryl or furan ring. Among these aryl rings *ortho*- and *para*-positions are favored. However, since in our case the *ortho*-position is already occupied by a methoxy group, the aryl-attack predominantly occurs on the *para*- position. In the furan ring-attack, the furan ring electronic density is equally distributed between the remaining three carbon atoms still containing a hydrogen atom, meaning that the major regioselective factor in electrophilic aromatic substitution is sterical hindrance. In conclusion, the electrophilic reactions may comprise of furan ring-attack, O-attack, and aryl attack resulting in furfuryl-type polybenzoxazine, phenoxy-type polybenzoxazine and phenolic type of polybenzoxazine (Scheme 1) (9, 27, 28). At higher temperatures phenoxy structure is transformed into a phenolic structure by rearrangement (stage 2) (29). Among this, stage 2 could also be the consequence of the diffusion-controlled step in the curing reaction (30). The shape of the first peak appeared as symmetrical, whereas the second peak was less exothermic and broader (Figure 1) indicating that rearrangement takes place over the wide temperature interval.

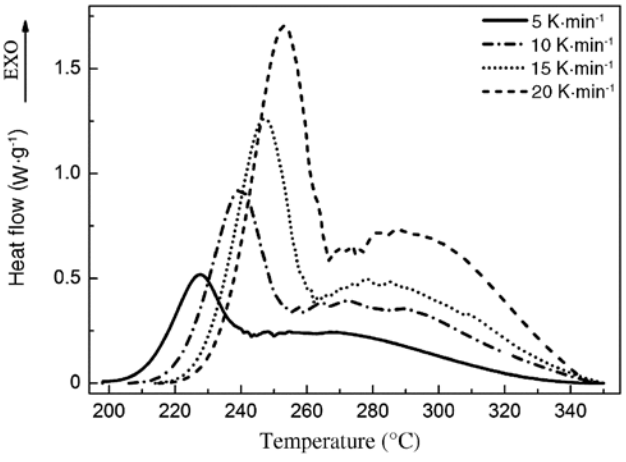
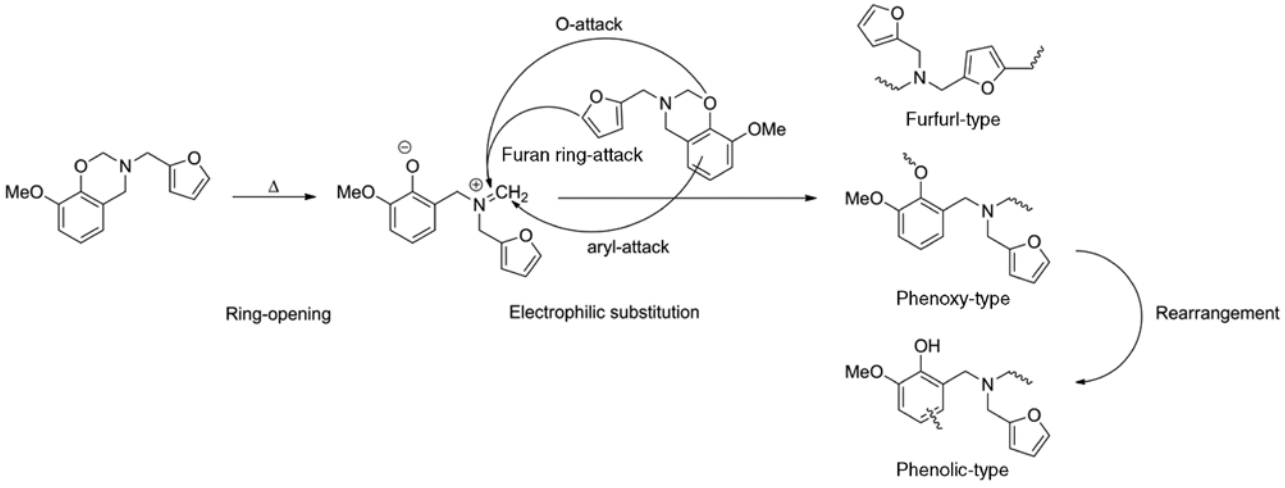


Figure 1: Normalized DSC thermograms of guaiacol based benzoxazine at different heating rates.

As non-isothermal DSC thermograms consisted of overlapped peaks, polymerization at a constant temperature 150°C was performed varying the curing time, namely 0, 15, 30, 60, 120 and 180 min. After the isothermal curing process at different curing times was performed, non-isothermal DSC experiment of a cured sample at a heating rate of 10 K min^{-1} was done. As expected, by increasing the curing time the exothermic peak at lower temperature decreased and at 120 and 180 min even completely disappeared until only a broad exothermic signal remained. The remaining signal in particular belongs to the rearrangement reaction of phenoxy to phenolic structure and the diffusion-controlled step, as the temperature at isothermal polymerization is not high enough for the proceeding of the mentioned reactions in defined experimental time in isothermal conditions.

3.2 Kinetic model

To study the curing kinetics of each stage separately, exothermic signals of DSC scans were deconvoluted and fitted by the OriginPro program using the Pearson



Scheme 1: Polymerization mechanism of guaiacol based benzoxazine.

VII distribution, which gave the best DSC peaks fitting and deconvolution results. In doing so, two overlapping exothermic peaks were separated. Narrower peak signal (stage 1) at lower temperature and broader peak at higher temperature (stage 2) could be observed. As a result, each exothermic peak could be studied individually and its distinct kinetics characteristic could be examined.

After completing the deconvolution and fitting process of exothermic signals for all heating rates we started with an individual kinetic investigation of each peak under non-isothermal conditions. The first apparent activation energy was calculated using the Kissinger method to determine the average activation energy and the isoconversional Flynn-Wall-Ozawa method for the assessment of the apparent activation energy over the entire conversion range. When using the Kissinger method the average activation energy for stage 1 was 113.8 kJ mol^{-1} and for stage 2 117.5 kJ mol^{-1}, whereas the results of the Flynn-Wall-Ozawa calculations over the entire conversion range are presented in Figure 2. Although the results of the Kissinger method showed similar average activation energy, the Flynn-Wall-Ozawa method showed constant value of the activation energy for the first stage, whereas the values for the second stage increased with the degree of conversion. The behavior of the increasing E_a in the case of the second stage could be explained by diffusion-controlled reaction kinetics due to the decrease in molecular mobility. However, the activation energy in the range of degree of conversion of 0.2–0.7, where the reaction rates are the highest, is similar to the one determined by the Kissinger method. For that reason apparent average activation energy provided by Kissinger was used in further studies. Among that, activation energy of the first stage, related to benzoxazine ring-opening is in the range of other kinetic studies of benzoxazine curing processes (6, 20, 31).

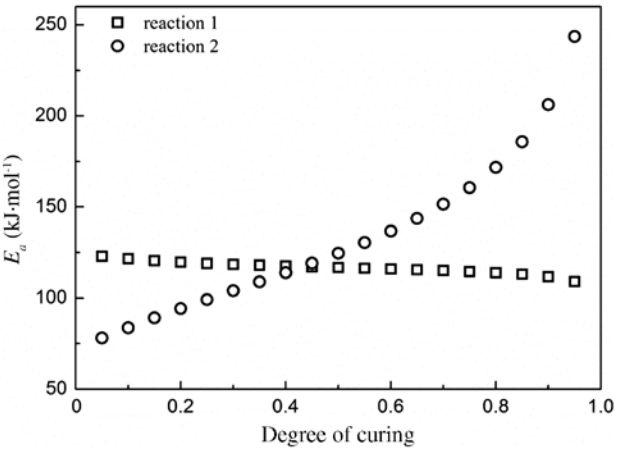


Figure 2: Values of the apparent activation energy determined by the Flynn-Wall-Ozawa method.

Ring-opening polymerization of benzoxazine tends to possess autocatalytic reaction kinetics, which is often described by the Šesták-Berggren autocatalytic model (Eq. [8]) (32).

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^{n}\alpha^{m} \quad [8]$$

In order to approve the autocatalytic nature of stage 1 the verification was made by using the Friedman method (Eq. [9]). Eq. [9] is derived from Eq. [5] for the simplest n^{th} order reaction.

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

Consequently, in the n^{th} order the kinetics relationship should yield a straight line of which the slope represents

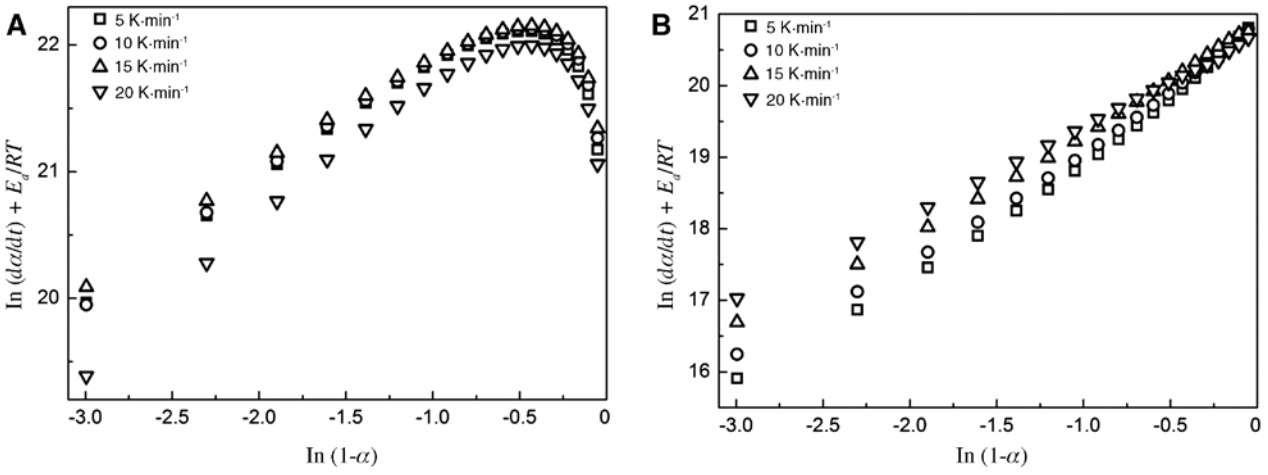


Figure 3: Results of the Friedman method applied over the experimental data of deconvoluted peaks for stage 1 (A) and stage 2 (B).

the value of the order, when in the case of autocatalytic process the Friedman plot would show a maximum of ln(1-α) approximately around -0.51 to -0.22, which is similar to α of about 0.2–0.4 (18). When performing the Friedman method over the deconvoluted exothermic signal of stage 1, the obtained results showed the maximum at around 0.44, which fell in the mentioned region and proved the autocatalytic nature for the first stage (Figure 3A). Similarly, the same method was also performed over the experimental data for the second deconvoluted peaks at different heating rates. Contrary to the stage 1, the result of the applied procedure indicated a straight line over the whole range of the degree of curing proving the n^{th} order kinetics of a stage 2 (Figure 3B).

Whereas the order of the reaction and pre-exponential factor for stage 2 could now be determined from the y-axis and from the slope of the line, for autocatalytic kinetics due to the non-linearity often a different approach is used. For obtaining kinetic parameters used in the Šesták-Berggren autocatalytic model frequently Malék statistic method is applied, although the kinetic parameters could be obtained by nonlinear regression analysis using least squares approximation from the Eq. [10], linearized form of Eq. [8] by taking the logarithm on both sides.

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)=\ln A-\left(\frac{E_a}{RT}\right)+m\ln(\alpha)+n\ln(1-\alpha) \qquad [10]$$

However, we used the Malék statistic method to get initial values for further non-linear regression analysis in order to obtain the best fitting results between experimental and calculated data. The Malék statistical analysis is straightforward by solving two special functions $y(\alpha)$ (Eq. [11]) and $z(\alpha)$ (Eq. [12]).

$$y(\alpha)=\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\exp(x) \qquad [11]$$

$$z(\alpha)=\pi(x)\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\frac{T}{\beta} \qquad [12]$$

where x is the reduced activation energy, and $\pi(x)$ is the expression related to the temperature integral, which can be well approximated using the equation of Senum and Yang, Eq. [13].

$$\pi(x)=\frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120} \qquad [13]$$

The variation of $y(\alpha)$ and $z(\alpha)$ values with conversion exhibit maxima at α_M and α_p^{∞}, respectively, while α_p is taken as the maximum of the DSC signal. However, the obtained values are not only useful in further calculation of kinetic parameters but also for determination of reliability of the Šesták-Berggren autocatalytic model following prescribed conditions: $0<\alpha_M<\alpha_p$ and $\alpha_p^{\infty}\leq 0.632$. The determined values for the studied stage 1 are as follows: α_p=0.4996, α_p=0.3642 and α_p^{∞}=0.5111, which proved the aforementioned criteria. Furthermore, the kinetic parameters could be obtained with regard to the ratio $p=m/n=\alpha_M/(1-\alpha_M)$ and transformation of Eq. [10] into Eq. [14]:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)=\ln A-\left(\frac{E_a}{RT}\right)+n\ln\left[\alpha^p(1-\alpha)\right] \qquad [14]$$

From the linear relationship of the $\ln(\mathrm{d}\alpha/\mathrm{d}t\cdot\exp[E_a/(RT)])$ vs. $\ln[\alpha^p(1-\alpha)]$ the average kinetic parameters A, n and m could easily be evaluated for different heating rates, where n is determined from the slope, A as a value on y-axis and m from the ratio $p=m/n$, once the value of n is known: $A=1.40\times10^{10}$ s^{-1}, n=1.2185 and m=0.6979 with

overall order of reaction $n+m=1.9164$. The found kinetic parameters with previously obtained E_a were then used in the proposed Šesták-Berggren autocatalytic model and compared to the experimental data. As expected, using the obtained kinetic parameters in a Šesták-Berggren autocatalytic model showed a slight deviation of the calculated data from experimental due to the variation of the data during the Malék statistical analysis. For that reason, we applied least squares approximation using Eq. [8] for experiments at all heating rates simultaneously, where we used previously found kinetic parameters for an initial iteration guess at fixed E_a value. Eventually, with new values, similar to the statistically derived, the explicit reaction rate equation for stage 1 at non-isothermal conditions can be written by Eq. [15]:

$$\frac{d\alpha_1}{dt}=1.32\times10^{10}\exp\left(-\frac{113810}{RT}\right)(1-\alpha)^{1.2176}\alpha^{0.6776} \quad [15]$$

Finally, the model calculated data are now in good agreement with the deconvoluted data for stage 1 as shown in Figure 4 ($R^2=0.9933$). In such a manner the ring-opening of a guaiacol based benzoxazine accompanying the electrophilic substitution involving furan ring-attack, O-attack and aryl-attack was adequately described by the Šesták-Berggren autocatalytic model.

After completing the kinetic investigation of stage 1 we continued to examine the characteristics of stage 2. From the procedure by Friedman kinetic analysis we have already identified that the stage 2 followed n^{th} order reaction mechanism (Eq. [16]).

$$\frac{d\alpha}{dt}=A\exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \quad [16]$$

Accordingly, the pre-exponential factor A and n were determined directly from the Friedman plot having the average value of $A=9.84\times10^8$ s^{-1} and $n=1.4717$. Once again, analytically determined kinetic values were used as the initial guess in least squares approximation by using Eq. [16] providing the final equation for stage 2 (Eq. [17]) with which relatively satisfactory agreement ($R^2=0.9733$) of the model with experimental data was achieved (Figure 5).

$$\frac{d\alpha_2}{dt}=9.54\times10^8\exp\left(-\frac{117500}{RT}\right)(1-\alpha)^{1.4060} \quad [17]$$

In conclusion, experimental curves and predicted curves of separated stage 1 and stage 2 emerged showing the overall curing process. From Figure 6 it can be observed

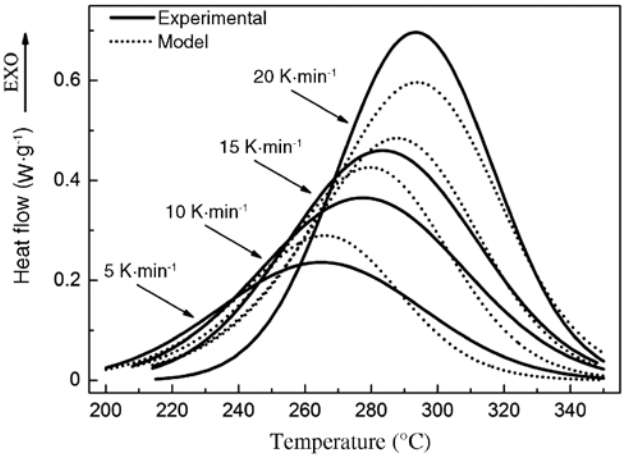


Figure 5: Comparison of the experimental and calculated data corresponding to the curing process of guaiacol based benzoxazine of stage 2 at different heating rates.

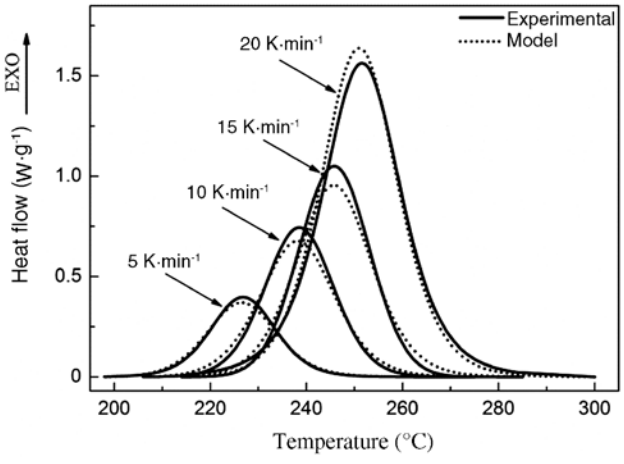


Figure 4: Comparison of the experimental and calculated data corresponding to the curing process of guaiacol based benzoxazine of stage 1 at different heating rates.

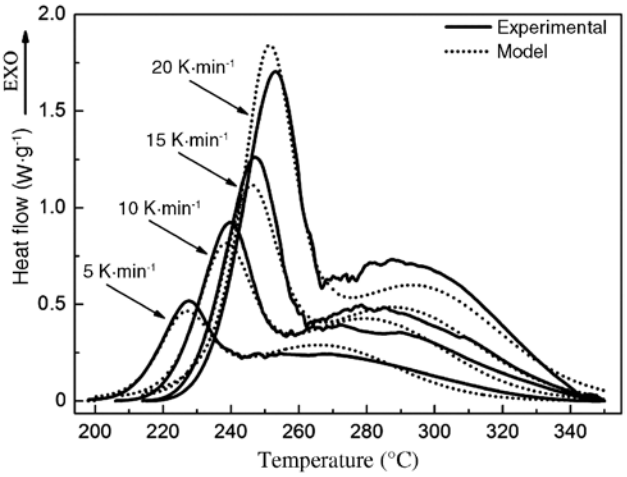


Figure 6: Comparison of the experimental and calculated data corresponding to the total curing process of guaiacol based benzoxazine at different heating rates.

that DSC curves fit relatively well with the experimental data using the obtained models. Figure 6 shows the summarized version of modeling results for both stages compared to the experimental data.

With the use of the deconvolution, we showed that total curing reaction consisted of two overlapped peaks, from which the first at lower temperature is associated to ring-opening and electrophilic substitution and could successfully be described by the Šesták-Berggren autocatalytic model. On the contrary, with the kinetic analysis we approved that rearrangement of phenoxy to phenolic structure and diffusion controlled step (stage 2) followed the n^{th} order of the reaction.

4 Conclusion

The curing reaction of guaiacol based benzoxazine was studied. The exothermic signals of non-isothermal DSC curing showed two dominant stages of the curing process, namely stage 1 and stage 2 due to the presence of double peaks on the DSC thermograms. Overlapped exothermic signals were deconvoluted and fitted by Pearson VII distribution integrated in the OriginPro program. Accordingly, stage 1 was attributed to the benzoxazine ring-opening and electrophilic substitution involving furan ring-attack, O-attack and aryl attack, whereas stage 2 was associated with the rearrangement of phenoxy structure towards the phenolic structure and to the diffusion-controlled step. The first stage was proved to be autocatalytic by the Friedman method and by accompanying the Malék statistical method the Šesták-Berggren autocatalytic model was used in the mathematical modeling of exothermic signals and kinetic parameters were appropriately derived. However, the second stage was proved to follow n^{th} order kinetics and kinetics parameters were derived thereafter. Evidently, the proposed kinetic model of the curing of guaiacol based benzoxazine was in a satisfying agreement with non-isothermal DSC results.

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