



REVIEW

**Formation study of Bisphenol A resole by HPLC, GPC and curing kinetics by DSC**



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**Abstract** The formation study of Bisphenol A (BPA) resole resins catalyzed by sodium hydroxide has been studied by HPLC, GPC. Resoles have been synthesized under controlled conditions: 90 °C, F/BPA = 1.5 (R1), 2.0 (R2), and 2.5 (R3). The resole with the high molar ratio has shown lower BPA content remained in the final product. The changes in molecular weights of Bisphenol A (BPA)–formaldehyde reaction have been identified by GPC as a result of measurements, an increase in molecular weight has been observed with an increase of reaction time and molar ratio. Curing reaction kinetics of resins as a function of molar ratio have been studied by differential scanning calorimetric DSC technique. The activation energies increased with an increase in molar ratio and molecular weights.

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## 1. Introduction

Thermosetting resins, such as phenolics and epoxies are generally used as adhesive and coating materials either alone or as a mixture with other polymers (Petrie, 2000). In order to utilize Bisphenol A (BPA) resins more efficiently in adhesives/coating systems and to develop new phenolic adhesives, it is important to realize the reaction of BPA with formaldehyde (Pilato, 2010; Gardziella et al., 2000). Resoles oligomers are prepared using an excess of formaldehyde over phenolic derivatives under basic conditions. In order to study the structures and kinetics of resoles, several analytical techniques have been utilized including: high performance liquid chromatography (HPLC), gel permeation chromatography (GPC), carbon and proton nuclear magnetic resonance spectroscopy ( $C^{13}$ -NMR and  $H^1$ -NMR), differential scanning calorimetric (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) (Gardziella et al., 2000).

It was realized that high pressure liquid size exclusion (SEC) or GPC are the best techniques to evaluate molecular weight distribution of the phenolic resins. The molecular weight distribution (MWD) has a major role to characterize the performance capabilities of the phenolic resins such as cure speed, viscosity, green strength development, substrates penetration and adhesion (Dillard et al., 2000). Therefore, the growth of molecular weight with the time of reaction for BPA–formaldehyde resole syntheses has been monitored by using GPC with monodisperse polystyrene as calibration standards (Gardziella et al., 2000). The higher molecular oligomers go around the smaller pores in packing column and elute faster. As a result, they come out at lower retention time (volumes). On the other hand, the smaller molecular oligomers stay in the pores and elute slower; hence, they have a longer retention time (Gibson et al., 2002).

In addition, in order to analyze the cure process of these thermosetting resoles, differential scanning calorimeter (DSC) has been used. This procedure has measured the reaction activation energy and the rate constants as a function of temperature (Alonso et al., 2004; Ghaemy et al., 2010; Lei et al., 2006).

The aim of this paper is to explain the synthesis of BPA–formaldehyde resole resins, the molecular weight achievable and their curing kinetic parameters. In addition, the use of these resoles in adhesives or coating formulations and their mechanical tests will be published in the future papers.

## 2. Experimental

### 2.1. Materials

Formaldehyde (37% solution in water) was obtained from Surechem products Ltd., On the other hand, Bisphenol A (BPA) (99.9%), sodium hydroxide (99.9%), phosphoric acid (85%), hydroxylamine hydrochloride, hydrochloric acid, acetonitrile, and unstabilized tetrahydrofuran (THF) were obtained from Merck. Deionized water was prepared by our lab apparatus.

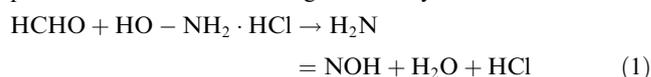
### 2.2. Synthesis of BPA formaldehyde resoles using sodium hydroxide as a catalyst

Resole-type BPA resins were prepared at varying formaldehyde–BPA molar ratios (F/BPA: 1.5, 2.0, and 2.5, R1, R2, and R3 respectively) in the presence of NaOH (0.017 mol per 1 mol of BPA), where the pH was kept at 8.2.

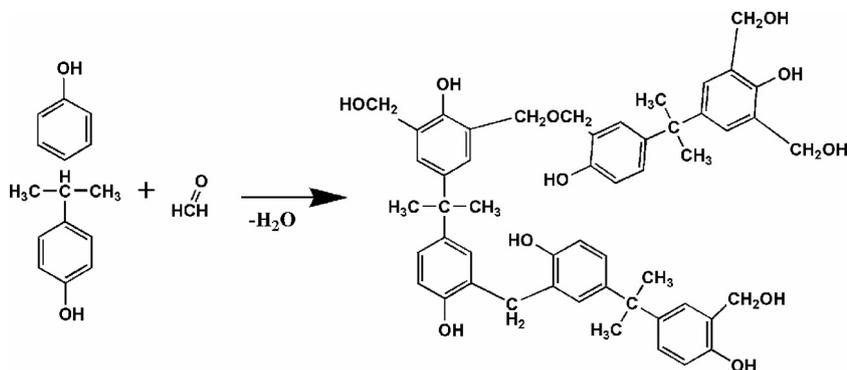
BPA formaldehyde solution and catalyst were placed in the glass reactor with magnetic stirrer, thermometer and reflux condenser. The mixture was stirred and heated to 90 °C (heating rate: 2.5–3.5 °C/min). Samples were taken during synthesis every 10 min. Zero time was defined when the condensation temperature reached (90 °C). The reaction stopped after two hours, cooled to 70 °C and then neutralized with a solution of phosphoric acid 41% until pH reached 6.0. The contents of the reactor were then subjected to a vacuum to strip the water from the reaction mixture at 75–80 °C until a total extraction of water. The scheme of the reaction of BPA with formaldehyde is proposed in Fig. 1 as follow:

### 2.3. Determination of formaldehyde by hydroxylamine hydrochloride method (DIN EN ISO 9397)

The free formaldehyde was determined by an oximation reaction with hydroxylamine hydrochloride. The formed hydrochloride acid from this reaction has been determined by potentiometric titration using sodium hydroxide solution.



Samples (0.2–0.5 g) were taken from the reaction mixture and poured into a beaker. Then, they were dissolved by 50 ml of a mixture (three volumes of propan-2-ol, and one volume of water) using a magnetic stirrer. The solution was adjusted to



**Figure 1** The reaction of Bisphenol A with formaldehyde.

pH 3.5 with 0.1 M HCl (for neutralized resins). Twenty-five milliliters of hydroxylamine hydrochloride solution (10% w/w in water) was stirred for 10 min. The sample was then back-titrated to pH 3.5 with 0.1 M NaOH (DIN EN ISO 9397, 1997).

#### 2.4. High performance liquid chromatography

High performance liquid chromatography was used to quantitatively determine the free BPA during the addition and condensation reactions that remained in the mixture reaction. An analysis was conducted with Merck-Hitachi L-7100 chromatography equipped with an U.V. detector set at 280 nm. The analytical column was an EMR ODS (250 mm × 4.6 mm, 5 μm). The mobile phase A was acetonitrile and mobile phase B was water. The system was run in linear gradient. From zero to 20 min, phase A would change from 25% to 50%. While from 20 to 25 min phase A would change from 50% to 100%. The change would be held for 5.0 min, then after 30 min, it would decrease from 100% to 25% for 10 min. The change would be held again for another 5 min to stop completely at 45 min. The chromatographic analysis was performed at 25 °C with flow rate of 1.0 ml/min and injection volume of 20 μl (Quanwei et al., 2006).

The chromatograms are shown in Figs. 2 and 3.

#### 2.5. Molecular weight and molecular distribution determined via GPC

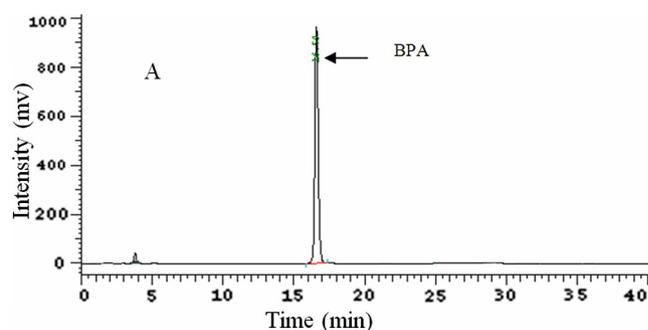
The GPC instrument was purchased from Shimadzu, Japan. It consists of LC-20AD pump and equipped with RID-10A refractive index detector. The conditions for the measurement of molecular weight of resin are given below.

**Standards:** Polymer Lab narrow polystyrenes standards (162D, 615D, 1270D, 3360D). Mobile phase: THF, flow rate: 1.0 ml/min. temperature: 25 ± 2 °C. Columns: polymer Lab PL gel 5 μm Mixed-C, PL gel 3 μm 100 in series. Internal Standard: sulfur, the injection volume: 200 μl.

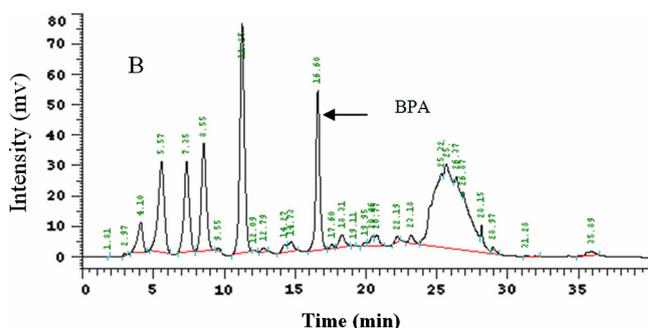
The molecular weight distribution and with it number – and weight average molecular weights can be calculated as follows (Chi-san, 1995):

Number – average molecular weight:

$$M_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum_{i=1}^N A_i}{\sum_{i=1}^N \frac{A_i}{M_i}} = \frac{\sum h_i}{\sum \frac{h_i}{M_i}} \quad (2)$$



**Figure 2** Chromatogram of standard Bisphenol A.



**Figure 3** Chromatogram of sample from the mixture of reaction for R3 at 120 min (B).

Weight – average molecular weight:

$$M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\sum_{i=1}^N A_i M_i}{\sum_{i=1}^N A_i} = \frac{\sum_{i=1}^N h_i M_i}{\sum_{i=1}^N h_i} \quad (3)$$

Polydispersity

$$D_p = \frac{M_w}{M_n} \quad (4)$$

where

- $n_i$ : The number of molecules of molecular weight  $M_i$ ,
- $M_i$ : Molecular weight,
- $A_i$ : Slice area at each interval of molecular weight  $M_i$ ,
- $h_i$ : Peak height at each interval of molecular weight  $M_i$ .

The resins were examined according to ASTM D 5296 (ASTM D5296, 2005).

## 2.6. DSC measurements

The calorimetric measurements of resins were performed on LINSEIS DSC PT10 Platinum series calorimetric; using copper pans with 120  $\mu$ l can withstand vapor pressures up to 10 MPa at four different heating rates (7.5, 10.0, 12.5, and 15.0) between 50 and 280  $^{\circ}$ C. The resins were mounted in a vacuum dried oven at 40  $^{\circ}$ C for 48 h in order to remove the moisture,

### 2.6.1. Kinetic methods

Thermal analysis system was used to study the cure reactions of pure BPA/F resins. The total area under the exothermal curve, based on the extrapolated baseline, was used to determine the heat of cure. One of the most commonly used techniques for cure kinetic studies of thermoset materials is DSC (Brown and Gallagher, 2008; Cheng, 2002; Menczel and Prime, 2009).

The equation of the kinetic models for thermoset polymers that clarifies the conversion rate at constant heating rate can be expressed as follows (Lei et al., 2006):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (5)$$

where

$k(T)$  is the rate constant (that depends on the temperature  $T$  according to Arrhenius law) ( $s^{-1}$ ).

$f(\alpha)$ : is a function of  $\alpha$  only. It relates to the reactant concentration and it is assumed to be independent of temperature and dependent on kinetic approach applied.

The rate constant  $k(T)$  can be expressed by an Arrhenius equation as follows:

$$K = Ae^{\frac{E_a}{RT}} \quad (6)$$

where  $A$  is the pre-exponential factor ( $s^{-1}$ ),  $E_a$  is the activation energy ( $J mol^{-1}$ ),  $R$  is the gas constant ( $J mol^{-1}K^{-1}$ ), and  $T$  is the absolute temperature (K).

For dynamic curing practice with constant heating rate, the temperature increases with the rise of cure time. The correlation between  $\frac{d\alpha}{dt}$  and  $\frac{dx}{dt}$  can be expressed as:

$$\frac{d\alpha}{dt} = \left(\frac{dT}{dt}\right) \frac{d\alpha}{dT} \quad (7)$$

where  $\frac{dT}{dt}$  is the heating rate (K/min) and is simplified by  $\beta$ .

The essential assumption to use in DSC for thermoset cure is that the measured heat flow  $\frac{dH}{dt}$  is proportional to the rate of conversion or rate of cure ( $\frac{d\alpha}{dt}$ ), as Eqs. (8) and (9):

$$\alpha = \frac{(\Delta H_T)_t}{\Delta H_0} \quad (8)$$

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_0} \frac{dH}{dt} \quad (9)$$

where  $(\Delta H_T)_t$  is the heat of reaction at a curing time ( $t$ ).

$\Delta H_0$  is the total exothermic heat of the cure reaction.  
 $\frac{dH}{dt}$  is the heat flow (peak height under the exothermal curve at temperature ( $T$ )).

Substituting Eq. (6) into (5) yields:

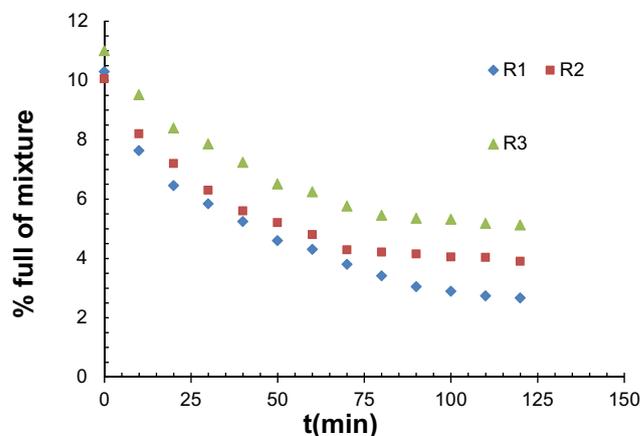


Figure 4 Disappearance of formaldehyde by the titration method.

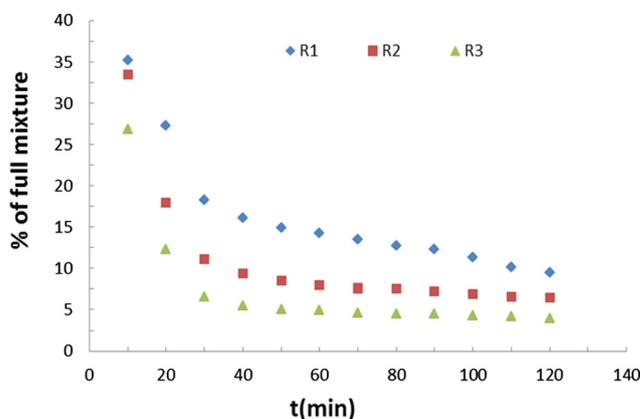


Figure 5 Decrease of Bisphenol A by HPLC.

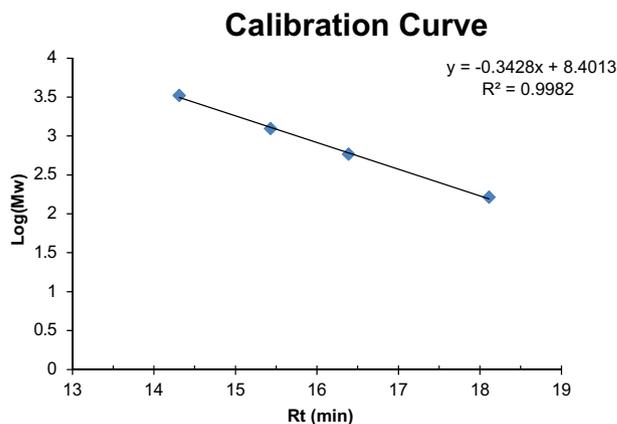


Figure 6 GPC calibration plot.

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}}f(\alpha) \quad (10)$$

One of the non-isothermal methods to characterize the curing kinetic ( $E_a$ ,  $A$ , and  $k$ ) is achieved from multiple heating rate method such as Ozawa's method. It is utilized by plotting  $\log \beta$

**Table 1** GPC calibration table.

	Mw	Mn	Mw/Mn	Mw × Mn	(Mw × Mn) <sup>1/2</sup>	Rt (min)	Log (Mw)
Standard (1)	3360	3240	1.03	108,86,400	3299.45	14.31	3.51
Standard (2)	1270	1200	1.06	15,24,000	1234.50	15.43	3.09
Standard (3)	615	544	1.13	334,560	578.41	16.39	2.76
Standard (4)	162	162	1.00	26,244	162	18.11	2.21

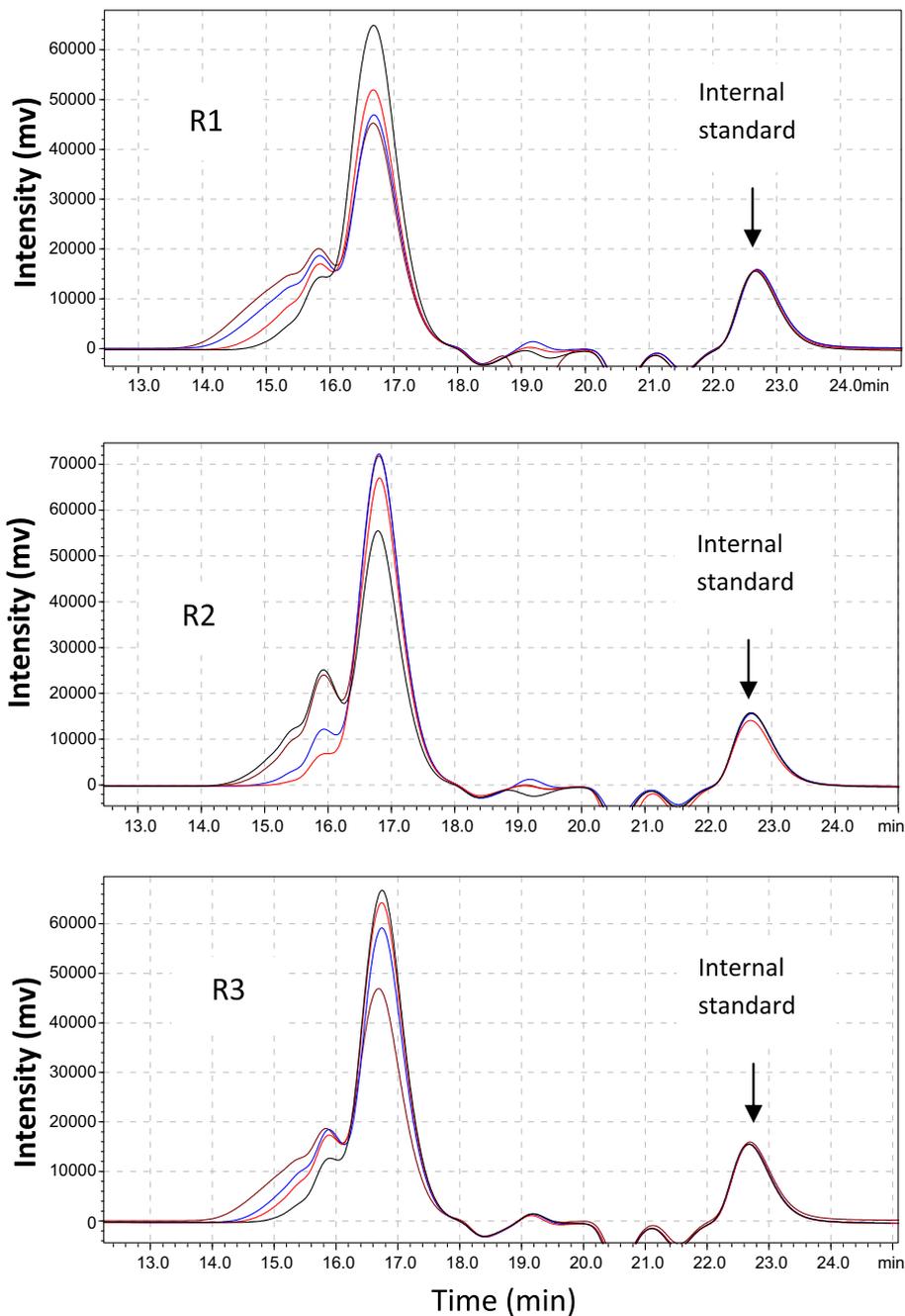


Figure 7 GPC chromatograms of BPA resins R1, R2 and R3 as a function of time (30, 60, 90 and 120 min).

(heating rate, K min<sup>-1</sup>) versus 1/T, where T is the peak maximum in Kelvin (Ozawa, 1970). Consequently, the curing activation energy can be calculated from the slope, as follows:

$$E_a \cong -2.19R \left[ \frac{d \log \beta}{d^1/T} \right] \tag{11}$$

Another method is Kissinger method which is used by plotting  $-\ln\left(\frac{\beta}{T^2}\right)$  (heating rate,  $\text{K min}^{-1}$ ) versus  $1/T$ , where  $T$  peak maximum in Kelvin (Kissinger, 1957). The curing activation energy can be calculated from the slope, as following equation:

$$-\ln\left(\frac{\beta}{T^2}\right) = \frac{E_a}{RT} - \ln\left(\frac{kR}{E_a}\right) \quad (12)$$

The Arrhenius pre-exponential factor ( $A$ ) can be calculated as follows

$$A = \frac{\beta E_{ac}^{E_a}/RT}{RT^2} \quad (13)$$

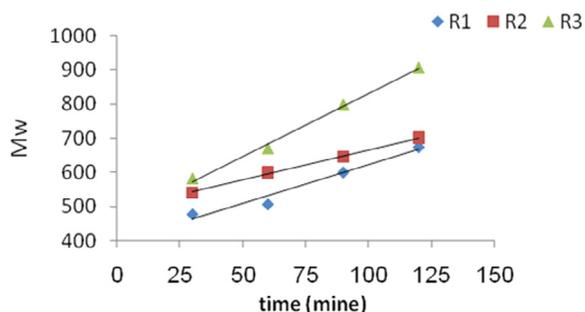
### 3. Results and discussion

#### 3.1. Determination the remaining formaldehyde

Fig. 4 exhibits the disappearance of free formaldehyde versus condensation time. The decrease in the concentration of formaldehyde in resoles R1 is close to that for resole R2 until 60 min of condensation times. Then R2 becomes higher at the end of the reaction. While concentration of formaldehyde in resole R3 is higher throughout the reaction time. It is found that the concentration of free formaldehyde increased with an increase in the ratio of formaldehyde to BPA.

**Table 2** Qualitative molecular weights and polydispersities of BPA resins.

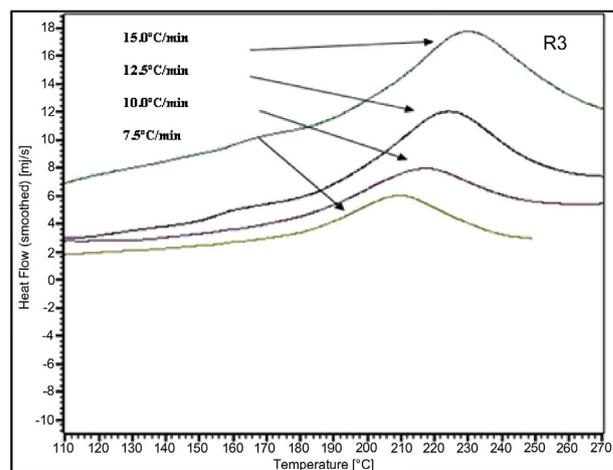
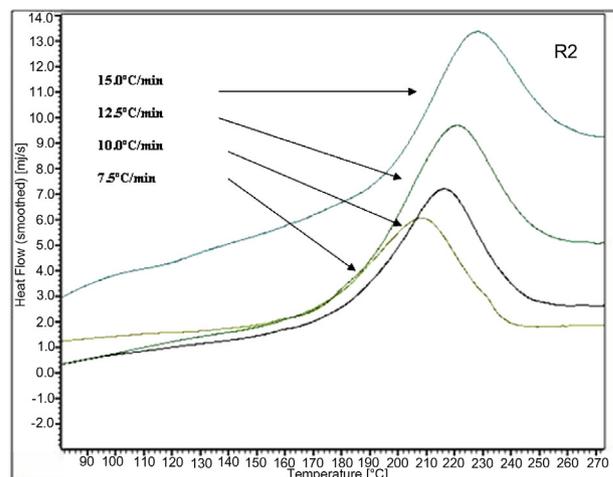
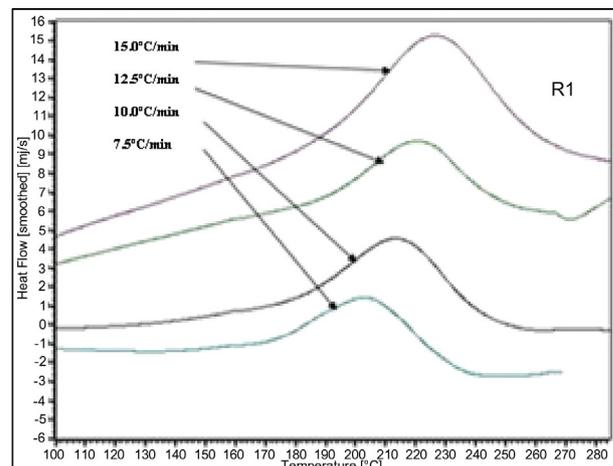
Time (min)	$M_n$	$M_w$	Dp
<i>(R1)F:BPA = 1.5:1.0</i>			
30	434.46	478.52	1.10
60	447.16	507.66	1.14
90	487.77	600.60	1.23
120	524.24	674.27	1.29
<i>(R2)F:BPA = 2.0:1.0</i>			
30	473.57	540.80	1.14
60	498.23	600.37	1.21
90	514.78	646.33	1.26
120	536.74	701.36	1.31
<i>(R3)F:BPA = 2.5:1.0</i>			
30	501.24	581.87	1.16
60	535.41	669.71	1.25
90	573.67	797.82	1.39
120	612.08	905.75	1.48



**Figure 8** The growing of Mw with time.

#### 3.2. Determination of the remaining Bisphenol A

Fig. 5 shows the disappearance of BPA for three prepolymers quantitatively followed by HPLC. It is observed that R3 is the fastest consumption of BPA followed by R1, and R2. This phenomenon means that an increase of the molar ratio F:BPA in the reaction mixture would reach faster to a steady



**Figure 9** Dynamic DSC curves R1, R2, and R3.

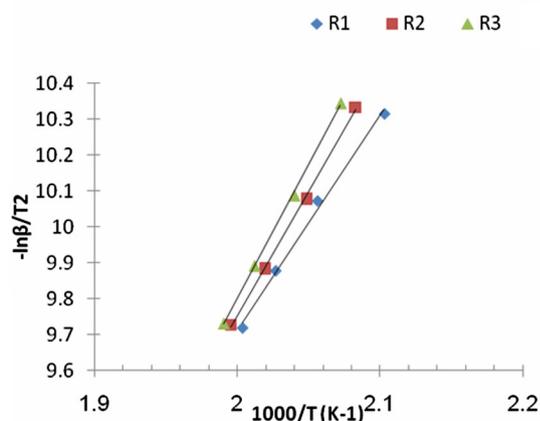


Figure 10 Plotting of  $\ln\left(\frac{\beta}{T^2}\right)$  versus  $1/T$  for resins.

Table 3 DSC data for curing BPA/F at different heating rates.

Resoles	$\beta$ ( $^{\circ}\text{C}/\text{min}$ )	$T_p$ ( $^{\circ}\text{C}$ )	The equation	$E_a$ (kJ/mol)
R1	7.5	202.4	$y = 6.012x - 2.316$	49.99
	10	213.2	$R^2 = 0.994$	
	12.5	220.2		
	15	225.9		
R2	7.5	207	$y = 6.953x - 4.156$	57.81
	10	215	$R^2 = 0.999$	
	12.5	222		
	15	228		
R3	7.5	209.4	$y = 7.424x - 5.046$	61.72
	10	217.1	$R^2 = 0.999$	
	12.5	223.9		
	15	229.3		

value of BPA concentration. In addition, it is observed that a constant amount of BPA remains in the reaction mixture after 60 min for all resoles.

### 3.3. Molecular weight determination via GPC

The calibration graph is shown in Fig. 6. The GPC calibration details are given in Table 1. GPC chromatograms of R1, R2, and R3 are shown in Fig. 7. For all resins, it is found that the peaks are shifted toward lower elution times as the average molecular weights increased.

By plotting average molecular weight versus time ( $t$ ) for all series, a linear increase of Mw as function of time is taken a place as shown in Table 2 and Fig. 8. Furthermore, it is found that the Mw is increased with an increase in the molar ratio.

### 3.4. Thermal analysis calculations

Fig. 9 shows DSC thermographs for BPA/F resoles at four different heating rates. All the curves show one sharp exothermic peak proportional to the heating rate. The exothermic peak shifted toward higher temperature as the heating rate is increased (see Fig. 10).

From Table 3, Arrhenius activation energies for BPA/F cure reaction were determined by using DSC according to ASTM E 698 (ASTM E 698, 2001), plotting  $-\ln\left(\frac{\beta}{T^2}\right)$  versus

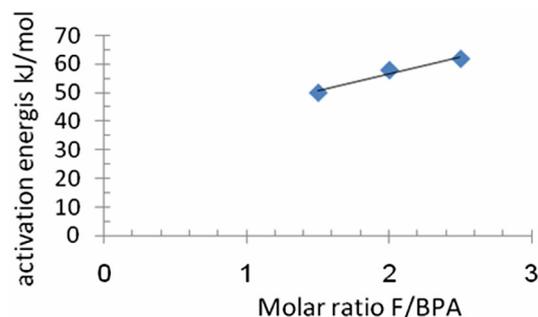


Figure 11 Changes of  $E_a$  versus increase of molar ratio.

$1/T$  as shown in Fig. 9, and using Eq. (11) to calculate  $E_a$ . Fig. 11 shows changes of  $E_a$  versus increase in molar ratio.

## 4. Conclusion

Comparison of resoles (R1, R2, and R3) from HPLC data noted that R3 has the lowest concentration BPA remaining than the other resoles, where the reaction consumes most of the BPA. Gel permeation chromatography GPC is an useful tool to evaluate the BPA resins during the formation of resoles. The growing of molecular weights that result from the addition and condensation reactions has been evaluated. GPC data have also shown the molecular weights of the resins increase when the molar ratio F/BPA increases. Curing reaction was analyzed by DSC at different curing rates. The activation energy values of the cure reaction increased as a function of increasing molar ratio of F/BPA. This phenomenon is explained due to the need for higher energy to present an increase in the crosslink density when molar ratio is increased.

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