Cure kinetics and thermal properties of novel bismaleimide containing phthalide cardo structure

Xuhai Xiong[a], Ping Chen[a,b,∗], Jinxiang Zhang[a], Qi Yu[b], Baichen Wang[b]

[a] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China
[b] Liaoning Key Laboratory of Advanced Polymer Matrix Composites Manufacturing Technology, Shenyang Aerospace University, Shenyang 110136, China

ARTICLE INFO

ABSTRACT

A novel bismaleimide containing phthalide cardo structure (BMIP) was mixed with 2,2′-diallyl bisphenol A (DABPA), and the cure behavior of the mixture was studied by Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The FTIR results demonstrated the cure reaction below 200 °C progressed preferentially via alternating copolymerization of maleimide and allyl groups. The DSC thermogram of the prepolymer showed three different cure regimes in the temperature range of 100–350 °C and the 2nd exothermic peak was predominant. The kinetic parameters of the 2nd curing process were evaluated using various kinetic models: Kissinger and Ozawa–Flynn–Wall, and the apparent activation energies obtained from two methods were consistent with each other. Thermal properties of the cured network were characterized by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Experimental results exhibited that the onset decomposition temperature ($T_{5\%}$) was ~431 °C and char yield at 600 °C was ~39.1%. In addition, the glass-transition temperature (T_g) reached 274 °C based on the tan δ peak temperature.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Bismaleimide (BMI) resins are a promising and relatively young class of thermosetting polymers [1]. They play an increasingly important role in high-tech industries due to the fact that their cured products have good electrical properties, lower coefficient of thermal expansion, excellent fire and moisture resistance, superior thermal and thermal-oxidative stability, and high glass transition temperature and mechanical strength [2–9]. However, the inherent brittleness, limited durability and poor impact resistance of the pure resins, resulting from high crosslink density and rigid molecular skeleton, hamper the further application in the aerospace and electronic industries [10]. Hence, many modification methods have been developed to overcome the above-mentioned drawbacks [11–13]. It was reported that the most successful modification method was the copolymerization of BMIs with allyl-substituted aromatic compounds, which not only could be able to enhance the toughness of BMIs but also endowed the resultant resins with better process flexibility and lower cost [14–16]. Based on the 4,4′-bismaleimidodiphenyl methane (BMPM) and 2,2′-diallyl bisphenol A (DABPA), numerous high performance modified BMI resins were developed, such as QY8911, Matrimid 5292 and BASF 5260 [17].

Despite the 2,2′-diallyl bisphenol A modified BMI resins win great honors for their outstanding properties, there is still not unambiguous information about the mechanism and kinetic feature of their cure reaction. Undoubtedly, aside from dependence on the molecular structure of various ingredients in the system, the properties of polymeric materials such as T_g, modulus and toughness also depend strongly on the extent of cure and the cure pathway which is controlled by the time of cure and the cure temperature [16,18,19]. Therefore, the optimization of polymer properties calls for reliable curing kinetic parameters and a clear picture of the chemical transformations which occur during curing. In fact, many efforts have been made to investigate the curing pathways and kinetics of BMPM/DABPA systems. Mijovic and Andjolic studied the isothermal cure of BMPM/DABPA using remote in situ real time fiber optic near-infrared spectroscopy in the 140–250 °C range [2]. They reported the principal reaction was alternating copolymerization involving maleimide and allyl double bonds, and maleimide homopolymerization occurred only in the initial stages of reaction at temperatures above 200 °C. Phelan and Sung characterized the cure behavior by FT-IR, fluorescence, and UV-reflectance spectroscopy and discussed various reaction pathways [16]. Rozenberg et al. reported the cure kinetics and mechanism of equifunctional BMPM/DABPA revealed by a combination of many analytical techniques [20]. In addition, isothermal and nonisothermal DSC methods were often employed for kinetic analysis of BMPM/DABPA cure [4,5,14,17]. According to these studies, the following reaction types have been proposed to be involved in the curing process: Ene, Diels–Alder, homopolymerization, alter-
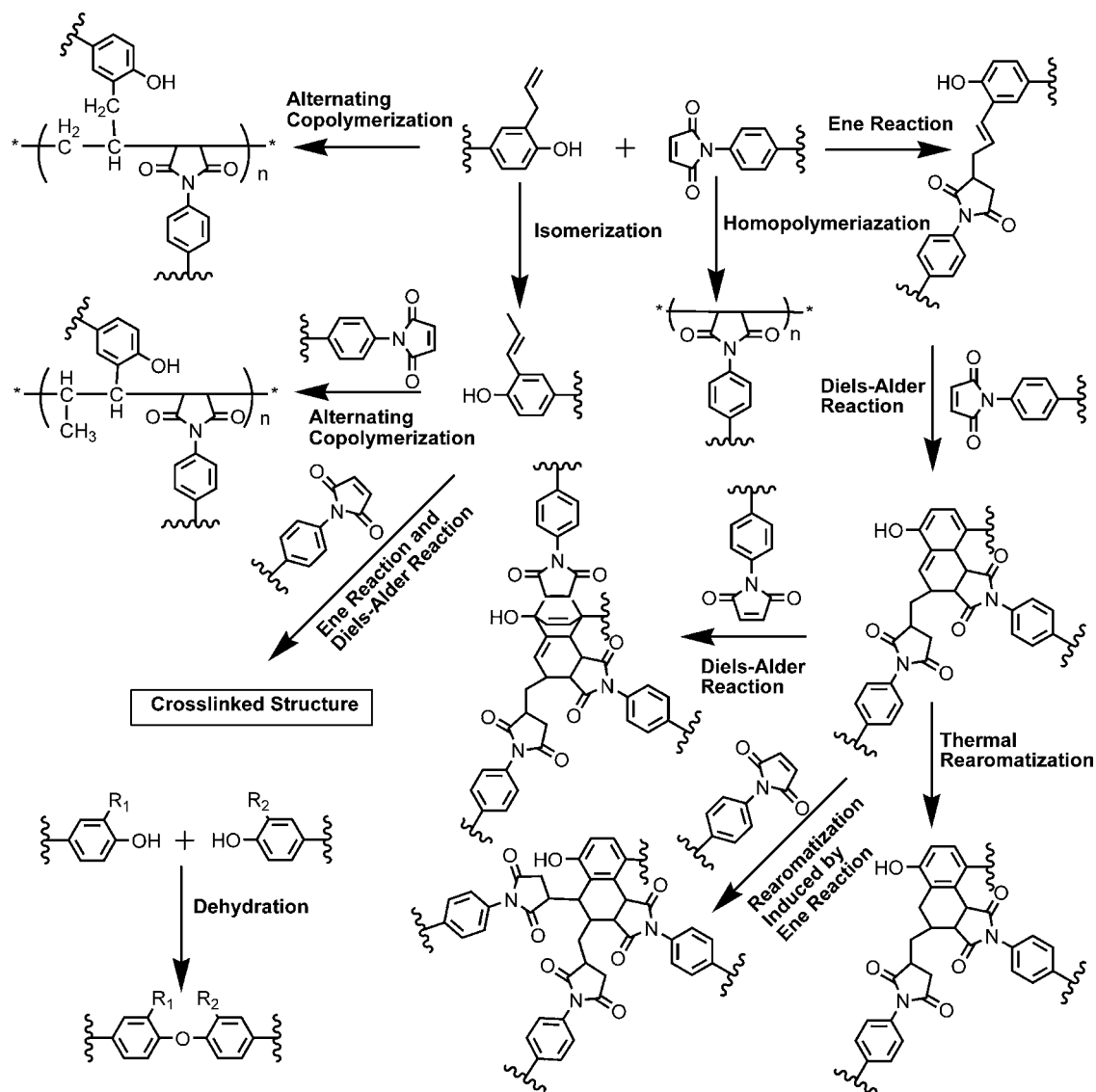
Fig. 1. Proposed curing mechanisms for BMI/DABPA resin.

nating copolymerization and rearomatization. The proposed curing pathways are outlined in Fig. 1.

In the previous research, we designed and synthesized a chain-extended BMI monomer containing phthalide cardo structure (BMIP) [21]. The monomer shows an advantageous combination of properties, such as good solubility, lower melting point and favorable cost. Nevertheless, its high melt viscosity and high cure temperature disfavor preparation of good-quality products. To solve these manufacturing limitations, DABPA was chosen to copolymerize with BMIP. The objective of this study was to provide the information about the mechanism and kinetics of curing for equimolar BMIP/DABPA resin investigated by FTIR and nonisothermal DSC. Furthermore, the thermal properties of the blend resin were characterized by DMA and TGA.

2. Experimental

2.1. Materials

Commercially available 2,2′-diallyl bisphenol A (DABPA) was provided by Laizhou City Laiyu Chemical Co., Ltd. (Shangdong, China). BMIP was synthesized according to the reported method [21].

2.2. Preparation of BMIP–DABPA blend

The structures of BMIP and DABPA are shown in Fig. 2. The prepolymer BMIP/DABPA was prepared by mixing an equimolar amount of crushed BMIP and DABPA at 150 °C under vigorous mechanical stirring for about 10 min, and then a homogeneous,
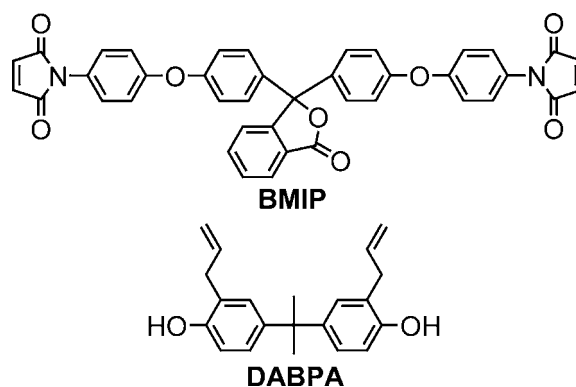

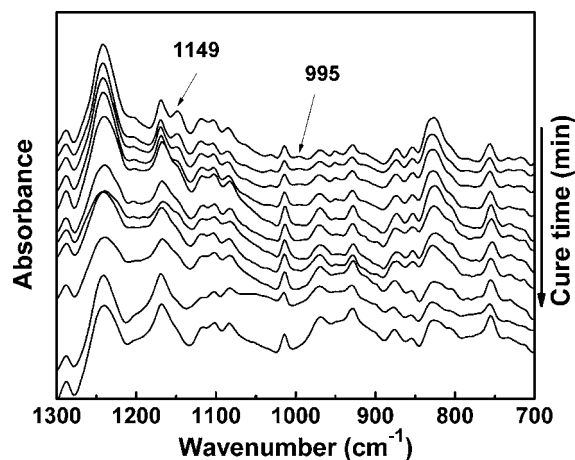Fig. 2. Chemical structures of BMIP and DABPA.

Fig. 3. FTIR spectra of BMIP/DABPA resin at various times during isothermal cure at 180 °C. Cure times were 0, 10, 30, 60, 120, 180, 240, 300, 360, 420, and 480 min.

visually transparent mixture was obtained. The mixture was degassed at 150 °C under vacuum to remove trapped air and then poured directly into preheated (150 °C) Teflon moulds and thermally cured in an air convection oven at 180 °C for 1 h, 200 °C for 2 h plus a post-cure period at 250 °C for 6 h. Finally, the casting was removed from the mould and characterized.

2.3. Characterization

Fourier transform infrared (FTIR) spectra (KBr) were recorded on a Nicolet-20DXB IR spectrophotometer. 32 scans were signal averaged with a resolution of 4 cm^{-1} at room temperature.

Differential scanning calorimetry (DSC) measurements were conducted with an NETZSCH DSC 204 instrument. About 7–9 mg samples were used at a heating rate of 10 °C/min under a flow of nitrogen (20 mL/min).

Dynamic mechanical analysis (DMA) was done on a TA Instruments Q800 DMA with an amplitude of 20 μm, driving frequency of 1.0 Hz, and a temperature ramp rate of 5 °C/min in nitrogen atmosphere. The specimen was cut to dimensions of 40 mm × 6 mm × 2.5 mm for the single cantilever mode.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 thermal analyzer and the sample (around 5 mg) was heated from 25 to 600 °C at a heating rate of 20 °C/min, under the purified nitrogen flow rate of 60 mL/min.

3. Results and discussion

3.1. IR characterization of cure reaction

Fourier transform infrared (FTIR) analysis is a useful tool to study cure mechanism and kinetics by monitoring the intensity change of the characteristic absorption bands. Herein, FTIR spectroscopy was employed to determine the extents of various reactions involved in BMIP/DABPA copolymerization process at lower temperatures (<200 °C). At elevated temperature (>200 °C), it was difficult to follow the kinetic behavior because the cure reaction rate was too fast to obtain well distinguished spectra. Fig. 3 shows the typical IR spectra of BMIP/DABPA during isothermal cure at 180 °C. The spectra taken at various stages of cure were shifted along the ordinate for clarity. It can be seen that the absorption band at 1149 cm^{-1}, attributable to the C–N–C stretching vibration of the maleimide group, decreases with the polymerization time, indicating the conversion of BMIP. Another evidence for the consumption of the BMI unsaturation can be found from the gradual disappearance of the absorbance band centered at 3100 cm^{-1}, which is assigned to the

Table 1
DSC peak maximum temperature of BMIP/DABPA prepolymer at different heating rates.

β (K/min)	T_{p1} (°C)	T_{p2} (°C)	T_{p3} (°C)
5	111.2	240.6	326.2
10	120.2	257.2	342
15	123.5	269.8	351.5
20	128.2	274.5	357.2

=C–H stretching. The allyl unsaturation presents two characteristic modes in the =C–H wagging region. One is found at 995 cm^{-1} and is due to a *trans* –HC=CH– wagging, while the other, at 912 cm^{-1}, arises from a vinyl =CH$_2$ wagging. The latter was often used to evaluate the conversion of allyl groups [6,16,17]. Unfortunately, it suffers from heavy interference in the present system under investigation and hence appears as a shoulder of the absorption peak at 927 cm^{-1}. Therefore, the consumption of DABPA allyl groups has to be measured from the peak at 995 cm^{-1} although it shows a weak intensity.

Quantitative evaluation of the reaction kinetics was conducted by following the change of absorbance peaks at 1149 cm^{-1} and 995 cm^{-1}. The methyl absorption at 2964 cm^{-1} did not change during the cure process and can thus be used as an internal reference band. The extent of cure reaction (α) at any time, t, was calculated using the following equation:

$$\alpha = 1 - \left(\frac{A_r/A_{\mathrm{ref}}}{A_r/A_{\mathrm{ref}}} \right)_0 \tag{1}$$

where $(A_r/A_{\mathrm{ref}})_t$ is the ratio of the areas of reactive (r) and reference (ref) peaks at cure time t corrected for thickness and $(A_r/A_{\mathrm{ref}})_0$ is the ratio of the areas of reactive (r) and reference (ref) peaks at cure time zero corrected for thickness.

The normalized extent of reaction based on the consumption of carbon–carbon double bonds is shown in Fig. 4 as a function of time for isothermal cure at 130, 180 and 200 °C. From Fig. 4a, all isothermal conversion curves first increase sharply and then level off and the rate of reaction increases with increasing curing temperature. The conversion ratio of maleimide to succinimide reaches approximately 90% and do not show increasing trend after BMIP/DABPA underwent about 200 and 100 min of isothermal cure at 180 and 200 °C, respectively, while the consumption of maleimide is nearly 60% after 600 min of isothermal cure at 130 °C. As shown in Fig. 4b, the pattern of the loss of allyl groups is similar to that of maleimide. To further elucidate the relationship between rates of conversion of maleimde and allyl groups, we made a plot (in Fig. 5) of maleimide group conversion (extracted from Fig. 4a) as a function of ally group conversion (extracted from Fig. 4b), with temperature as a parameter. It is apparent from Fig. 5 that the consumption of maleimide and allyl groups shows a fairly strict 1:1 correlation regardless of the temperature. This observation suggests that the cure reaction below 200 °C progressed preferentially via alternating copolymerization of maleimide and allyl groups. By contraries, the homopolymerization of bismaleimide and isomerization reaction of the allyl to the propenyl form are neglectable. An analogous conclusion was made through the study of BMPM/DABPA curing process using near-infrared spectroscopy [2].

3.2. DSC characterization of cure reaction

Fig. 6 shows the dynamic DSC thermograms of BMIP/DABPA prepolymer scanned at different heating rates and the characteristic results are listed in Table 1. At all heating rates, the exotherms show three temperature regimes: (i) in the 100–150 °C range, the exothermic peak, which will disappear if mixing time is prolonged during the prepolymer preparation, is associated with
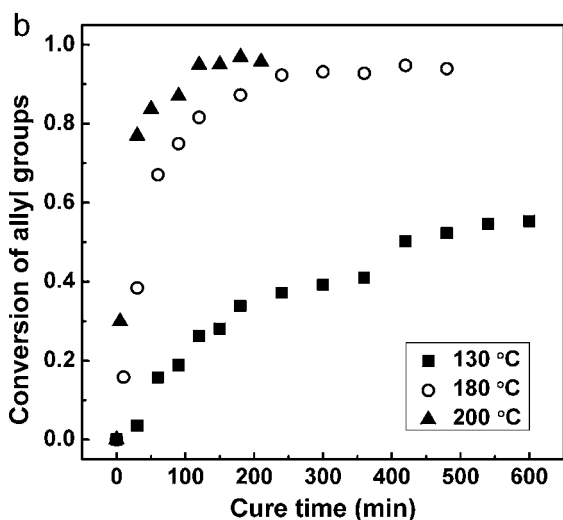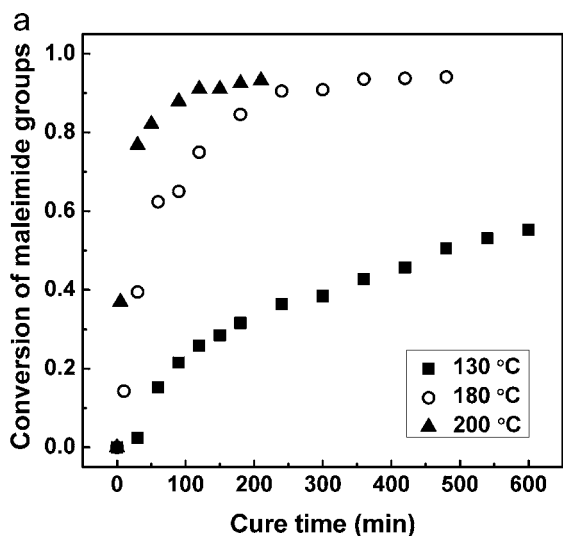
Fig. 6. DSC exotherms for BMIP/DABPA cure at different heating rates.

the Ene reaction; (ii) the principal exothermic peak located at 150–300 °C is assigned to the following reactions (Fig. 1): Ene reaction, copolymerization, Diels–Alder reaction, BMIP homopolymerization, isomerization of the allyl groups as well as dehydration of the hydroxyl groups; (iii) above 300 °C, the residual unreacted groups further react, such as homopolymerization of allyl group [17]. In addition, it is observed that the all exothermic peaks associated with the curing reaction shift to higher temperatures as the heating rate increases.

The kinetic analyses of three stages were done by Kissinger method based on the multiple heating rates. The activation energy (E_a) was estimated using Kissinger equation [14,22,23]:

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + \ln\left(\frac{AR}{E_a}\right) \tag{2}$$

where β is the heating rate(K/min), T_p is the peak maximum temperature (K), R is the gas constant.

The typical kinetic plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ by Kissinger equation were drawn. According to the plots shown in Fig. 7, the values of the activation energy were obtained by the determination of the value of the slope. The E_a values of the three curing processes are 100.2, 83.6 and 128.8 kJ/mol, respectively. The second curing process shows the lowest E_a value, suggesting the reactions more easily progressed in this temperature region. The variation of E_a demonstrates the different reaction mechanisms for the three curing stage and the trend is in good agreement with the fact that the

Fig. 4. (a) The conversion of maleimide group determined by FTIR at 1149 cm⁻¹ as a function of cure time for BMIP/DABPA isothermal cure at different temperatures. (b) The conversion of ally group determined by FTIR at 995 cm⁻¹ as a function of cure time for BMIP/DABPA isothermal cure at different temperatures.
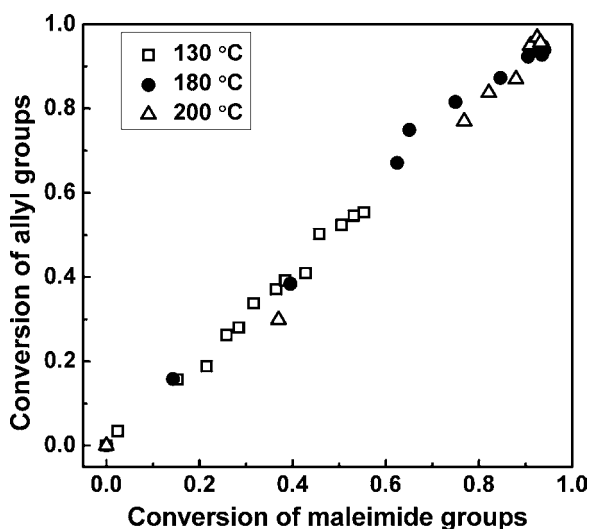

Fig. 5. Comparison of the consumption of maleimide and allyl groups during BMIP/DABPA isothermal cure at different temperatures.
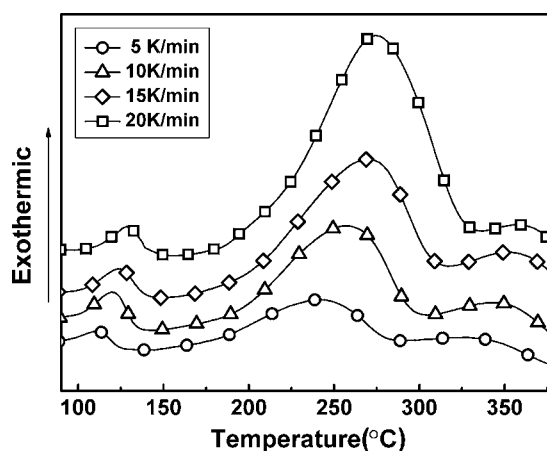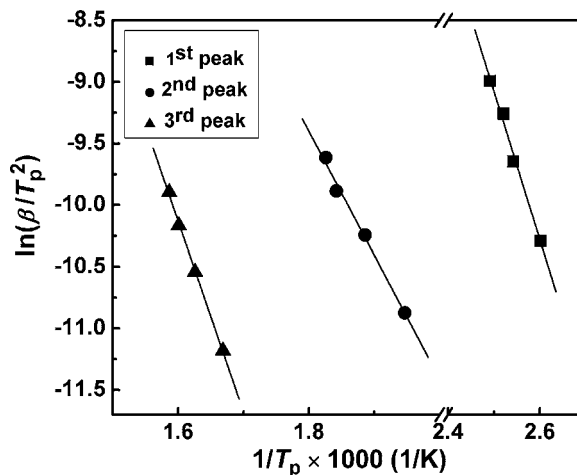

Fig. 7. Kinetic plots of three cure process for BMIP/DABPA resin based on Kissinger equation.
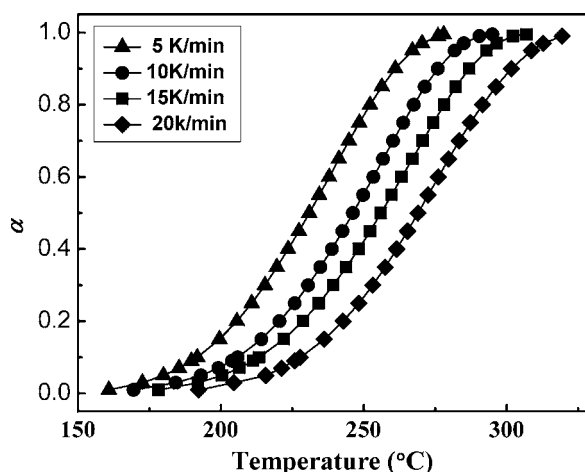
Fig. 8. Fractional conversion as a function of temperature for various heating rates.

Ene reaction is required to overcome the higher activation energy barrier than the analogous Diels–Alder reaction because of stereoelectronic requirement of breaking the allylic C–H σ-bond [24]. Additionally, the polymerization of allyl group, thermally initiated at high temperature, is also difficult because of the resulting allyl radical possesses an ability to stabilize itself by resonance [25]. Therefore, allyl polymerization shows higher apparent activation energy. The E_a of allyl homopolymerization achieves 121 kJ/mol calculated according to the Kissinger equation, which has been reported by Wang et al. when they have studied the kinetic of the curing of allyl poly (phenylene oxide) [26]. The E_a value of 3rd cure process of the system under consideration is nearly equal to that of allyl homopolymerization. The agreement of two E_a values is also an evidence that exothermic peak located at the highest temperature region is attributed to the polymerization of residual allyl groups.

As shown in Fig. 6, the 2nd cure process is predominant, and hence its state of cure has a profound impact on properties of the resulting cured resin. Although the Kissinger method has been applied for kinetic analysis, it only produces a single value of the activation energy for the whole process. The obtained result is believable only if E_a is constant throughout the process. As aforementioned, the 2nd cure process in which many reactions occur is very complicated, and no variety of E_a with cure reaction progress is unrealistic. Isoconversional kinetic analysis is capable of yielding a dependence of the activation energy on the extent of conversion [23,27–31]. Analysis of this dependence allows for untangling complex mechanism of cure processes and for predicting kinetics [18,27]. Furthermore, the 2nd exothermic peak, which is completely free from being overlapped, can be separated from adjacent peaks and analyzed solely. Therefore, it is suitable that this cure process was investigated by the means of an isoconversional method.

To perform isoconversional analysis, the original DSC data on 2nd exothermic peak was transformed into the fractional conversion (α) versus temperature curves at various heating rates, and the corresponding plots are shown in Fig. 8. The α values were obtained by the integration of the 2nd exothermic peak based on the following equation:

$$\alpha = \frac{H_\alpha}{H_{total}} \tag{3}$$

where H_α is the fractional enthalpy and H_{total} is the total enthalpy of the cure reaction.

It is clear from Fig. 8 that all α values increase very slowly at the beginning of curing and when the samples were heated to given

temperatures, the α values show a sharply increase and then level off. Moreover, to obtain the same α value, the required temperature is increased with increasing heating rate.

The Ozawa–Flynn–Wall method, a model-free isoconversional method based on data recorded for various heating rates, was used to obtain the activation energies (E_a) for different conversion levels (α). Ozawa–Flynn–Wall Equation is expressed as follows [32]:

$$\log(\beta) = \log\left(\frac{AE_a}{R}\right) - \log[g(\alpha)] - c - l\left(\frac{E_a}{RT}\right) \tag{4}$$

where β is the heating rate, c and l are couple tabulated coefficients, and $g(\alpha)$ is integrated form of the conversion dependence function and independent from the scanning rate at a fixed value of the variable α. The critical point in kinetic analysis using the Ozawa–Flynn–Wall method consists in the accurate setting of the coefficients c and l. The most frequently used values are: $c = 2.313$ and $l = 0.4567$, if $E_a/RT = 28$–50, or $c = 2.000$ and $l = 0.4667$ when $E_a/RT = 18$–30 [33]. For BMIP/DABPA system under consideration, E_a/RT is in the range of 13–20, which is significantly less, so we considered $c = 1.600$ and $l = 0.4880$ [34]. The activation energy can be calculated from the slope of the linear plot of $\log(\beta)$ against $1/T$. Fig. 9 shows the dependence of E_a on α. It can be seen that the E_a values exhibit systematic variation within the range of 84–98 kJ/mol. The E_a firstly decreases in the initial cure stage ($\alpha < 0.1$), reaches a slowly increasing plateau in the region $\alpha = 0.1$–0.7, and increases significantly after α value reaches about 0.7 especially near the end of cure. The similar phenomenon was observed during the course of studying the cure kinetic behavior of other thermosetting systems and some different explanations were given [34–40]. For the present system, the decreasing E_a at $\alpha < 0.1$ may associate with the diffusion control which is induced by melt viscosity [30]. This is because the molecular weight increases slowly at low conversion, but the viscosity decreases drastically with increasing temperature, which may result in an increase in mobility of the molecular chains. Additionally, an apparent increase in E_a values at $\alpha > 0.7$ is because the growing molecular chains lose their mobility as the degree of cure increase, which may be an indication of the reaction mechanism from chemical kinetic control to diffusion control induced by the vitrification [37–40]. Alternatively, the sharply increasing E_a at the final cure stage may be ascribed to the occurrence of side reactions, such as thermal rearomatization which is initiated at higher temperature [27,34–36]. The mean value of activation energies in the plateau region is 85.9 kJ/mol, which is comparable to the result obtained based on Kissinger method.
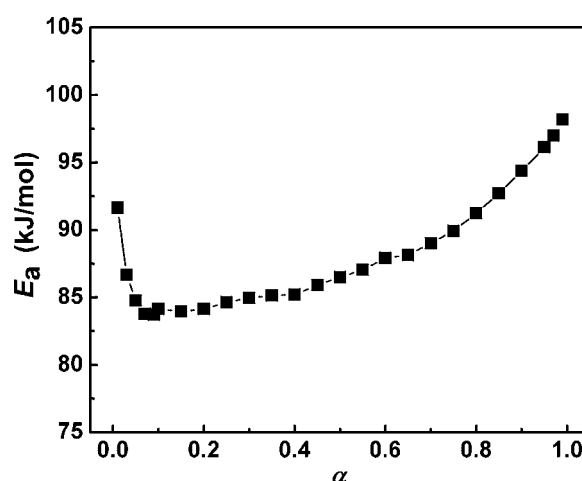

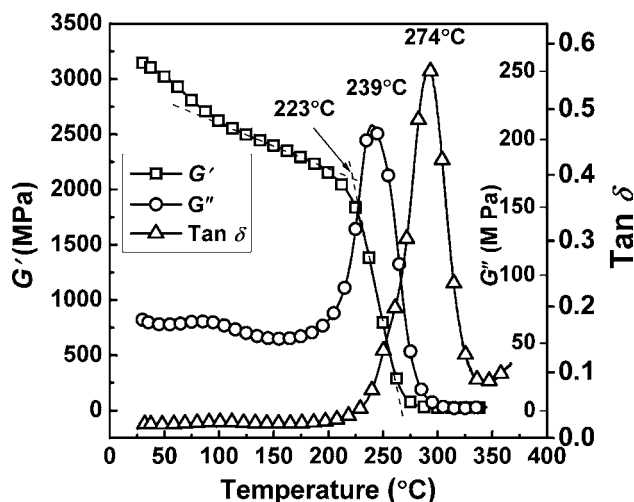**Fig. 9.** Dependence of the activation energy on the extent of conversion.

Fig. 10. DMA thermograms for cured BMIP/DABPA resin.

3.3. Thermal properties of cured BMIP/DABPA

The thermal mechanical behavior of cured BMIP/DAPBA was investigated by dynamic mechanical analysis (DMA). Fig. 10 shows the temperature dependence of storage modulus (G'), loss modulus (G'') and loss tangent (tan δ) of the polymer. From G'–T curve in Fig. 10, the cured resin experienced one-step obvious physical transition, and possesses high bending modulus in the glassy region. The curve of G'' versus T shows two relaxation peaks. Firstly, the strong α relaxation peak at 239 °C is due to the motion of network chain segments. Secondly, the fairly broad weak β relaxation peak located in the 50–100 °C may be due to packing defects in the glassy state, whose relaxation intensity decreases after aging at enhanced temperature and increases dramatically after one water absorption–desorption cycle [41]. Furthermore, only one sharp and symmetrical tan δ peak centered at 274 °C is observed, indicating the formation of a homogeneous network structure of BMIP/DABPA.

The dynamic TG and DTG thermograms of BMIP/DABPA copolymer are shown in Fig. 11. The 5% and 30% mass loss temperatures ($T_{5\%}$ and $T_{30\%}$), temperature at the maximum rate of decomposition (T_{max}) and char residue at 600 °C were chosen as the thermal stability parameters and are compiled in Table 2. As seen from Fig. 11, the cured resin exhibits a high level of thermal stability
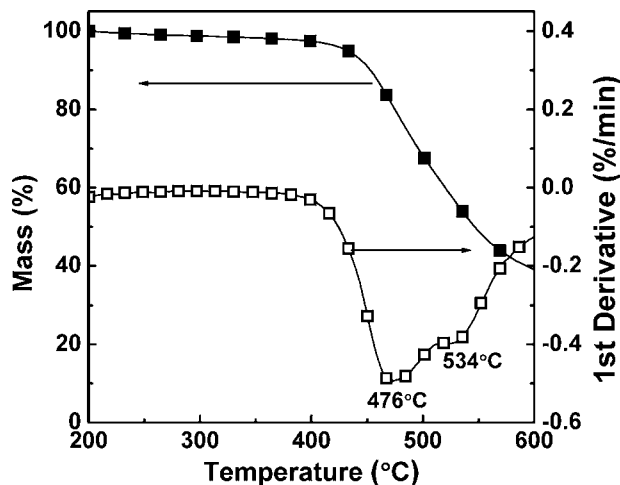

Fig. 11. TGA thermograms for cured BMIP/DABPA resin.

Table 2
TGA analysis of cured BMIP/DABPA resin.

Copolymer	$T_{5\%}$[a] (°C)	$T_{30\%}$[b] (°C)	T_{max}[c] (°C)	RW[d] (%)
BMIP/DAPBA	432	495	476	39.1

[a] 5% weight loss temperature.
[b] 30% weight loss temperature.
[c] Temperature at maximum rate of weight loss.
[d] Char yield at 600 °C.

with char residue at 600 °C of 39.1%, and the onset decomposition temperature ($T_{5\%}$) is as high as 431 °C. Moreover, the cured network of BMIP/DABPA underwent two-stage decomposition reaction and the inflection temperatures of the two stages are 476 and 534 °C, respectively. The first stage could be due to the degradation of the aliphatic chain structures derived from allyl group, and the second stage should be attributed to the aryl and the heterocyclic structures derived from maleimide in the cured resins.

4. Conclusions

A novel BMI resin was developed based on biamaleimide containing phthalide cardo structure and 2,2′-diallyl bisphenol A. The curing mechanism and kinetics of the prepolymer were monitored using FTIR and DSC. The FTIR observation showed that the alternating copolymerization of maleimide and allyl groups was more favored than the homopolymerization of BMI monomer and the isomerization reaction of the allyl to the propenyl form below 200 °C. The DSC thermogram of the prepolymer showed three cure regimes in the range of 100–350 °C. The apparent activation energies with respect to individual cure regime obtained by Kissinger method were 100.2, 83.6 and 128.8 kJ/mol, respectively. Furthermore, the 2nd exothermic peak was separated from other peaks and analyzed independently by the integral isoconversional method, viz. Ozawa–Flynn–Wall method. The average values of the apparent activation energy in the plateau region was 85.9 kJ/mol. The cured resin of BMIP/DABPA exhibited good thermal properties. The DMA results showed that $G' > 2$ Gpa in the whole glassy region and the glass-transition temperature (T_g) reached 274 °C based on the tan δ peak temperature. The TGA showed the onset decomposition temperature ($T_{5\%}$) and temperature at the maximum rate of decomposition (T_{max}) reached 431 °C and 476 °C.

References

[1] H.D. Stenzenberger, Adv. Polym. Sci. 117 (1994) 165.
[2] J. Mijovic, S. Andjelic, Macromolecules 29 (1996) 239.
[3] J. Fan, X. Hu, C.Y. Yue, Polym. Int. 52 (2003) 15.
[4] Z.S. Guo, S.Y. Du, B.M. Zhang, Z.J. Wu, J. Appl. Polym. Sci. 9 (2004) 3338.
[5] F.Y.C. Boey, X.L. Song, C.Y. Yue, Q. Zhao, J. Polym. Sci. Part A: Polym. Chem. 38 (2000) 907.
[6] E. Martuscelli, P. Musto, G. Ragosta, G. Scarinizi, Polymer 37 (1996) 4025.
[7] I.K. Varma, R. Tiwari, J. Therm. Anal. 32 (1987) 1023.
[8] C. Gouri, C.P.R. Nair, R. Ramaswamy, Polym. Int. 50 (2001) 403.
[9] M. Frigione, J.M. Kenny, Adv. Polym. Technol. 24 (2005) 253.
[10] M. Sunitha, C.P.R. Nair, K. Krishnan, K.N. Ninan, Thermochim. Acta 374 (2001) 159.
[11] F.W. Huang, Z.X. Rong, X.N. Shen, Polym. Eng. Sci. 48 (2008) 1022.
[12] M. Abbate, E. Martuscelli, P. Musto, G. Ragosta, J. Appl. Polym. Sci. 65 (1997) 979.
[13] Y.J. Han, G.X. Liao, Y.J. Xu, G.P. Yu, X.G. Jian, Polym. Eng. Sci. 49 (2009) 2301.
[14] Y. Xiong, F.Y.C. Boey, S.K. Rath, J. Appl. Polym. Sci. 90 (2003) 2229.

[15] X. Hu, J. Meng, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 994.
[16] J.C. Phelan, C.S.P. Sung, Macromolecules 30 (1997) 6845.
[17] R.J. Morgan, E.E. Shin, B. Rosenberg, A. Jurek, Polymer 38 (1997) 639.
[18] N. Sbirrazzuoli, S. Vyazovkin, Thermochim. Acta 388 (2002) 289.
[19] D. Rosu, F. Mustata, C.N. Cascaval, Thermochim. Acta 370 (2001) 105.
[20] B.A. Rozenberg, E.A. Dzhavadyan, R.M. Morgan, E. Shin, Polym. Adv. Technol. 13 (2002) 837.
[21] X.H. Xiong, P. Chen, Q. Yu, N.B. Zhu, Polym. Int. 59 (2010) 1665.
[22] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[23] A. Catalani, M.G. Bonicelli, Themcochim. Acta 439 (2005) 126.
[24] W. Carruthers, Some Modern Methods of Organic Synthesis, 3rd edition, Cambridge University Press, Cambridge, 1986, p. 244.
[25] A. Matsumoto, Prog. Polym. Sci. 26 (2001) 189–257.
[26] L.H. Wang, Q.Y. Xu, D.H. Chen, J. Appl. Polym. Sci. 102 (2006) 4111.
[27] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 2 (2006) 1515.
[28] N. Sbirrazzuoli, S. Vyazovkin, Macromol. Chem. Phys. 20 (2003) 1815.
[29] S. Vyazovkin, N. Sbirrazzuoli, Macromolecules 29 (1996) 1867–1873.
[30] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Chem. Phys. 20 (2000) 199.
[31] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 2 (1999) 387.
[32] C.D. Doyle, Nature 207 (1965) 290.
[33] J.Y. Li, P. Chen, Z.M. Ma, J. Appl. Polym. Sci. 111 (2009) 2590.
[34] V.L. Zvetkov, Polymer 42 (2001) 6687.
[35] N. Sbirrazzuoli, A.M. Mija, Thermochim. Acta 447 (2006) 167.
[36] F. Dimier, N. Sbirrazzuoli, Polym. Eng. Sci. 44 (2004) 518.
[37] I. Mondragon, L. Solar, Thermochim. Acta 417 (2004) 19.
[38] M.R. Kessler, S.R. White, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 2373.
[39] J. Ruiz, A. Mantecon, V. Cadiz, J. Appl. Polym. Sci. 87 (2003) 693.
[40] L. Callau, A. Mantecon, J.A. Reina, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 2337.
[41] L.R. Bao, A.F. Yee, C.Y.C. Lee, Polymer 42 (2001) 7327.