

Synthesis and characterization of a novel bisphthalonitrile containing benzoxazine

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Abstract. The novel bisphthalonitrile containing benzoxazine (BPNBZ) has been synthesized using bisphenol-A, 4-aminophenoxylphthalonitrile and paraformaldehyde. The structure of the monomer was supported by FTIR spectroscopy, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectra, which have exhibited that the reactive benzoxazine ring and cyano groups exist in molecular structure of BPNBZ. The cure reaction of BPNBZ was monitored by the disappearance of the nitrile peak and the tri-substituted benzene ring that is attached with oxazine ring peak at 2231, 951 cm^{-1} . The thermal polymerization of the BPNBZ was studied by differential scanning calorimetry (DSC) and dynamic rheometer. It was shown that the bisphthalonitrile containing benzoxazine had completely cured with two-stage polymerization mechanisms according to oxazine ring-opening and phthalonitrile ring-forming. The thermal decomposition behaviors of the polymer were examined by thermogravimetry analysis (TGA) in nitrogen and in air. The materials achieve char yields above 73% under nitrogen at 800°C and above 78% under air at 600°C, which exhibited the cured resin has good thermal stability and thermo-oxidative stability.

Keywords: thermosetting resins, thermal properties, thermal polymerization, bisphthalonitrile containing benzoxazine

1. Introduction

The aerospace industry and space programs have created new demands for even higher temperature polymers. There has been increasing interest in phthalonitrile polymers [1–7], owing to their excellent thermal and thermo-oxidative stability, high char yield, good chemical inertness, abrasion resistance, and flame resistance. But, there are several challenges to overcome with regard the processing of these materials with higher melting temperature and high processing temperature.

In recent years, the development of the benzoxazine-based family of phenolic resins has attracted significant attention. The attractive characteristics of benzoxazine polymers include low melt viscosity, no release of volatiles during cure and no need

for harsh catalysts, high thermal stability, good mechanical properties, excellent electrical properties and molecular design flexibility [14–16]. So in order to achieve low melt temperature of phthalonitrile, the presence of aromatic oxazine in the phthalonitrile molecular structure is necessary [11]. In this paper, we report on the synthesis of a bisphthalonitrile monomer containing benzoxazine and the properties of its polymer. Thermal polymerization of this monomer is relatively easy, because of the active benzoxazine ring in the backbone [8–11]. The focus of this research develops a novel bisphthalonitrile containing benzoxazine which expected that this bisphthalonitrile will contribute to the cross-link network formation by its own ring-forming polymerization.

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2. Experimental

2.1. Materials

All chemicals were used as received. Paraformaldehyde (CP), toluene (99.5%), N-N-dimethylformamide (DMF, 99.5%), potassium carbonate (99%), and 1,4-dioxane (99%) were obtained from Tianjin BODI Chemicals. 4-nitrophthalonitrile (99%) was obtained from Alpha Chemical (Dezhou) Co. Ltd. 4-Aminophenol (CP) was obtained from Sinopharm Chemical Reagent Co., Ltd. Bisphenol-A was obtained from Tianjin Guangfu Fine Chemical Research Institute. All solvents used were certified A.C.S grade and used as received.

2.2. Synthesis

2.2.1. Synthesis of

4-aminophenoxyphthalonitrile

To a 250 ml three neck round-bottom flask equipped with a mechanical stirrer, refluxing condenser, and 4-nitrophthalonitrile (34.6 g, 0.2 mol), 4-Aminophenol (21.8 g, 0.2 mol), potassium carbonate (30 g.), and DMF (120 ml) were added. The reaction mixture refluxed at 85°C for 6 h. After 6 h, the mixture was precipitated into dilute NaOH (1 mol/l) using an additional funnel with slow addition rate. The brown precipitate was filtered and dried in vacuum oven at 70°C shown in Figure 1. Melting point (T_m):134°C; typical IR data: 3457 cm^{-1} ($-\text{NH}_2$), 2231 cm^{-1} ($-\text{CN}$), 1247 cm^{-1} (stretch, C–O–C), 1493 cm^{-1} (1, 2 and 4 substitution of benzene ring), 830 cm^{-1} (1, 4 substitution of benzene ring).

2.2.2. Synthesis of the novel bisphthalonitrile containing benzoxazine (BPNBZ)

To a 250 ml three neck round-bottom flask equipped with a mechanical stirrer, refluxing condenser, the 4-aminophenoxyphthalonitrile (23.4 g, 0.1 mol), bisphenol-A (11.4 g, 0.05 mol), and Paraformaldehyde (6 g, 0.2 mol) were dissolved in 40 ml of 1,4-dioxane and 20 ml of toluene and the reaction mixture refluxed at 110°C for 5 h. Then, the solvent was evaporated using a vacuum pump, and the crude product was obtained. Then, the crude product was dissolved in DMF and precipitated into the dilute NaOH (1 mol/l). The brown precipitate was filtered through a glass filter under vacuum and dried in vacuum oven at 70°C, and the purified bisphthalonitrile containing benzoxazine (BPNBZ) was obtained, shown in Figure 1 [11]. The typical IR characteristics data: 2231 cm^{-1} ($-\text{CN}$), 1503, 951 cm^{-1} [12, 13] (tri-substituted benzene ring that is attached with oxazine ring), 1247, 1032 cm^{-1} (stretch, C–O–C) [12, 13], 1086, 830 cm^{-1} (stretch C–N–C) [12], 1420 cm^{-1} (CH_2 antisymmetric stretch); $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 1.621–1.627 (CH_3), 4.615–4.629 (CH_2); 5.350 ($\text{N-CH}_2\text{-O}$), 6.740–6.745 (N-Ar-H), 6.762–6.907 (ortho to N-Ar-). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) δ (ppm): 31.05 (CH_3), 41.83 ($\text{C}(\text{CH}_3)_2$), 51.03 ($\text{Ar-CH}_2\text{-N}$), 79.10 ($\text{N-CH}_2\text{-O}$), 115.46 ($\text{Ar-C}\equiv\text{N}$), 121.01 ($\text{C-CH}_2\text{-N}$), 143.44 (C_{11}), 146.94 (C_8), 162.35 (C_7).

2.2.3. Thermal polymerization of the monomer

The BPNBZ monomer could be polymerized by heating. The conditions of the BPNBZ polymeriza-

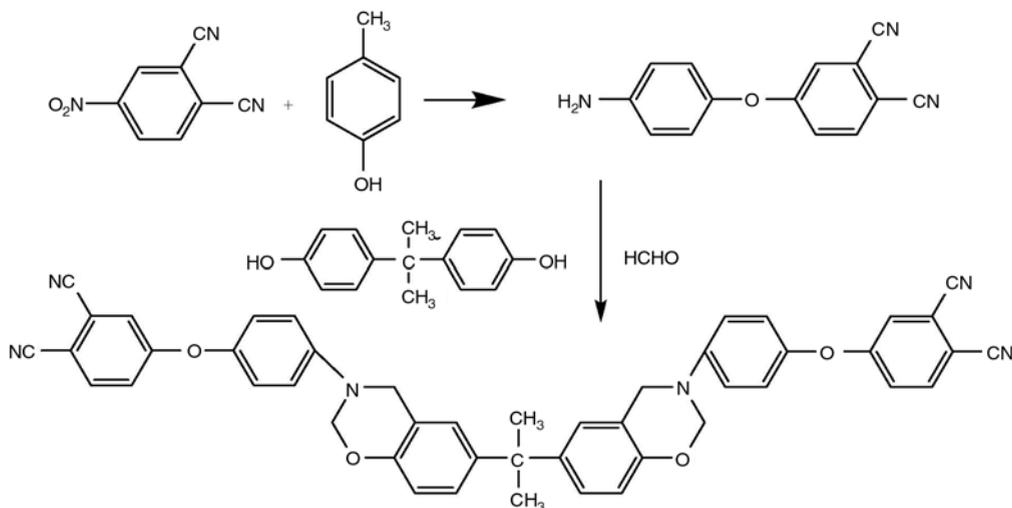


Figure 1. The synthesis of the bisphthalonitrile containing benzoxazine

Table 1. The cured schedule of the prepolymer and polymer

Sample	Time and temperature
b	160°C-12h
c	160°C-12h 180°C-12h
d	160°C-12h 180°C-12h 200°C-8h
e	160°C-12h 180°C-12h 200°C-8h 220°C-6h
f	160°C-12h 180°C-12h 200°C-8h 220°C-6h 250°C-6h

tion were listed in Table 1. The cured samples were heated at 160°C for 12 h, 180°C for 12 h, 200°C for 8 h, 220°C for 6 h and 250°C for 6 h consecutively. A hard shiny blue-black solid was obtained.

2.2.4. Characterizations

The structure of monomer and resins were characterized in KBr pellets at Shimadzu FTIR8400S. The resins with different cured extent were prepared in DSC by heating from 50 to 180 (b), 200 (c), 220 (d), 250 (e) and 275°C (f) at a heating rate 10°C/min respectively.

¹H-NMR and ¹³C-NMR spectra were obtained using a Bruker AV400 nuclear magnetic resonance spectrometer (NMR) at a proton frequency of 400 MHz and the corresponding carbon frequency. The solvent is CDCl₃.

The thermal behaviors of monomer and resins were investigated by the differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA). The differential scanning calorimetry (DSC) was performed on TA Instruments Modulated DSC-Q100 with a heating rate of 10°C/min and a nitrogen flow rate of 50 ml/min. All samples were crimped in hermetic aluminum pans with lids. The thermogravimetry analysis (TGA) was performed on the TA instruments Q50 thermogravimetric analyzer with a heating rate of 20°C/min and a nitrogen flow rate of 50 ml/min or an air flow rate of 50 ml/min.

The dynamic rheological measurements were carried out using TA Instruments AR-G2 Oscillatory Rheometer with a heating rate of 10°C/min and the frequency of 10 Hz under air atmosphere.

3. Results and discussion

3.1. Characterization of structure of BPNBZ and resin

The structure of BPNBZ as shown in Figure 1 was verified by ¹H-NMR and ¹³C-NMR spectroscopy

and the corresponding spectrum was shown in Figure 2 and 3. In ¹H-NMR, resonances appearing at 4.63 and 5.35 ppm are assigned to the methylene protons in the oxazine ring of BPNBZ [13]. The prominent resonance at 1.621 and 1.627 ppm in the aromatic frequency corresponds to methyl of the monomer. Furthermore, the structure of the monomer is confirmed by using ¹³C-NMR and the corresponding chemical shifts are shown in Figure 3, according to chemical shift values, the peak at 79.5 ppm indicates the characteristic resonance of –CH₂– in oxazine ring, and the peak at 115 ppm is the characteristic resonance of –CN. Along with the excellent agreement between the calculated and observed data of the elemental analysis for the purified sample, it shows that the targeted compounds were obtained in high purity [13].

The FTIR spectrum of BENBZ is shown in Figure 4a. The appearance of –CN at 2231 cm⁻¹ and tri-substituted benzene ring that is attached with oxazine ring at 1503, and 951 cm⁻¹ can be observed. The band at 1247 cm⁻¹ is assigned to the C–O–C antisymmetric, while the band at 1032 cm⁻¹ is assigned to the C–O–C symmetric stretch [12, 13]. The antisymmetric and symmetric stretch of the C–N–C is observed at 1086, 830 cm⁻¹. These results show a novel bisphthalonitrile containing benzoxazine could be synthesized by this technique.

The FTIR spectra of resins are shown in Figure 4. The peaks at 951, 1503, 2231, 1360, 1521, 1640 and 3280 cm⁻¹ show changes in intensity as a function of cure temperature. To observe the thermal polymerization and curing reaction mechanisms of BPNBZ, we use the non-isothermal polymerization techniques by DSC instrument scanning to schedule program, so as to explain the way of thermal polymerization and the structures of crosslinked networks. From these results, the changes of all characteristic peaks are no apparent when scanning from 50 to 180°C using non-isothermal polymerization reactions by DSC instrument (Figure 4b), the intensity of the peak at 951 and 1503 cm⁻¹ decreased faintly after scanning to 200°C shown in Figure 4c. At the same time, the peak attributed phenolic hydroxyl group at 3300–3400 cm⁻¹ was enhanced, suggesting the polymerization reaction of oxazine ring-opening appears (Figure 4d). After scanning to 250°C, the band of tri-substituted benzene ring that is attached with oxazine ring disap-

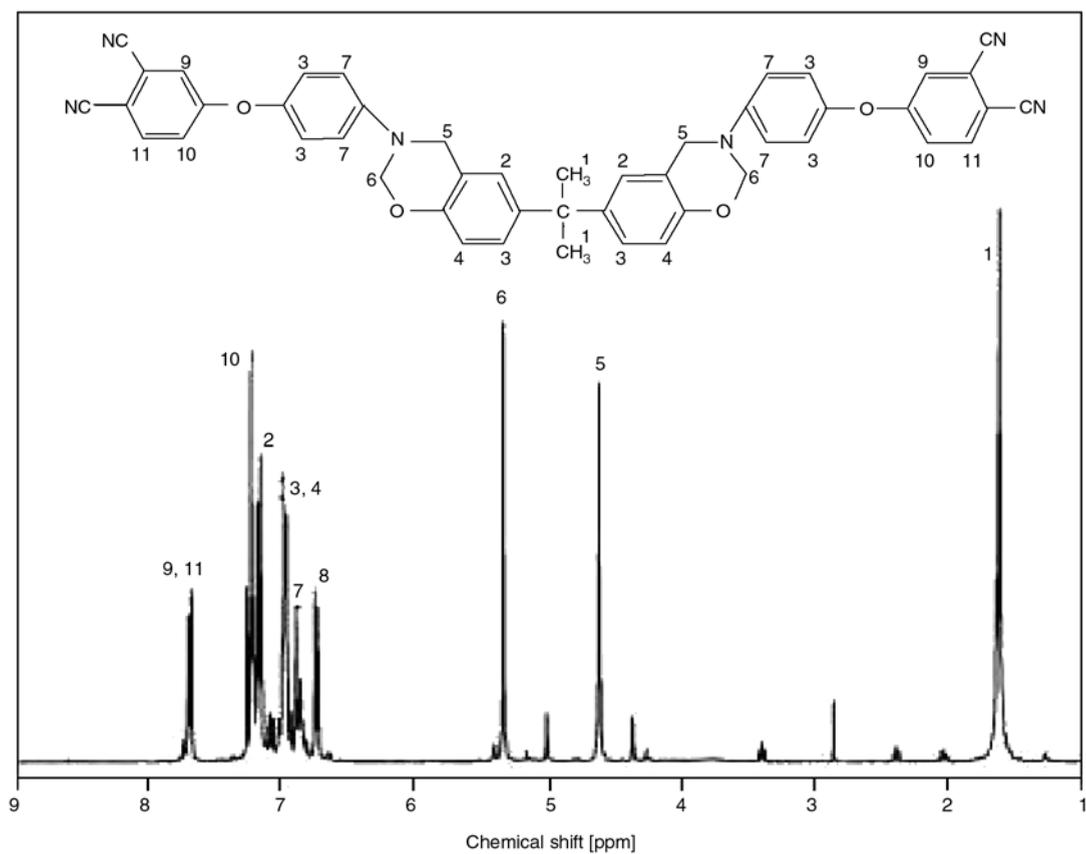


Figure 2. ¹H-NMR spectrum of BPNBZ in CDCl₃

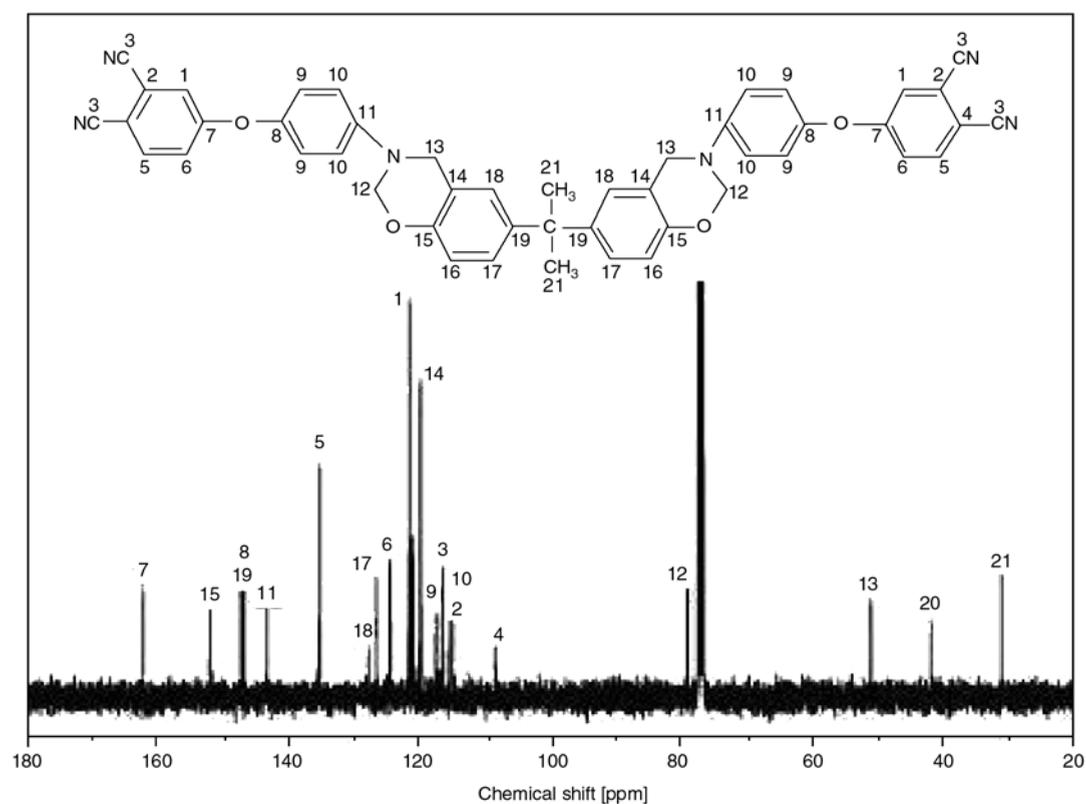


Figure 3. ¹³C-NMR spectrum of BPNBZ in CDCl₃

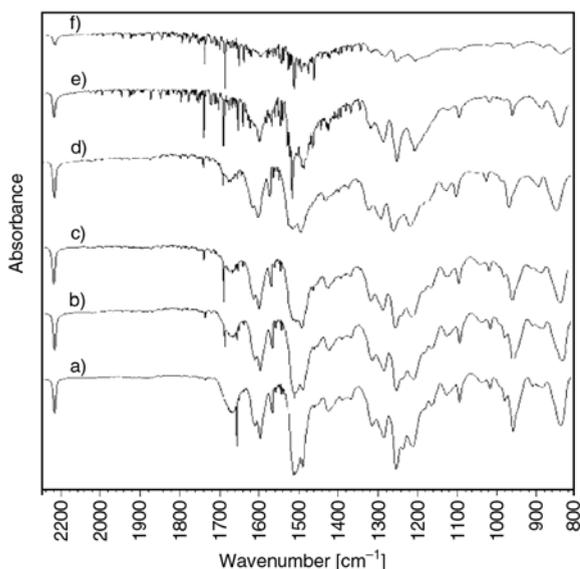


Figure 4. FTIR spectra of the monomer (a), partially cured resin (b), (c), (d), (e) and (f)

pears at 1503 cm^{-1} and the prominent band of tetra-substituted appears at 1500 cm^{-1} , suggesting benzoxazine polymerization via ring-opening is complete. According to the decrease of intensity of the peak at 2231 cm^{-1} and the appearance of new peaks at 1521 , 1360 , 1637 ($-\text{C}=\text{N}-$) and 3275 cm^{-1} ($\text{N}-\text{H}$), which are contributed to the characteristic absorptions of triazine and phthalocyanine, suggest the polymerization reaction of $-\text{CN}$ groups has happened, as shown in Figure 4e. The Figure 5 indicates the typical FTIR spectra of the ring-forming proceedings of $-\text{CN}$ groups, the reactions are enhanced with the elevating of temperature. After scanning to 275°C , the peak of $-\text{CN}$ at 2231 cm^{-1} decreases clearly, shown in Figure 4f. These spectral observations suggest that multiple reaction

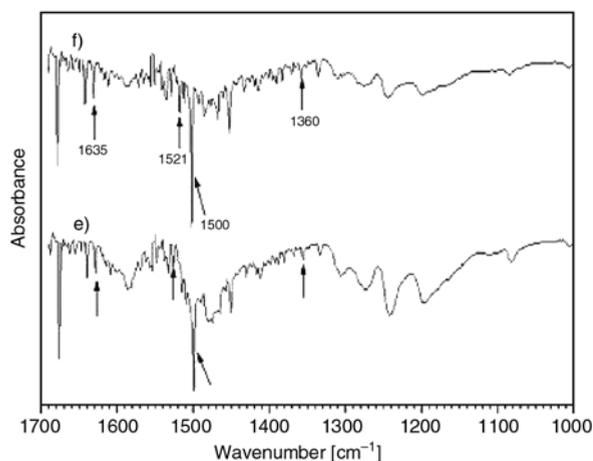


Figure 5. FTIR spectra of the pre-cured resins

mechanisms may be operational in the cure reactions of bisphthalonitrile containing benzoxazine.

3.2. DSC and TGA analysis

The thermal polymerization reactions of the monomer were studied by DSC as shown in Figure 6a. The DSC trace has two well resolved polymerization peaks. The first polymerization peak at the temperature range from 170 to 265°C is mainly attributed to the oxazine ring-opening polymerization, and the second peak at the temperature range from 265 to 300°C owes to the bisphthalonitrile ring-forming polymerization. This result was supported by the FTIR spectra results. From Figure 6, the cured extent of resin increased as a function of cure temperature and time, the peaks decreased with the increase of time and temperature. The resins with different cured extent are shown in Table 1, we found that the first peak had eliminated after curing at 200°C for 8 h (Figure 6d), and from Figure 6e and f, the second peak had eliminated basically after curing at 220°C for 6 h and 250°C for 5 h. There is a peak at the temperature range from 325 to 360°C , the temperature 325°C is post-cure temperature and the 360°C is the initial decomposition temperature, which can be support by the TGA results. As these results, it means that the bisphthalonitrile containing benzoxazine had completely cured with two-stage polymerization mechanisms according to oxazine ring-opening and phthalonitrile ring-forming.

The TGA curves of the polymers as shown in Figure 7. The initial decomposition temperatures (T_{id}) of the polymer under nitrogen and air are about

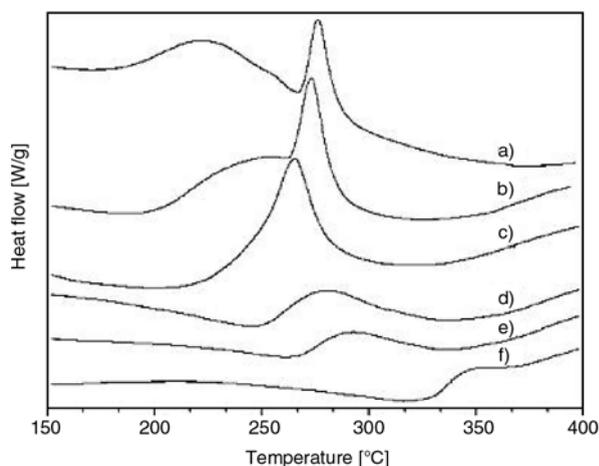


Figure 6. The DSC curves of the monomer (a) and the pre-cured resin (b), (c), (d), (e) and (f)

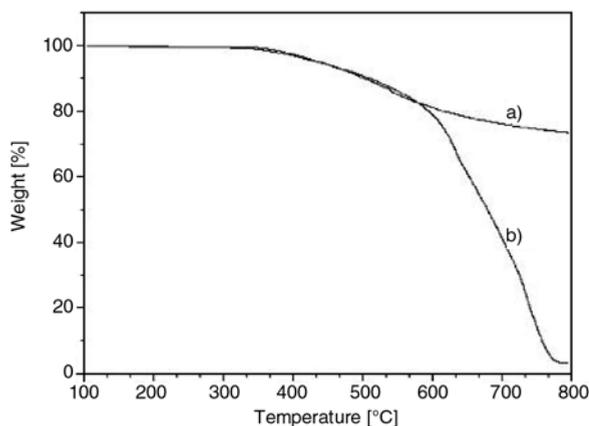


Figure 7. The TGA curves of the polymer a) in N_2 , b) in air

343.38 and 354.06°C, respectively. The temperatures at weight loss 5 and 10% in nitrogen atmosphere are 437.50 and 504.59°C and in air atmosphere are 434.63 and 504.29°C, respectively. The char yield at 800°C under nitrogen is 73.65% and at 600°C under air is 78.66%. In Table 2, the thermal properties of BPNBZ are summarized and compared to other phthalonitrile. The thermal properties of BPNBZ under nitrogen are as well as or decrease slightly than the other two monomers, but there is a significant improvement of the BPNBZ thermal properties under air than the other two. Therefore, the BPNBZ can be used for making heat-resistance high performance composites.

3.3. The rheological behavior

Figure 8 is relationship between rheological behaviors and temperature under curing process of bisphthalonitrile containing benzoxazine. Two transitions of G' appear from 200 to 300°C and two cross

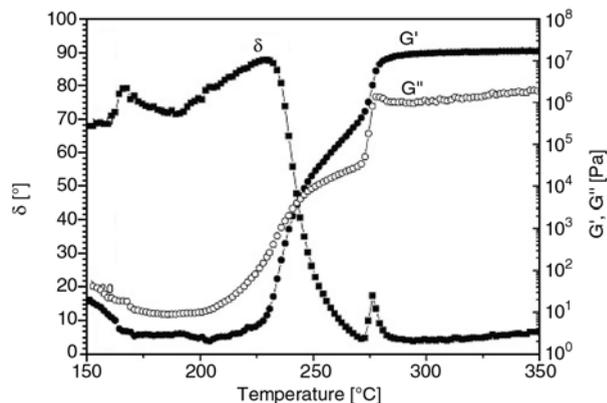


Figure 8. The rheological behaviors of the BPNBZ under non-isothermal curing

points of G' and G'' were observed at 242.7 and 276.1°C, respectively. The G'' has two apparent peaks. The first peak ranges from 200.9 to 242.7°C, and the second peak ranges from 242.7 to 276.1°C. The Delta curve appears two sharp peaks; the temperature of peak top is 230.7 and 276.1°C respectively. As these results, the former suggests primary polymerization of oxazine ring-opening, and the later suggests the bisphthalonitrile polymerizations of nitrile groups. So, it means that the bisphthalonitrile containing benzoxazine had completely cured with two-stage polymerization mechanisms which are consistent with the DSC results.

4. Conclusions

The novel bisphthalonitrile containing benzoxazine (BPNBZ) has been synthesized using bisphenol-A, 4-aminophenoxylphthalonitrile and paraformaldehyde. The structure of the monomer was supported by FTIR spectroscopy, 1H -NMR, and ^{13}C -NMR

Table 2. summary of TGA results

Monomer	Nitrogen			Air		
	T _{5%}	T _{10%}	Char yield [wt%] 800°C	T _{5%}	T _{10%}	Char yield [wt%] 600°C
	437	505	73	434	504	78
	414	505	73	378	420	0
	544	596	80	390	450	75

spectra, which have exhibited that the reactive benzoxazine ring and cyano groups exist in molecular structure of BPNBZ. The cure reaction mechanism of BPNBZ was monitored by the disappearance of the nitrile peak and the tri-substituted benzene ring that is attached with oxazine ring peak at 2231, 951 cm^{-1} . The bisphthalonitrile containing benzoxazine polymer possesses excellent thermal stability, thermal-oxidation stability and high char yield in nitrogen and air. The materials char yields achieved 73% at 800°C under nitrogen and 78% at 600°C under air. The temperatures at weight loss 5% and 10% under air are 434.63 and 509.29°C, respectively. According to the observations of thermal polymerization by DSC and dynamical rheology, the curing process of bisphthalonitrile containing benzoxazine has two stages polymerization mechanisms according to oxazine ring-opening and phthalonitrile ring-forming. The cured extent is a function of temperature and time. It can be used as a matrix of advanced composites.

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