Synthesis and Curing Behavior of a Novel Benzoxazine-Based Bisphthalonitrile Monomer

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ABSTRACT: A novel bisphthalonitrile containing benzoxazine units (BZ-BPH) was synthesized via a solventless method from 4,4′-dihydroxybiphenyl, paraformaldehyde, and 4-aminophenoxylphthalonitrile. The chemical structure of BZ-BPH was confirmed by ^{1}H-NMR and ^{13}C-NMR analyses. The curing behavior was investigated with DSC, FTIR, TGA, and rheology techniques. The monomer manifested a two-stage thermal polymerization pattern. The first stage was attributed to the ring-opening polymerization of benzoxazine moiety, and the second to the polymerization of phthalonitriles. Study about the effect of the catalysts including 4,4′-diaminodiphenylsulfone and FeCl₃ on the polymer-

ization of BZ-BPH was performed, and the result indicated that the addition of these agents could increase the curing rate and lower the curing temperature. Additionally, the cured product showed excellent thermal and thermo-oxidative stability, the high char yield was 76.0% by weight at 800°C in nitrogen atmosphere and 81.2% by weight at 600°C in air, and temperature at 5% weight loss ($T_{5\%}$) in nitrogen and air was 477.9°C and 481.7°C, respectively. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1469–1475, 2010

Key words: phthalonitrile; benzoxazines; curing of polymer; catalysts; thermo properties

INTRODUCTION

Aerospace industry and spaceprograms have created new demands for even higher temperature matrix resins for advanced performance composites. There has been increasing interest in phthalonitrile resins, owing to their excellent thermal and thermo-oxidative stabilities, high char yield, good chemical inertness, abrasion resistance, and flame resistance.[1–10] These polymers are derived by heating the phthalonitrile derivatives for an extended period of time at elevated temperatures by addition curing reaction of cyano groups from phthalonitrile derivatives. However, they usually suffer from poor processability. Initially the phthalonitrile monomers were cured alone by heating, and this procedure needed several days to obtain stable polymers.[2] Later, the curing reaction was found to be readily promoted in the presence of a small amount of curing additives such as organic amines[2–4] and phenols.[5,6] Because of the high temperature required for resin processing, curing additives, aromatic amines, or phenols generally of low molecular weight, tend to be volatile or

decomposed, therefore, causing void problems. On the other hand, to fabricate the fiber composites, the prepolymer was used to prepare the prepreg due to the poor adhesion and infiltration of the monomer for the fiber,[7,8] however, the prepolymer only had good solubility in some high boiling point solvent, such as dimethylformamide, *N*-methylpyrrolidone, which also brought difficulties in processing. So in the development of the phthalonitrile resin based composites, the technical challenge was to improve the processability of the phthalonitriles without significantly sacrificing their other desirable properties. Polybenzoxazines were a newly developed class of thermosetting resins derived from the ring-opening polymerization of their precursors. The attractive characteristics of benzoxazine polymers include low melt viscosity, no release of volatiles during curing and no need for harsh catalysts, easy processing, moderate curing conditions, high thermal stability, good mechanical properties, excellent electrical properties, and molecular design flexibility.[11–15]

Our object was to develop a new bisphthalonitrile monomer containing benzoxazine units for high performance composites with good processability and excellent thermal properties. In this new monomer, benzoxazine ring opening could produce phenolic hydroxyl groups, which could serve as the curing agent, and then promote the phthalonitrile polymerization at moderate curing conditions. We prepared the monomer via a solventless synthesis and its

polymerization was extensively studied by using DSC, TGA, and FTIR. This article concerns the synthesis, characterization, polymerization, and thermal properties of the resultant polymer. The effect of commonly used catalysts including $FeCl_3$ and 4,4′-diaminodiphenylsulfone (DDS) on the polymerization of BZ-BPH was also investigated.

EXPERIMENTAL

Materials

All chemicals were used as received. Paraformaldehyde (CP), toluene (99.5%), N-N-dimethylformamide (DMF, 99.5%), potassium carbonate (99%), and dichloromethane, NaOH, hydrochloride, and $FeCl_3$ were obtained from Tianjin BODI Chemicals. 4-Nitrophthalonitrile (99%) was obtained from Alpha Chemical (Dezhou) Co. 4,4′-Diaminodiphenylsulfone was obtained form Sinopharm Chemical Reagent Co. 4,4′-Dihydroxybiphenyl and 4-aminophenol were obtained form Tianjin Guangfu Fine Chemical Research Institute. All solvents used were certified A.C.S grade and used as received.

Synthesis of the novel bisphthalonitrile containing benzoxazine (BZ-BPH)

To synthesize BZ-BPH, first 4-aminophenoxylphthalonitrile (BZN) was prepared as follows. N-N-dimethylformamide (DMF; 50 mL), 4-nitrophthalonitrile (10.8 g, 62 mmol), and 4-aminophenol (7.1 g, 65 mmol) were stirred until a solution was formed. Stirring was continued as anhydrous potassium carbonate (16.0 g, 116 mmol) was added in 4-g increments over 4 h, and the resulting mixture was stirred overnight at room temperature. The reaction mixture was filtered, and the filtrate was added dropwise to 700 mL of 1N NaOH water solution to precipitate 13.1 g of golden-yellow product. Melting point (T_m): 134°C; typical IR data: 3457 cm^{-1} ($-NH_2$), 2231 cm^{-1} ($-CN$), 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).

Then BZ-BPH was prepared by the melt reaction method. Briefly, BZN (27.9 g, 0.3 mol), 4,4′-dihydroxybiphenyl and 4-aminophenol were mixed together in a mortar for 15 min until the powder was homogeneously mixed. The powder was put into a flask that has been preheated in an oil bath at 160°C, and kept for 25 min at the same temperature. The as-synthesized product was dissolved in dichloromethane and purified by washing with 3N NaOH solution several times and then with 2 L distilled water. The solvent was then evaporated by a rotary evaporator, and the sample was dried in a vacuum oven overnight at 50°C. Yield about 60%.

Characterization

^{1}H-NMR and ^{13}C-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 was $CDCl_3$. FTIR spectra were obtained with a PerkinElmer spectrum GXA spectrophotometer at a resolution of 4 cm^{-1}. DSC was performed on TA Instruments Modulated DSCQ100 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. 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 at a frequency of 1 Hz and a strain of 0.5%.

RESLULTS AND DISCUSSION

Synthesis of BZ-BPH

The synthesis of BZ-BPH is shown in Scheme 1. The chemical structure of the monomer was confirmed by ^{1}H-NMR and ^{13}C-NMR. In ^{1}H-NMR as shown in Figure 1, signals of oxazine ring hydrogens were observed at 5.33 ppm (s, O—CH_2—N) and 4.55 ppm (s, Ar—CH_2—N—), respectively. No signals appeared at around 3.10 and 3.60 ppm, attributable to the opened structures of oxazine ring, which confirmed the purity of the monomer.[11] The aromatic protons appeared as multiple at 6.77–7.16 ppm. Furthermore, the structure of the monomer was confirmed by ^{13}C-NMR as shown in Figure 2, according to chemical shift values, the peak at 79.5 ppm indicated the characteristic resonance of —CH_2— in oxazine ring, and the peak at 115 ppm was the characteristic resonance of —CN. The results indicated the successful synthesis of the novel phthalonitrile monomer.

In addition, BZ-BPH monomer had good solubility in common organic solvents including toluene, petroleum ether, ethyl acetate, acetone, tetrahydrofuran, dichloromethane, chloroform, etc., which indicated its excellent solution processability.

Curing behavior of BZ-BPH

First the curing behavior of BZ-BPH was monitored with DSC. Figure 3(A) shows the nonisothermal DSC thermograms of BZ-BPH. For the monomer, two exotherms were observed [Fig. 3(A), curve a]: The broad exotherm at 230°C was followed by the sharp exotherm at 275°C. The first exotherm was considered to be due to the ring-opening of the benzoxazine ring, and the second exotherm to the addition reaction of the phthalonitrile groups. The
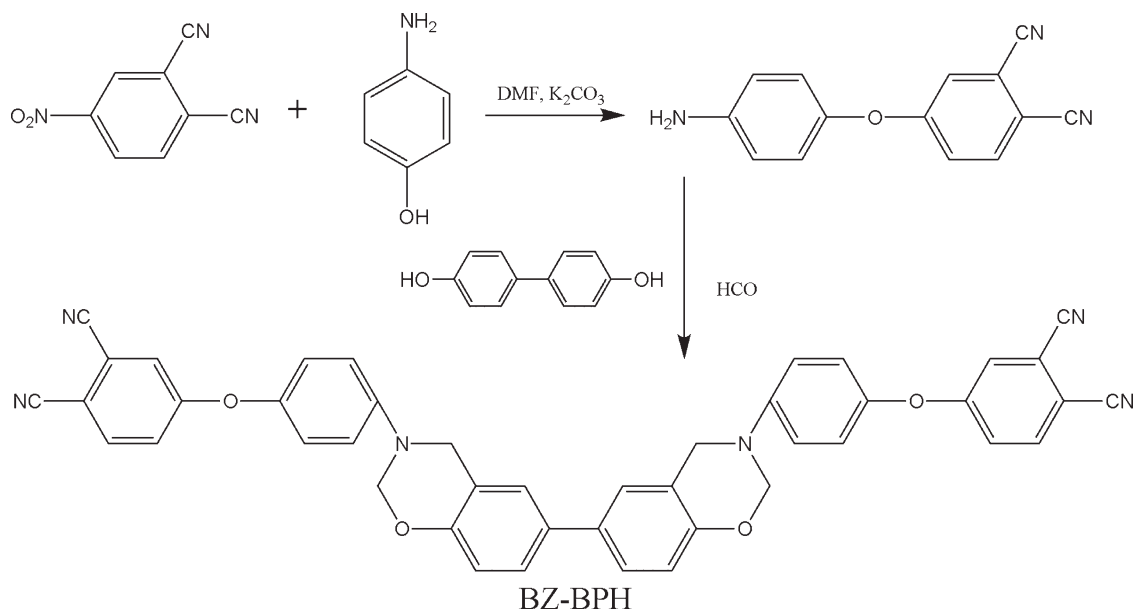
Scheme 1 Synthesis of BZ-BPH.

exothermic amount corresponding to the ring opening of benzoxazine ring decreased greatly after 180°C/30 min cure, and the exothermic amount of the second exotherm increased significantly, which was resulted from that the phenolic hydroxyl groups generated by the ring-opening reaction of benzoxazine ring could catalyzed the addition reaction of the phthalonitrile group.[5,6,16] The exothermic amount due to the benzoxazine ring decreased gradually. One exotherm remained after cumulative curing, and shifted to low temperature [Fig. 3(A), curves d,e], and the exothermic amount decreased with the increase of the heat treatment temperature. After the

cure cycle of 180°C/60 min, 200°C/60 min, a broad exotherm appeared and shifted to high temperature above 300°C gradually [Fig. 3(B)], as weight loss was no more than 1% as seen in TGA curves from Figure 3(B), these exotherms should be the post-curing of the phthalonitrile groups, not the thermal degradation. This phenomenon could be attributed to the steric hindrance of the crosslinked network, which restricted the mobility of the curing groups, and then induced the increase in the post-curing temperature.

FTIR was another means to study the curing behavior of BZ-BPH through monitoring of the
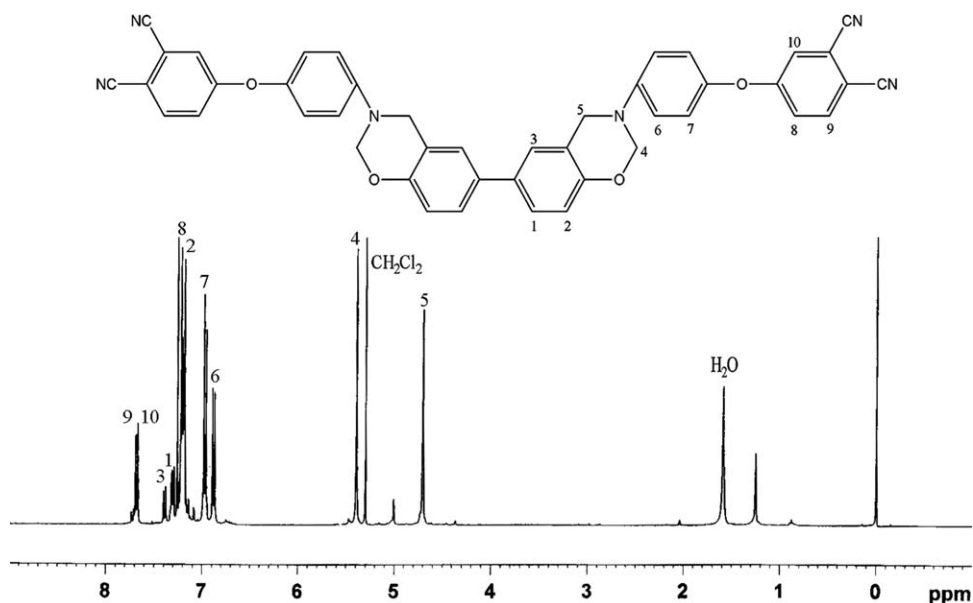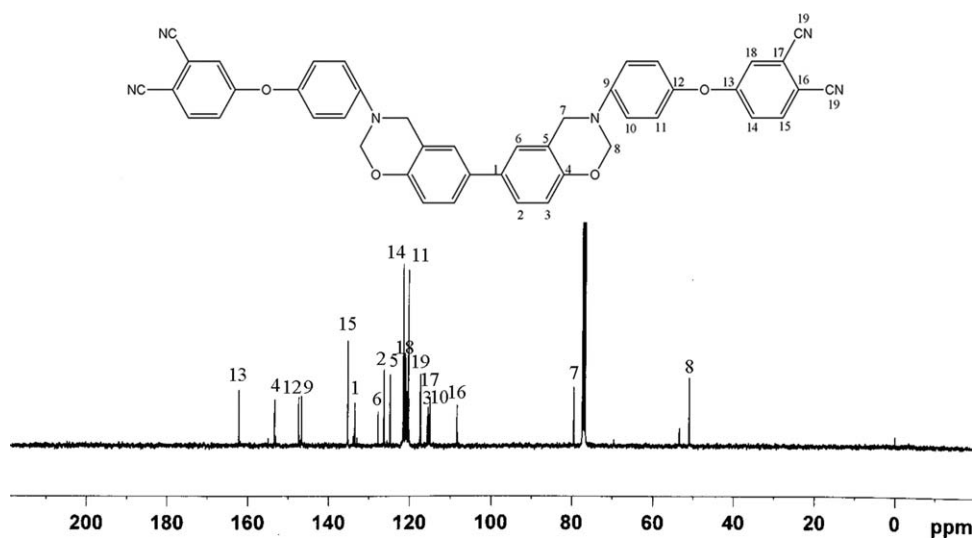

Figure 1 ^{1}H-NMR spectra of BZ-BPH.

Figure 2 [1]C-NMR spectra of BZ-BPH.

changes of the characteristic peak of benzoxazine ring and the phthalonitrile groups during the course of curing and post-curing. Figure 4 shows FTIR spectra of the monomer and the product after each cure. In the spectrum of BZ-BPH monomer, the peaks centered at 1507 cm^{-1} and 950 cm^{-1} were characteristic of the tri-substituted benzene ring in the benzoxazine structure, corresponding to the in-plane C—C stretching and the out-of-plane C—H deformation of tri-substituted benzene ring, respectively. The characteristic absorption band due to the benzoxazine ring gradually decreased and disappeared after the cure at 240°C/3 h indicating the completion of ring-opening at this stage. A decrease of the characteristic band of phthalonitriles at 2230 cm^{-1} (corresponding the stretching of C—N in cyano groups) indicated the reaction of phthalonitrile groups. Accordingly, post-curing at the higher temperature was required to achieve a higher level of polymerization. It was difficult to achieve full poly-

merization of these phthalonitrile groups even after post-curing at 320°C for 4 h due to the steric hindrance of the crosslinked network. On the other hand, new absorptions at 1619 cm^{-1} (corresponding the stretching of C—N in —C=N— species) appeared during the polymerization of the phthalonitrile groups, thus it was presumed that thermal polymerization of BZ-BPH formed mostly linear —C=N— species. Along with the result from the DSC studies, FTIR investigation indicated that bisphthalonitrile containing benzoxazine had cured through two-stage reaction including ring-opening of benzoxazine and addition of phthalonitrile groups.

A rheological cure analysis was carried out on BZ-BPH because rheology offers the more precise temperature region where real mechanical property build-up. Figure 5 is relationship between rheological behaviors and temperature under curing process of BZ-BPH. Two transitions of storage modulus (G') and loss modulus (G'') were observed. The tan
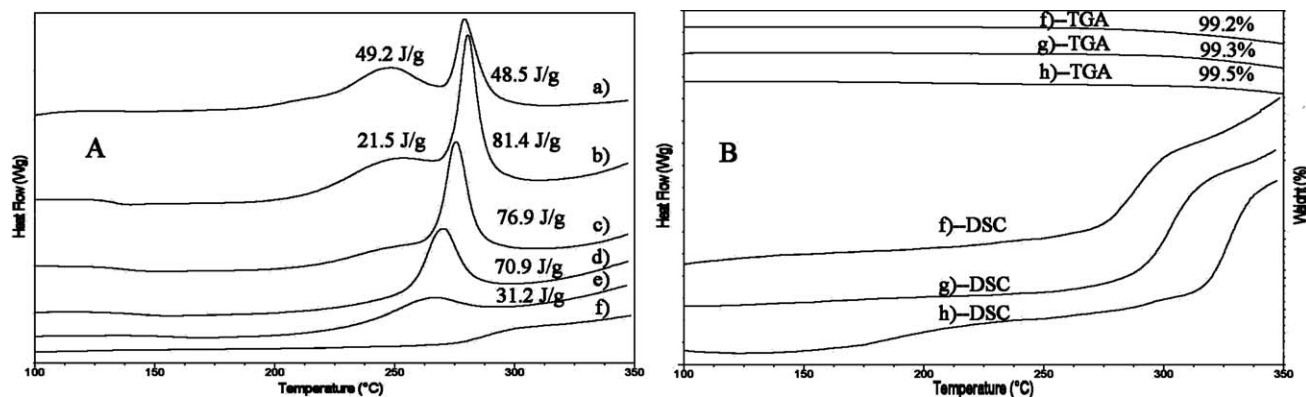

Figure 3 DSC and TGA curves of BZ-BPH after each cure stage. (a) BZ-BPH monomer, (b) 180°C/30 min, (c) 180°C/1 h, (d) 180°C/1 h, 200°C/30 min, (e) 180°C/1 h, 200°C/1 h, (f) 180°C/1 h, 200°C/1 h, 220°C/1 h, (g) 180°C/1 h, 200°C/1 h, 220°C/1 h, 240°C/1 h, and (h) 180°C/1 h, 200°C/1 h, 220°C/1 h, 240°C/1 h, 260°C/1 h.
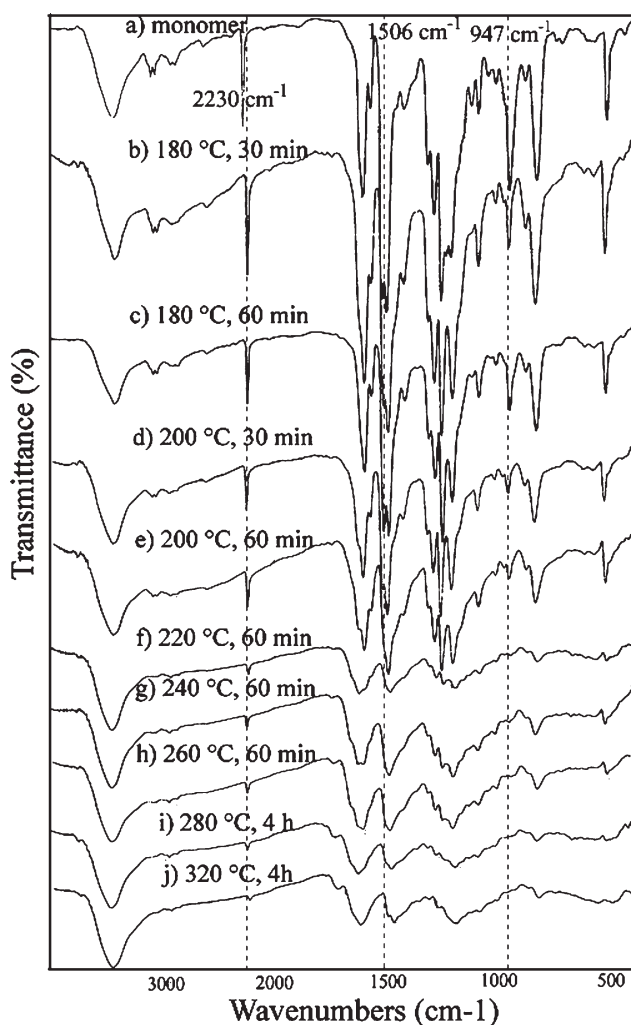
Figure 4 FTIR spectra of BZ-BPH after each cure stage.

(delta) curve appeared two peaks at 228°C and 268°C, respectively. As these results, the former suggests primary polymerization of oxazine ring-opening, and the later suggests the bisphthalonitrile poly-
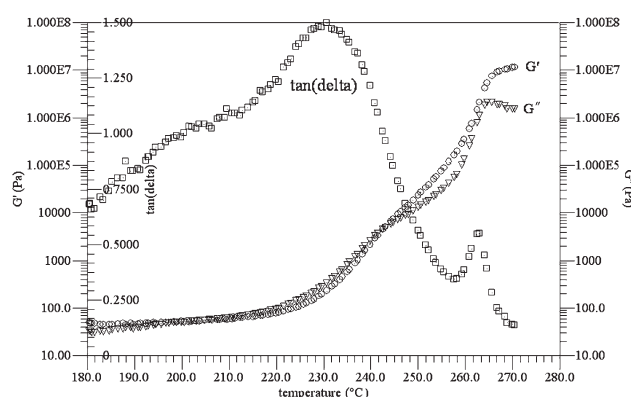
merizations of nitrile groups. The results indicated that the bisphthalonitrile containing benzoxazine cured with two-stage polymerization mechanisms which were consistent with the DSC results. Viscosity changes accompanying the cure reaction was also monitored by rheometric studies. It was important to know the initial curing behavior of the monomer to determine the processing parameters for fabricating fiber-reinforced polymer composites. Figure 6 shows the complex viscosity evolution with reaction time for the curing system over a range of processing temperatures at 160°C, 180°C, and 200°C. As expected, the initial complex viscosity varied inversely with temperature in the early stage of cure, causing the viscosity to be initially lower at higher temperatures. With the increase in the curing temperature, the viscosity underwent a more rapid viscosity increase, corresponding to the faster curing rates at higher temperature.

Affect of catalysts on the curing reaction

As mentioned in the published papers, amines were often used as curing agents to improve the reaction rate of the phthalonitrile groups.[2-4] In addition, various metal salts could also affect the polymerization of benzoxazine[17] and phthalonitrile.[18] Therefore, DDS and FeCl$_3$ were chosen as catalysts for the curing of BZ-BPH. First, the effect of the catalysts on the curing reaction was studied by DSC. Figure 7 shows DSC thermograms of neat BZ-BPH (a), the catalyzed system [DDS (b) and FeCl$_3$ (c)]. For the system containing DDS, the exotherm ascribe to the benzoxazine opening slightly shifted to a lower temperature, and the peak of the second exotherm due to the phthalonitrile reaction nearly did not change; the exothermicity of both exotherm increased
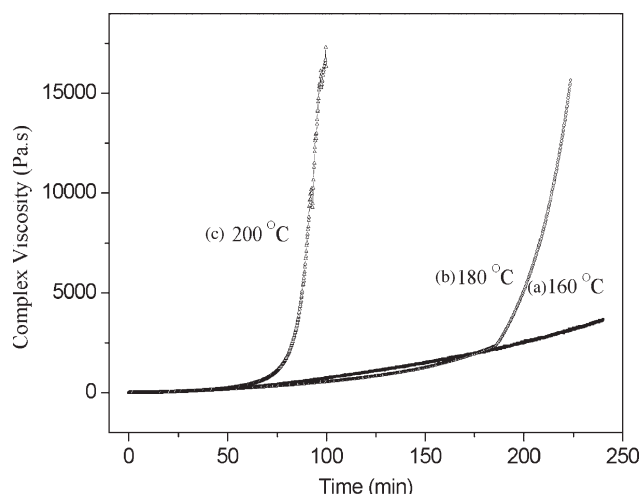

Figure 5 The rheological behaviors of the BZ-BPH under nonisothermal curing.

Figure 6 Complex viscosity versus the time at curing temperatures of (a) 160°C, (b) 180°C, and (c) 200°C.
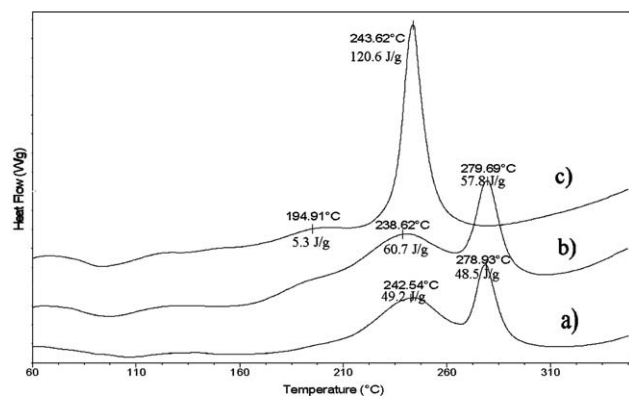
Figure 7 DSC thermograms of neat BZ-BPH (a), BZ-BPH in the presence of catalyst [DDS (b), and FeCl$_3$ (c)].

significantly. Addition of FeCl$_3$ brought significant effect on the curing of BZ-BPH, a small exotherm and a large exotherm were observed, and the main exotherm peak, which should be attributable to the polymerization of benzoxazine and phthalonitrile groups, was lowered by 35°C using this catalyst. Catalytic mechanism would be studied in detail in the future work. Additionally, rheological measurements were carried out to investigate the effect of the catalyst on the curing reaction of BZ-BPH.

Figure 8 shows the temperature dependence of storage modulus (G') of neat BZ-BPH (a), the catalyzed system [DDS (b) and FeCl$_3$ (c)]. It was seen that with DDS as catalyst the cure temperature slightly shifted to a lower temperature, and there was two-stage polymerization in this catalyzed system; with FeCl$_3$ as catalyst, the cure temperature shifted to a lower temperature significantly, and the two-stage polymerization became not obvious. Figure 9 shows the viscosity response with time at 180°C of the catalyzed and uncatalyzed system. When compared with the uncatalyzed system, the increase in the viscosity was rapid for the two catalysts, and the system using FeCl$_3$ as catalyst under-
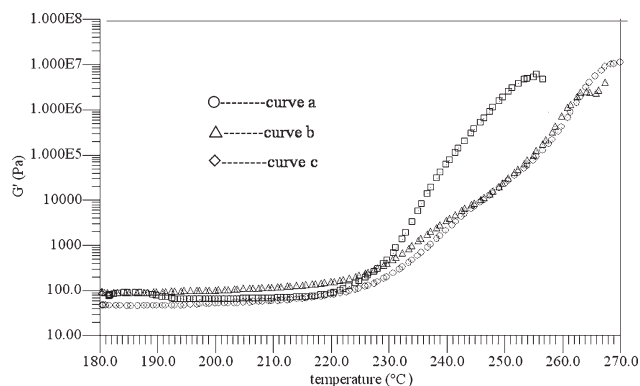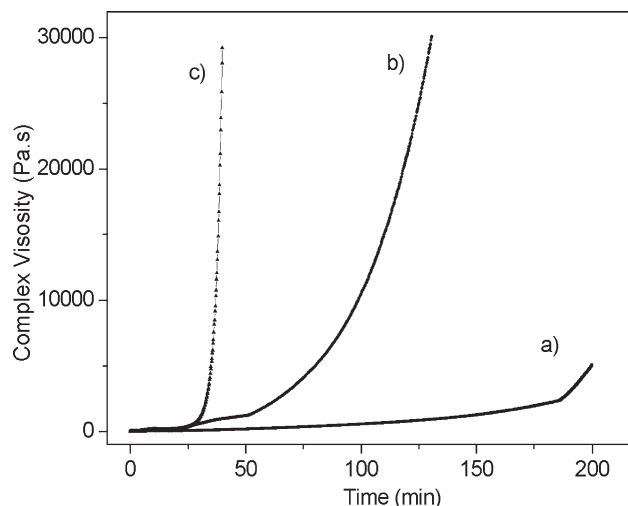

Figure 9 Complex viscosities versus the time at 180°C of neat BZ-BPH (a), BZ-BPH in the presence of catalyst [DDS (b) and FeCl$_3$ (c)].

went a more rapid viscosity increase, corresponding to the faster curing rates. Along with the results from DSC studies, it was indicated that using the catalyst could lower the curing temperature and reduce the curing time, compared with the neat BZ-BPH. According the results, proper catalyst could be chosen to prepare the composites using different processing methods.

Thermal and thermal-oxidative stability

The thermal and thermo-oxidative stability of the polymerized material was evaluated using TGA. The weight loss curves in nitrogen and air are shown in Figure 10. The temperatures at weight loss 5% and 10% ($T_{5\%}$ and $T_{10\%}$) in nitrogen atmosphere were
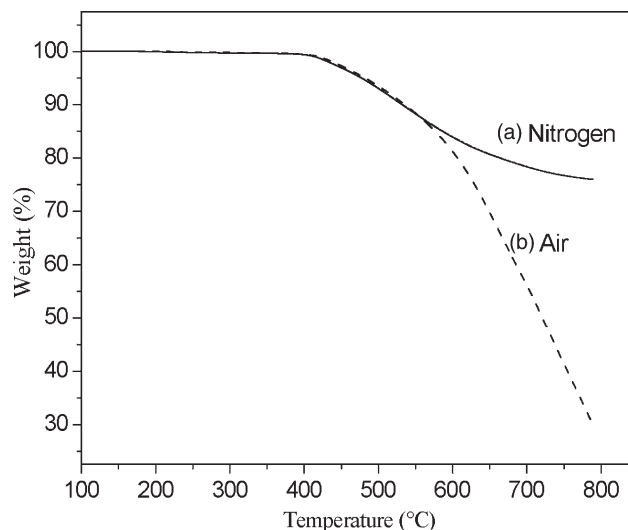

Figure 8 Storage modulus (G') as a function of temperature for the neat BZ-BPH (a), the catalyzed system [DDS (b) and FeCl$_3$ (c)].

Figure 10 TGA curves of the cured product in nitrogen (a) and air (b).

477.9°C and 533.6°C, respectively, and the char yield at 800°C was 76.0%. In air atmosphere, $T_{5\%}$ and $T_{10\%}$ were 481.7°C and 536.6°C, respectively, and the char yield was 81.2% at 600°C. For most of the thermosetting resins, thermo-oxidation process starts around 500 and 600 char yield equals zero. This indicated that the crosslinked units formed by the addition reaction of phthalonitrile groups were responsible for excellent thermal and thermo-oxidative stabilities and high char yield.

CONCLUSIONS

A bisphthalonitrile possessing benzoxazine unit which had good solubility in common organic solvent was synthesized and characterized. BZ-BPH underwent dual curing through benzoxazine ring-opening and phthalonitrile polymerization. In addition, the curing temperature could be lowed and the curing rate could be improved by using curing agents including DDS and FeCl$_3$. The cured product exhibit excellent thermal stability, thermal-oxidative stability and possessed high char yield in nitrogen and air. So, the resin was an ideal heat-resistant and ablation-resistant material.

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