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Diamine-functional bisphthalonitrile: Synthesis, characterization and its application in curing epoxy resin

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ABSTRACT

A novel bisphthalonitrile containing diamino group (BhPN) was successfully synthesized and characterized by FT-IR and ^{1}H NMR spectra. The BhPN monomer showed a self-promoted curing behavior and good processability confirmed by differential scanning analysis and rheological analysis, respectively, and its apparent activation energy was determined by the Kissinger's method. Thermogravimetric analysis and dynamic mechanical analysis indicated that the temperatures of 10% weight loss and glass-transition of BhPN polymer were in the ranges of 480–506 °C and 307–403 °C, respectively, which were significantly dependent on the curing temperature. Furthermore, the BhPN monomer was used as a new curing agent of bisphenol-A diglycidyl ether (DGEBA) and the possible curing mechanism was proposed. The thermal stabilities and viscoelastic properties of epoxy resins cured with different curing agents including BhPN and 4,4′-diaminodiphenyl methane (DDM) were made a detailed comparison. As a result, the cured DGEBA/BhPN system showed higher char yield, glass-transition temperature, and elasticity modulus compared to the DGEBA/DDM system because of the additional polymerization of cyano groups.

1. Introduction

In recent years, the applications for the functional polymeric materials have increased drastically with development of society and technology [1–4]. Phthalonitriles, a novel class of thermosetting resins, have many outstanding performance features, such as high glass transition temperature (Tg) [5], good thermal stability [6], excellent mechanical properties [7], superior flame resistance [8], near zero volumetric shrinkage on polymerization [9] as well as low water absorption [10]. Meanwhile, phthalonitrile monomers can be expediently synthesized via nucleophilic substitution reaction involving condensation from commercially available phenols or their derivatives and nitrophthalonitrile in the presence of weak base catalyst [11,12]. Furthermore, unlike polyimide, phthalonitriles have lower melt viscosity and are easy to be processed in a manner similar to epoxy resin [13]. Up to now, many phthalonitriles containing various functional groups such as imide [14], siloxane [15], phosphazene [16], naphthyl [17], allyl [18], alkyne [19,20], benzoxazine [21], and novolac [22] have been developed and applied in a wide range of fields.

The thermally polymerization reaction is typically used to produce phthalonitrile polymers. Cyano groups are allowed to be polymerized into heat-resistant heteroaromatic structures such as triazine, phthalocyanine, dehydrophthalocyanine and isoindoline [23–25]. Nevertheless, phthalonitriles are latent materials, requiring long curing time and high temperature for gelation [26,27]. Therefore, two kinds of approaches have been employed to promote polymerization. On one hand, the polymerization process can be accelerated with the assistance of curing additives, such as amines [28], metallic salts [29,30], phenols [31], anhydrides [32], and carboxylic acids [33]. Unfortunately, the mechanical properties and thermal stabilities of the polymers are reduced to some extent because of the the inherent volatility of the curing additives, e. g. aromatic amines. On the other hand, the curing conditions can be simplified by designing molecular structure with in-built, self-promoted curing groups (i.e. amino, benzimidazole or hydroxyl) [34–37]. As a matter of fact, the high molecular weight polymers can't be formed by the monofunctional self-promoted phthalonitriles due to their low concentration of cyano groups and they are rarely used alone. Further performance enhancement of self-promoted phthalonitrile is still strongly expected.

Epoxies are used widely as industrial materials because of their excellent processability, chemical resistance, good mechanical and adhesive properties [38–40]. However, aromatic amines, the major epoxy curing agents, are volatile and rather toxic to the user [41]. Similarly the epoxy resins cured with polyamide have a low Tg, poor thermal and

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thermal-oxidative stabilities. Our previous study [42] has shown that the copolymerization of epoxy resin with dissimilar thermosetting resin may allow the network structure to achieve higher crosslink density, superior heat and water resistance, and outstanding thermo-mechanical properties in comparison to the epoxy homopolymer.

Based on these considerations, the focus of the work presented in this article is to prepare a novel bisphthalonitrile derivative containing diamino group following a few simple steps. It is expected that the incorporation of diamine into bisphthalonitrile structure can significantly accelerate curing process without compromising thermal properties. The target monomer BhPN has a relatively low melting point and good processability, and shows a self-promoted curing behavior. For another purpose, we propose to utilize BhPN as epoxy harder to solve the problems mentioned above, complementing our previous publications [42,43]. The effect of various curing agents on curing behavior, thermal and thermo-mechanical properties of epoxy resin was investigated under the same conditions.

2. Experimental

2.1. Materials

Bisphenol-A and DGEBA (epoxide equivalent is 192 g/eq) were used as received from Shanghai Huayi resin Co., Ltd (China). Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 80 wt%) were purchased from Aladdin Reagent (Shanghai) Co., Ltd (China). 4-Nitrophthalonitrile was obtained from Shijiazhuang Alpha Chemical (China). DDM was kindly supplied by Shanghai Coking&Chemical (China). Other starting materials from commercial sources were of analytical-reagent grade and used without further purification.

2.2. Synthesis

2.2.1. Synthesis of 2,2′-bis(4-hydroxy-3-nitrophenyl)propane (abbreviated as BhN)

The bisphenol-A (11.4 g, 50 mmol) was added in batches over 30 min to a stirred solution of concentrated nitric acid (35 mL) and deionized water (95 mL), and the reaction mixture was stirred for extra 3 h at room temperature. Afterwards, the mixture was precipitated into deionized water. The precipitate was filtered, dried under vacuum and recrystallized from benzene to give BhN. The purified product is a yellowish crystal.

Yield: 84%; FT-IR (KBr, cm^{-1}): 3205, 2968, 1629, 1582, 1540, 1480, 1420, 1326, 1260; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 10.822 (s, 2H, —OH); 7.730, 7.724 (d, 2H, Ar—H); 7.355–7.327 (dd, 2H, Ar—H); 7.055, 7.033 (d, 2H, Ar—H); 1.612 (s, 6H, —CH_3).

2.2.2. Synthesis of 2,2′-bis(3-amino-4-hydroxylphenyl)propane (abbreviated as BhA)

The BhN (6.4 g, 20 mmol), absolute ethyl alcohol (80 mL), $FeCl_3$ $6H_2O$ (0.2 g) and activated carbon (1.5 g) were added into a 250 mL flask equipped with mechanical stirrer and reflux condenser. The $N_2H_4{\cdot}H_2O$ (15 mL) was added dropwise over a period of 30 min, and then reaction mixtures were refluxed at 75 °C for 5 h. After cooling to room temperature, the precipitate was filtered and recrystallized from diluted hydrochloric acid to give the product as an offwhite powder.

Yield: 92%; FT-IR (KBr, cm^{-1}): 3412, 3327, 2968, 1601, 1513, 1380, 1355, 1226, 874; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.672 (s, 2H, —OH); 6.526, 6.505 (d, 2H, Ar—H); 6.423, 6.417 (d, 2H, Ar—H); 6.306–6.280 (dd, 2H, Ar—H); 4.319 (s, 4H, —NH_2); 1.454 (s, 6H, —CH_3).

2.2.3. Synthesis of diamine-functional bisphthalonitrile (abbreviated as BhPN)

To a 100-mL, three-necked flask fitted with thermometer and nitrogen inlet was added successively BhA (5.16 g, 20 mmol), 4-nitrophthalonitrile (6.93 g, 40 mmol), pulverized K_2CO_3 (6.63 g, 48 mmol) and DMSO (50 mL). The reaction mixture was stirred continuously at 60 °C for 6 h under nitrogen atmosphere. After cooling, the mixture was poured into 0.1 mol/L sodium hydroxide aqueous solution. The precipitate was filtered and washed with deionized water until the filtrate was neutral.

Yield: 93%; FT-IR (KBr, cm^{-1}): 3472, 3375, 2230, 1624, 1590, 1508, 1486, 1245, 882; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.046, 8.024 (d, 2H, Ar—H); 7.612, 7.606 (d, 2H, Ar—H); 7.205–7.177 (dd, 2H, Ar—H); 6.871, 6.850 (d, 2H, Ar—H); 6.772, 6.767 (d, 2H, Ar—H); 6.531–6.505 (dd, 2H, Ar—H); 5.025 (s, 4H, —NH_2); 1.586 (s, 6H, —CH_3).

2.3. Processing methods

The preparation process of glass-fiber-reinforced BhPN composites was described as follows: a plain weave glass cloth was dried at 120 °C for 2 h before use, and then impregnated with the BhPN/DMF solution (25 wt%). The solvent was allowed to evaporate at 80, 120, and 150 °C (2 h each) in an oven. The impregnated clothes were stacked between two isolation films and hot-pressed with a 30-ton Carver compression molder. The samples were cured at 160 °C for 2 h, 200 °C for 2 h, and 250 °C for 3 h consecutively, and postcured at 375 °C for 2 h. Finally, the composite laminates with different curing degrees were cut into appropriate size for dynamic mechanical analysis (DMA). Same curing cycle was used for samples prepared for thermogravimetric analysis (TGA).

The samples consisted of DGEBA and curing agents (BhPN or DDM) were prepared by a melt-blending method. The resin mixtures containing stoichiometric amount of curing agent were heated to approximately 100 °C in a glass beaker, and stirred for a few minutes until homogeneous resin mixtures were formed. The mixtures were then poured into a metal mold treated with silicone-based mold-release agent. The degassed mixed resins were polymerized gradually at 180 °C for 3 h, 200 °C for 2 h, and 250 °C for 2 h in an air-circulating oven.

2.4. Characterization and measurements

FT-IR spectra were recorded on a BRUKER VECTOR 22 spectrometer and obtained at a resolution of 2 cm^{-1} at room temperature.

^1H NMR spectra were obtained using a BRUKER AVANCE 400 MHz spectrometer with tetramethylsilane as the internal standard and DMSO-d_6 as solvent.

Dynamic differential scanning calorimetric (DSC) study was performed on a TA Q20 Instruments at different heating rates of 5, 10, 15, and 20 °C/min and a constant nitrogen flow of 50 mL/min.

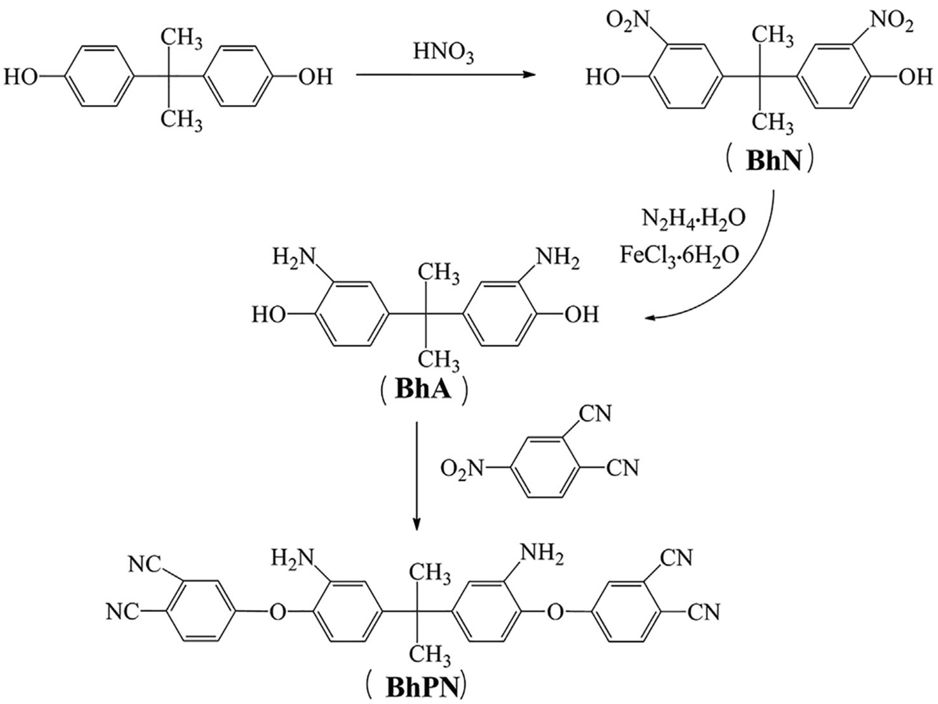
Rheological behavior of BhPN was obtained using a TA DHR-1 Rheometer equipped with disposable 25 mm parallel plate. The processing window was obtained at a frequency of 10 rad/s and a heating rate of 10 °C/min, and the measuring gap was set at 1000 μm under an oscillatory shear mode. Similarly, the gelation time as a function of time with constant temperature of 140, 160 or 180 °C was performed.

TGA tests of BhPN and epoxy polymers were carried out on a TA Q50 Instruments at a heating rate of 10 °C/min under nitrogen atmosphere from 50 to 800 °C.

DMA measurements in a single cantilever mode were performed on TA Q800 dynamic mechanical analyzer. The samples with a dimension of 35 mm × 8 mm × 2 mm were heated at a temperature ramp of 5 °C/min.

2.5. Theory section

The activation energy of polymerization (E_a) can be obtained by the Kissinger's method without a previous knowledge of the kinetic model. The Kissinger's equation can be expressed as shown in Eq. (1). Where β is the heating rate, A is the frequency factor, and R is the gas constant.



Scheme 1. Synthesis of diamine-functional bisphthalonitrile.

Variable T_p is the exothermic peak temperature obtained from DSC curves at different heating rates.

$$\mathrm{In}\left(\frac{\beta}{T_P^2}\right) = \mathrm{In}\left(\frac{\mathrm{A.R}}{\mathrm{E_a}}\right) - \frac{\mathrm{E_a}}{\mathrm{R}}\frac{1}{T_P} \tag{1}$$

According to the Van Krevelen's equation, there is a linear relationship between the limiting oxygen index (*LOI*) and char yield (Y_C) for halogen-free polymers as listed in Eq. (2).

$$LOI\,(\%) = 17.5 + 0.4Y_C \tag{2}$$

3. Results and discussion

3.1. Structural characterization

The intermediate BhA was simply prepared from bisphenol-A using nitration followed by reduction (Figs. S1 and S2). The BhPN monomer was designed and synthesized by a nucleophilic substitution reaction from the alkali salt of BhA and 4-nitrophthalonitrile at the presence of K_2CO_3, as depicted in Scheme 1. Its molecular structure was verified by ^{1}H NMR technique, and the corresponding spectrum is presented in Fig. 1. The peaks at 5.025 and 1.586 ppm belonged to primary amine and methyl protons, respectively, and other peaks at 6.505–8.046 ppm corresponded to aromatic protons. As shown in Fig. 2a, the FT-IR spectrum confirmed diamino unit at 3472 and 3375 cm^{-1}, and the typical absorption band at 2230 cm^{-1} was assigned to the stretching vibration of cyano groups [10,35]. These results show a novel diamine-functional bisphthalonitrile can be synthesized by this pathway.

3.2. Curing characteristics of BhPN monomer

The curing behavior of the pristine BhPN monomer was studied by DSC method at a temperature ramp of 10 °C/min, as depicted in Fig. 3a. The endothermic transition at 89 °C belonged to the melting point of BhPN. A sharp exotherm with a peak maximum around 233 °C was attributed to the thermal polymerization of cyano groups, while a weak exotherm located between 280 and 360 °C was assigned to the secondary cure process at higher temperature. In typical phthalonitrile, there is no obvious exothermic peak in the DSC curve owing to the extremely sluggish polymerization rate [44]. Therefore, a self-catalyzed curing behavior was realized for BhPN monomer, which could be thermally polymerized to a cross-linking network without addition of other curing additives. After the first heating scan, the quenched sample was heated again (second heating scan). However, the DSC curve of Fig. 3b didn't exhibit a glass-rubber transition, implying that the formation of a highly crosslinked, rigid polymer with little molecular mobility. As shown in Fig. 2b, after heated at 250 °C for 3 h, the characteristic absorption of primary amine was converted into secondary amine (3369 cm^{-1}). In addition, the new peaks at 1657, 1529, and 1030 cm^{-1} were attributed to the characteristic absorptions of C=N bond in isoindole ring, stretching vibrations in triazine and phthalocyanine ring, respectively [45]. However, the band at 2230 cm^{-1} didn't disappear completely demonstrated that a portion of cyano groups still

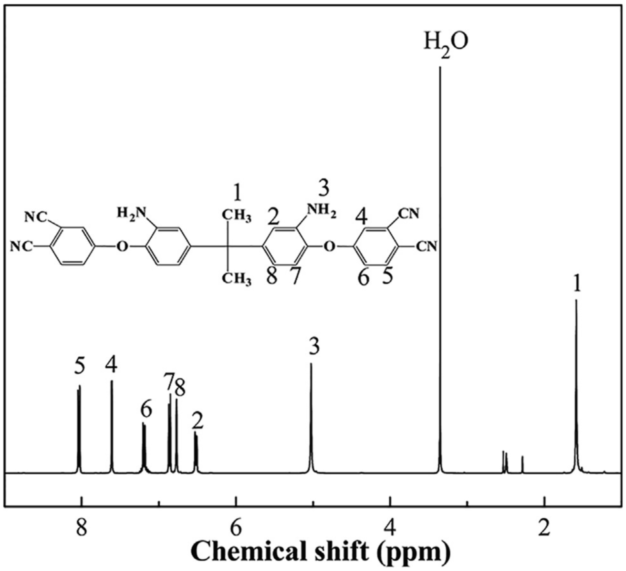


Fig. 1. ^{1}H NMR spectrum of BhPN in DMSO-d_6.

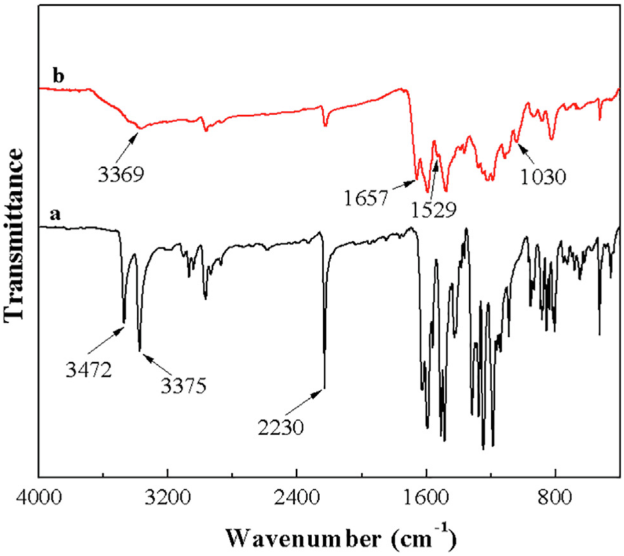


Fig. 2. FT-IR spectra of BhPN (a) monomer and (b) polymer after cured at 250 °C for 3 h.

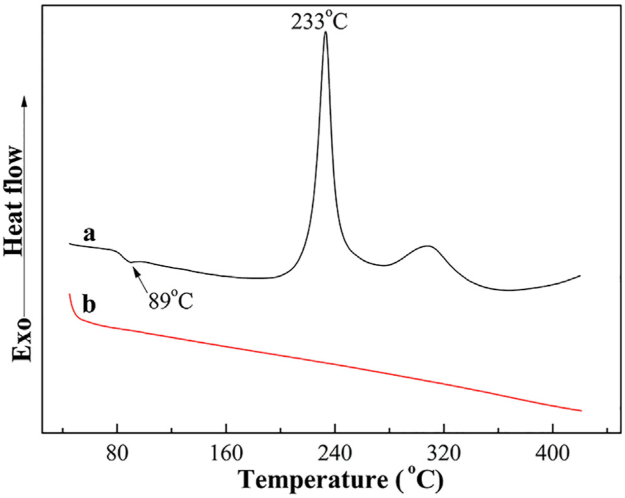


Fig. 3. DSC curves of BhPN monomer in the (a) first and (b) second heating scans.

remain unreacted because of the prevalence of steric factors. These spectral observations also indicate that the diamino unit in the backbone structure of BhPN can induce the polymerization of cyano groups to form thermoset.

Fig. 4 displays the DSC thermograms of BhPN monomer at different heating rates of 5, 10, 15, and 20 °C/min. The figure indicates that the initial polymerization temperature (T_i) and exothermic peak temperature (T_P) shift to higher temperature with the increasing heating rate. According to the Eq. (1), the activation energy of polymerization (Ea) can be determined from the slope of $\ln(\beta/T_P{}^2)$ versus $1/T_P$ plot (Fig. 5). Consequently, the calculated value of Ea was 72.86 kJ/mol, and the linear correlation coefficient was 0.999. The Ea value of BhPN is lower than those autocatalytic phthalonitriles reported in the literature (79.18–79.29 kJ/mol) [46]. These results indicate that BhPN has an improved polymerization activity due to the presence of higher amino concentration and the increased chance of molecular collisions.

3.3. Rheological behavior of BhPN monomer

In order to determine the processability of BhPN monomer, the complex viscosity as a function of temperature was tested from 80 to

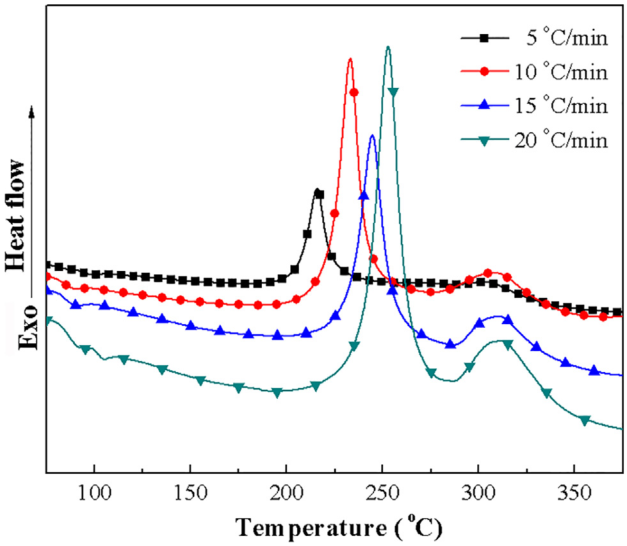


Fig. 4. DSC curves of BhPN at different heating rates.

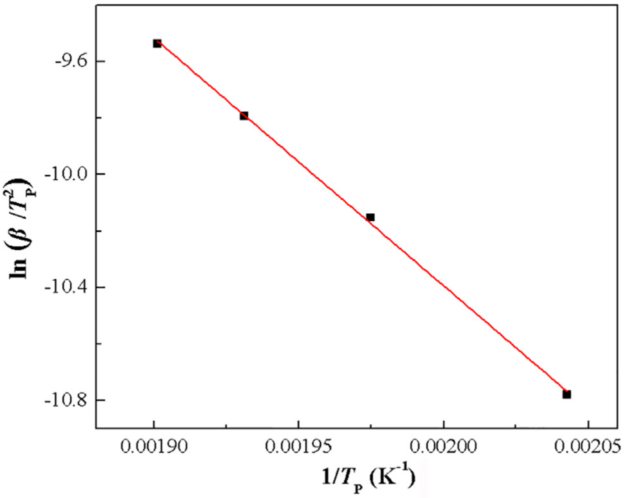


Fig. 5. Plot of $\ln(\beta/T_P{}^2)$ against $1/T_P$ by the Kissinger method.

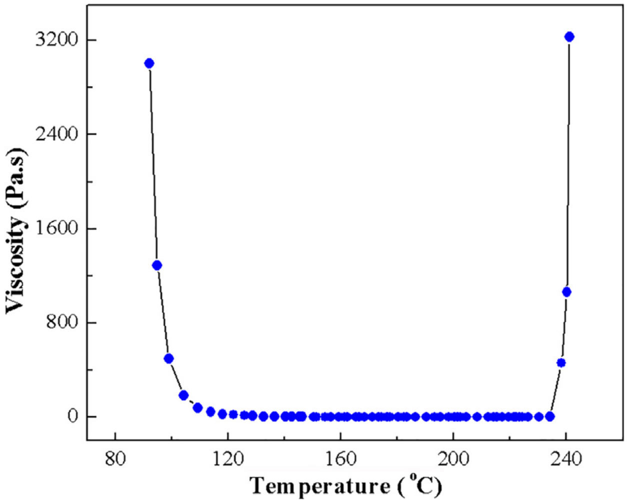


Fig. 6. Complex viscosity of BhPN as a function of temperature.

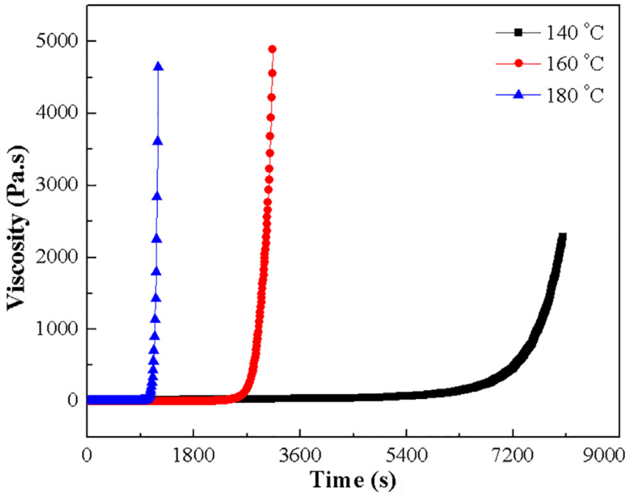


Fig. 7. Complex viscosity of BhPN as a function of time.

250 °C. As shown in Fig. 6, the viscosity gradually decreased with temperature and up to approximately 1000 Pa.s at 95 °C, indicating the liquefying temperature [47]. Next, a minimum melting viscosity varied from 0.1 to 1 Pa.s was observed at between 150 and 230 °C. At temperature above 240 °C, the rapid increase of viscosity revealed the polymerization of bisphthalonitrile catalyzed by diamino group. The relatively low melting viscosity and broad processing window are advantageous to the formation of complex composite structures by resin infusion or RTM process. The typical viscosity change of the pure BhPN as a function of time was measured as depicted in Fig. 7. As expected, the melt viscosity increased at faster rate with increasing processing temperature [11]. The viscosity of liquated BhPN at 140, 160, and 180 °C increased to 1000 Pa.s in about 130, 53, and 30 min, respectively. The viscosity studies reveal that the polymerization rate of the as-prepared self-catalyzed bisphthalonitrile can be easily controlled by varying the processing temperature.

3.4. Thermal properties of BhPN polymer

The thermal stabilities of BhPN polymers were evaluated by TGA in nitrogen atmosphere. Fig. 8 showed that the temperatures of 5% and 10% weight loss ($T_{5\%}$ and $T_{10\%}$) increased from 405 and 480 °C to 444 and 506 °C when the temperature rose from 250 to 375 °C, and a high char yield (Y_C) recorded as 75.18% and 76.53% at 800 °C, respectively. It is noteworthy that the higher curing temperature resulted in an improved thermal stabilities of the cured BhPN polymers. In order to determine the dynamic mechanical properties, the glass-fiber-reinforced BhPN composites were prepared by a prepreg-laminated method as mentioned in the experimental section. The final resin content in the composites was calculated to be 35 wt%. The plots of storage modulus and tanδ as a function of temperature are shown in Fig. 9. An approximated Tg value of 307 °C was observed upon heat treatment at 250 °C for 3 h, as determined by the peak temperature of tanδ. Another transition above 330 °C was mainly from further polymerization reaction of the unreacted cyano groups. When the sample was further heated at increased temperature of 375 °C, the Tg value was over 400 °C. The Tg values and decomposition data of BhPN polymers based on different curing degrees are summarized in Table 1.

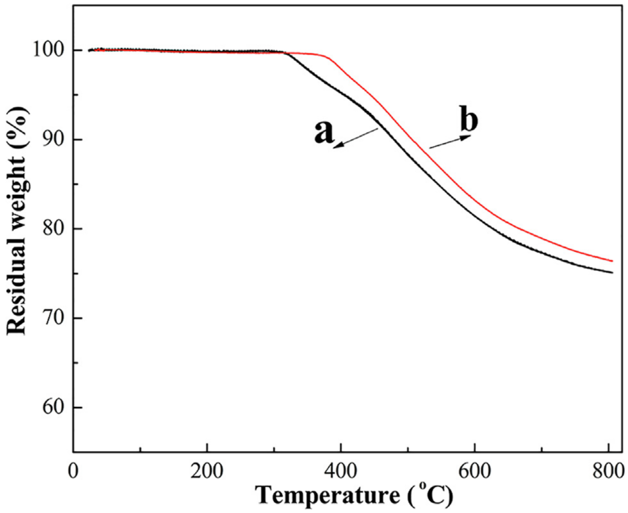


Fig. 8. TGA curves of BhPN polymers cured at (a) 160 °C for 2 h, 200 °C for 2 h, and 250 °C for 3 h and (b) postcured at 375 °C for 2 h.

3.5. Cure studies of epoxy resin

The polymerization profile of DGEBA/BhPN system was investigated by DSC method as noted in Fig. 10, and the results are summarized in Table 2. For comparison, DSC thermogram of DGEBA cured with DDM, one of the most commonly used epoxy curing agent, was also displayed. Both of the reactant compositions were mixed in equimolar ratio of amino to epoxy groups. In Fig. 10a, the DGEBA/DDM system showed a single exothermic transition at 166 °C corresponding to the polymerization of epoxy and amino groups. However, two overlapped exothermic peaks were observed for DGEBA/BhPN sample (Fig. 10b). The first exotherm appeared as a shoulder peak emerging at 162 °C because of the epoxy-amine reaction. The second exotherm peaked at 220 °C was ascribed to the polymerization reaction of cyano groups catalyzed with active-hydrogen. Moreover, the DGEBA/BhPN system showed a lower value (338 J/g) of polymerization heat compared to that of DGEBA/DDM system (437 J/g). These data reveal that the DGEBA can be cured with BhPN at a desirable polymerization rate and moderate temperature.

The structural change of DGEBA/BhPN blend during polymerization process was monitored by FT-IR as plotted in Fig. 11. The characteristic absorption band assigned to cyano groups gradually reduced with polymerization temperature, but didn't disappear at any curing stage. After curing 3 h at 180 °C, the band of epoxy ring at 915 cm^{-1} disappeared, suggesting epoxy polymerization via ring-opening was completed. At the same time, the new peaks at 1716, 1548, and 1012 cm^{-1} assigned to the characteristic absorptions of isoindoline, triazine and phthalocyanine, respectively, were observed. These results suggest that the polymerization reaction of cyano groups has occurred. After scanning to 200 and 250 °C, the alone peak attributed to isoindoline at 1715–1721 cm^{-1} was gradually enhanced. This is most likely that the hydroxyl groups generated by epoxy ring-opening can promote the polymerization of cyano groups and plenty of isoindoline rings were formed finally. The possible reaction mechanism is shown in Scheme 2.

3.6. Thermal properties of cured epoxy resin

The thermal stabilities of epoxy polymers were evaluated by TGA under nitrogen environment. As shown in Fig. 12, the DGEBA/BhPN polymer exhibited $T_{5\%}$ at 379 °C and maximum degradation temperature ($T_{\max}$) around 406 °C, which were 9 and 24 °C higher than that of DGEBA/DDM polymer, respectively. After heating the sample to 800 °C, the Y_C of DGEBA/BhPN sample was up to 41.4% and that of DGEBA/DDM was only 15.3%. According to the Eq. (2), the calculated *LOI* value of DGEBA/BhPN system achieved 34.06%, indicating that the flame retardancy of epoxy resin was significant improved using BhPN as curing agent.

As can be observed from Fig. 13a and Table 3, the storage modulus (E') of epoxy polymers in the presence of DDM and BhPN were 1953

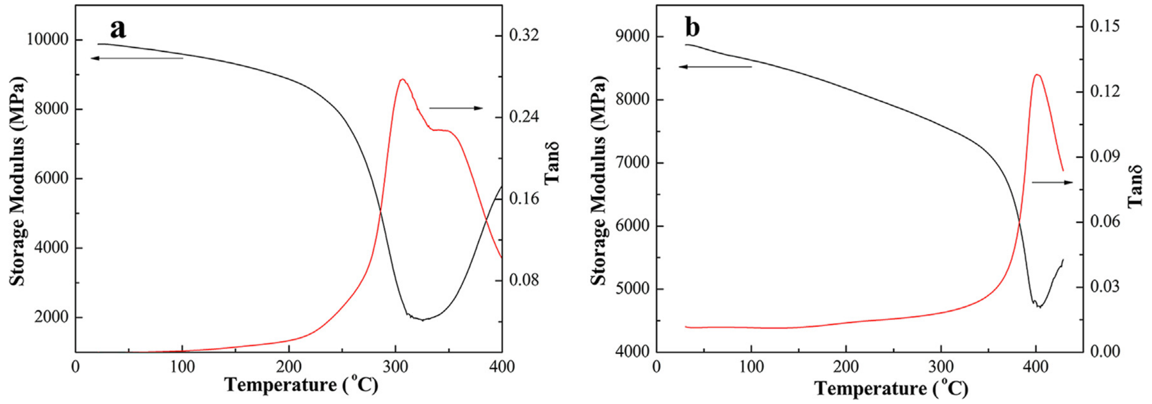


Fig. 9. DMA plots of BhPN composites cured at (a) 160 °C for 2 h, 200 °C for 2 h, and 250 °C for 3 h and (b) postcured at 375 °C for 2 h.

Table 1
TGA and DMA data of BhPN polymers.

Cure schedule	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Y_C at 800 °C (%)	Tg (°C)
160 °C, 2 h; 200 °C, 2 h; 250 °C, 3 h	405	480	75.18	307
160 °C, 2 h; 200 °C, 2 h; 250 °C, 3 h; 375 °C, 2 h	444	506	76.53	403

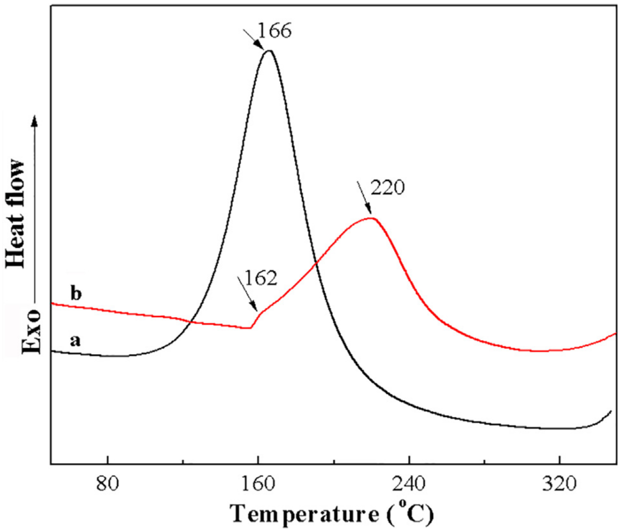


Fig. 10. DSC curves of DGEBA cured with (a) DDM and (b) BhPN.

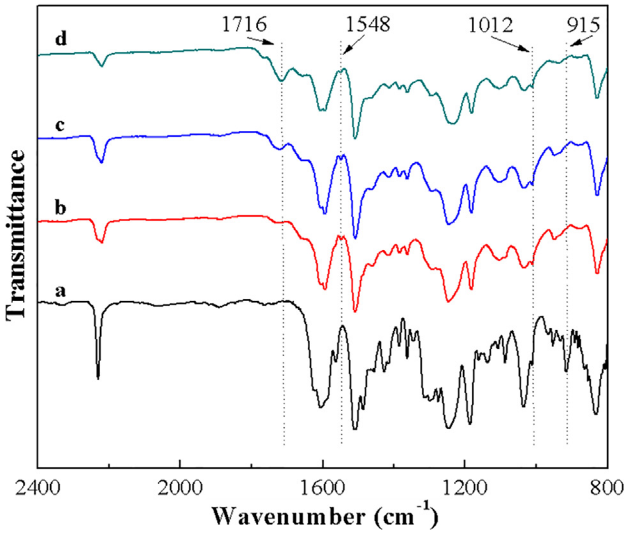


Fig. 11. FT-IR spectra of DGEBA/BhPN blends (a) at room temperature and cured at (b) 180 °C for 3 h, (c) 200 °C for 2 h, and (d) 250 °C for 2 h.

Table 2
DSC parameters of epoxy resins.

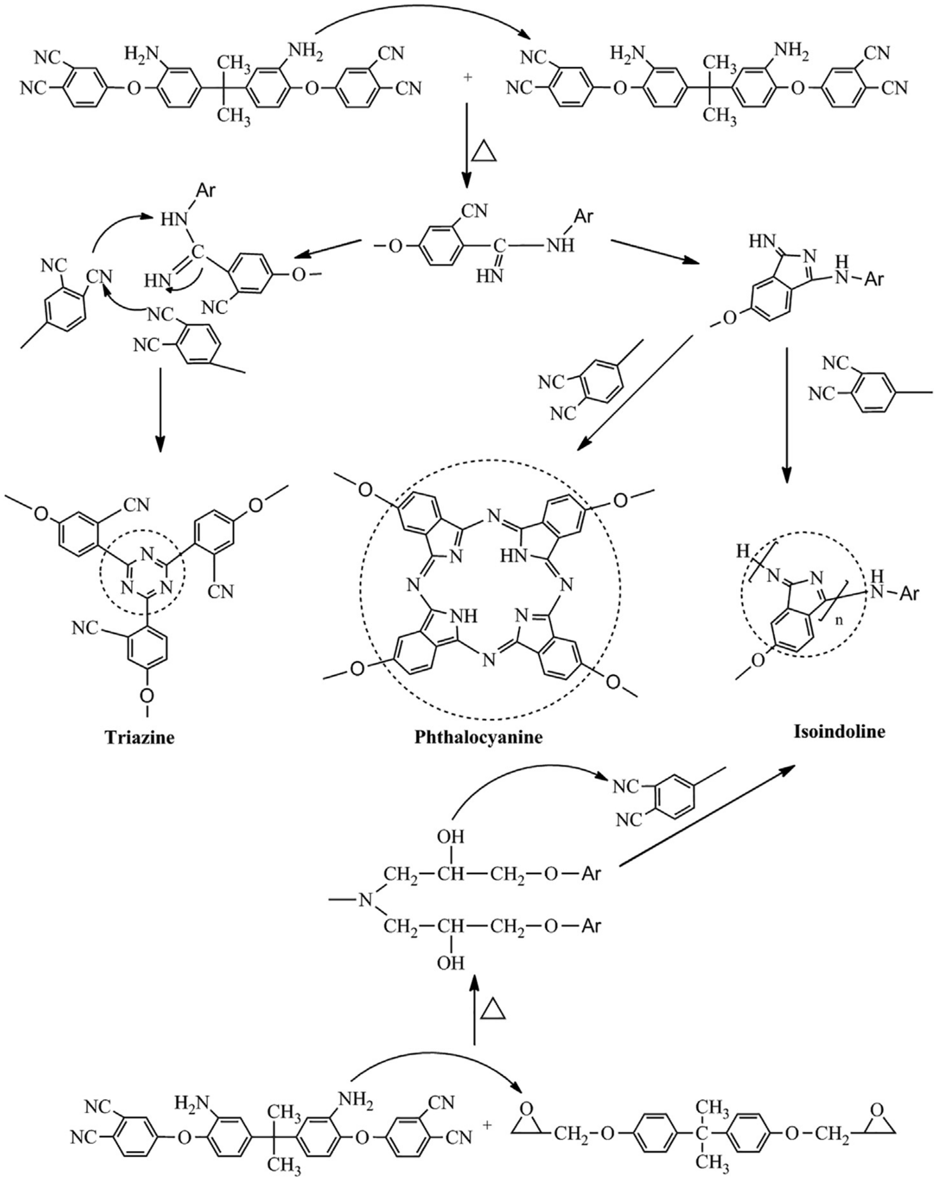
Samples	T_i (°C)	T_p^1 (°C)	T_p^2 (°C)	Polymerization heat (J/g)
DGEBA/DDM	130	166	–[a]	437
DGEBA/BhPN	156	162	220	338

[a] No T_p obtained.

and 2935 MPa at 40 °C, respectively. The modulus may be affected by the crosslinking density of epoxy resins [48]. As shown in Fig. 13b, the DGEBA/BhPN system exhibited a much higher Tg with a value of 253 °C than DGEBA/DDM system (193 °C). Furthermore, a single but wider tanδ peak for DGEBA/BhPN system was observed. This may be attributable to the concerted copolymerization between the epoxy and diamine-functional bisphthalonitrile, implying the formation of multiple cross-linked structures. Further studies on thermal degradation mechanism, mechanical properties, and microstructure evolution are under way.

4. Conclusions

In this paper, we have synthesized and characterized a novel bisphthalonitrile derivative containing diamino group. Its thermal behavior and curing characteristics were studied by DSC and FT-IR analysis. Results indicated that the BhPN monomer could be thermally polymerized in the absence of curing catalyst and the resultant crosslinking network was composed of heat-resisting heteroaromatic structure. The thermo-mechanical properties and thermal stabilities of the resulting BhPN polymers were improved with increasing post-cure temperature. Besides, the BhPN monomer was used to cure DGEBA epoxy resin, and the results revealed that the DGEBA/BhPN polymer showed higher thermal properties and Tg than DGEBA/DDM system owing to the existent cyano groups. Consequently, the diamine-functional bisphthalonitrile can be used not only as matrix resin for high performance composite, but also curing agent for the traditional epoxy component.



Scheme 2. Possible polymerization process between BhPN and DGEBA.

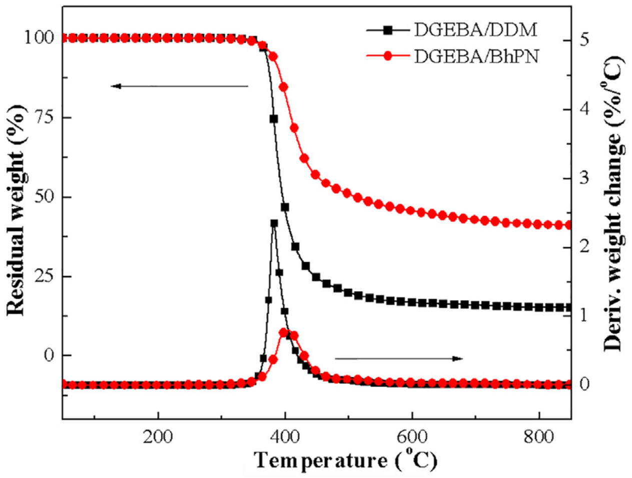


Fig. 12. TGA curves of DGEBA polymers in nitrogen.

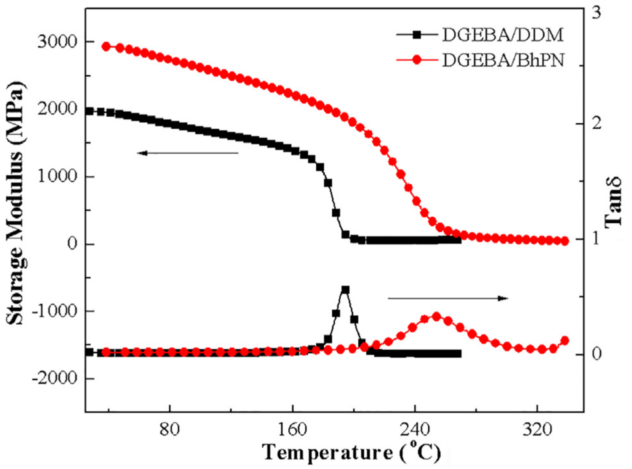


Fig. 13. DMA curves of DGEBA polymers.

Table 3
TGA and DMA data of epoxy resins.

Samples	TGA analysis					DMA analysis	
	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	Y_C at 800 °C (%)	*LOI* (%)	E′ at 40 °C (MPa)	Tg (°C)
DGEBA/DDM	370	375	382	15.3	23.63	1953	193
DGEBA/BhPN	379	390	406	41.4	34.06	2935	253

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Declaration of Competing Interest

None.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2019.109304.

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