

# Effect of Different Aromatic Amines on the Crosslinking Behavior and Thermal Properties of Phthalonitrile Oligomer Containing Biphenyl Ethernitrile

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**ABSTRACT:** To find a proper amine to promote the processability of phthalonitrile-based composites, three different aromatic amines: 4-aminophenoxypthalonitrile (APN), 2,6-bis(4-diaminobenzoyl) benzonitrile (BDB) and 4,4'-diaminediphenyl sulfone (DDS) were used as curing agents to investigate the crosslinking behavior and thermal decomposition behavior of phthalonitrile oligomer containing biphenyl ethernitrile (2PEN-BPh). Differential scanning calorimeter (DSC) and dynamic rheological analysis were employed to study the curing reaction behavior of the phthalonitrile/amine blends and prepolymers. The studies revealed that BDB was the preferred curing agent and the preferred concentration of BDB was 3 wt %. The thermal

properties of the 2PEN-BPh polymers were monitored by TGA, and the results indicated that all the completely cured 2PEN-BPh polymers maintained good structure integrity upon heating to elevated temperatures and these polymers could thermal stabilize up to over 550°C in both air and nitrogen atmospheres. Dynamic mechanical analysis (DMA) showed the glass transition temperature ( $T_g$ ) exceeded 450°C when the 2PEN-BPh polymer post cured at 375°C for 8 h. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2331–2337, 2011

**Key words:** aromatic amine; crosslinking behavior; phthalonitrile oligomer; thermal properties; glass transition

## INTRODUCTION

At the naval research laboratory (NRL), Keller's group had reported an important class of high performance polymers-phthalonitrile polymers in the 1980s. These polymers were used for aerospace, marine, and microelectronic industries<sup>1,2</sup> owing to their good mechanical properties, outstanding thermal and thermo-oxidative stability, superior moisture resistance, and fire resistance.<sup>3–10</sup> Many researches indicated that the polymerization temperature of neat phthalonitrile monomer was up to 375°C and the polymerization procedure needed several days under this condition to form stable polymers.<sup>2–4</sup> Gradually, it was found that the curing reaction could be promoted and the curing temperature could be lowered by adding a small amount of curing additives such as phenols,<sup>11</sup> organic amines,<sup>3</sup> strong organic acids,<sup>12</sup> strong organic acids/amine salts,<sup>13</sup> metals and their salts.<sup>14</sup>

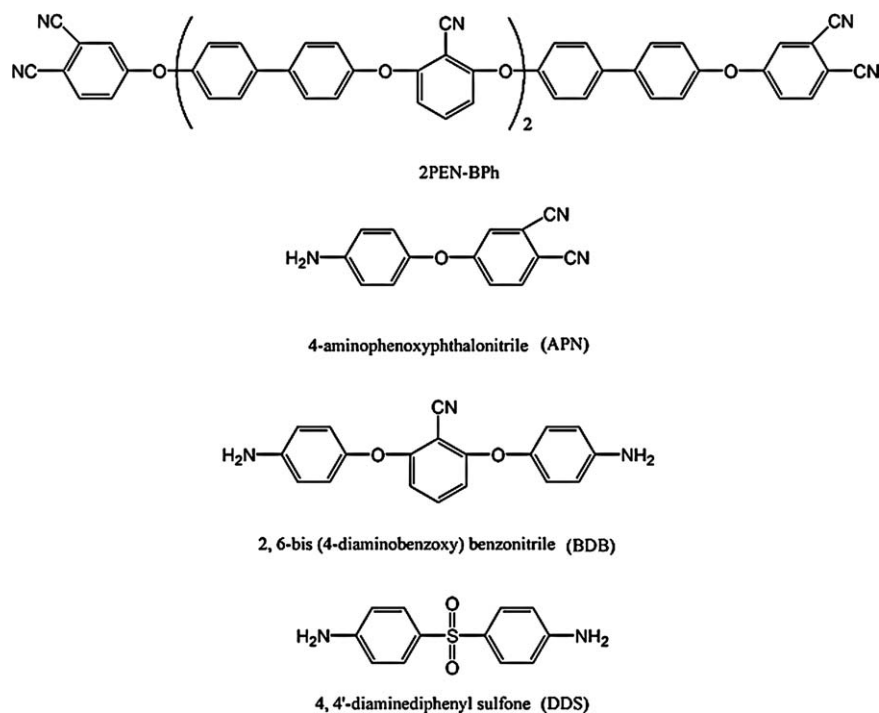
Biphenyl bisphthalonitrile (BPh) was the first phthalonitrile-based, high-temperature resin reported<sup>3,15</sup> and had been the most extensively stud-

ied phthalonitrile monomer. In spite of the advantages of BPh system, polymerization began immediately after the monomer melted (231–233°C) which resulted in a narrow processing window (~ 20°C). The narrow processing window prevented these resins from being fully utilized and also caused processing difficulties.<sup>10</sup>

To date, we had successfully synthesized an oligomer-2PEN-BPh<sup>16</sup> in our laboratory, which incorporated aromatic ether-containing linkages between the terminal phthalonitrile units.<sup>17,18</sup> The incorporation of linkages containing aromatic ether effectively lowered the melting temperature of monomer, but the curing rate of monomer was still very sluggish. Therefore, it was necessary to incorporate a curing agent to accelerate the curing process. Keller's group had studied phthalonitrile polymers and composites formulated with *m*-APB amine as the curing agent,<sup>6</sup> however, loss of amine from some volatility and thus a slowdown of cure had been observed when curing thin sections in an open mold.<sup>1</sup> Based on this idea, try to find curing agents that did not volatilize at elevated cure reaction temperatures and that were less reactive relative to *m*-APB was a key to promote the processability of phthalonitrile-based composites.<sup>1</sup>

In this article, one nitrile side chain-containing diamine (BDB) and one sulfone-containing diamine

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**Figure 1** Chemical structures of the 2PEN-BPh oligomer and the curing agents.

(DDS) were chosen as curing agents. For the sake of comparison, one amine containing a single amino-group (APN) was also chosen as curing agent. With such amines, the curing reaction behavior and thermal decomposition behavior of 2PEN-BPh oligomer was investigated in detail. The curing behavior was studied by differential scanning calorimeter (DSC) and dynamic rheological analysis. The thermal decomposition behavior of fully cured 2PEN-BPh resin was monitored by TGA.

## EXPERIMENTAL

### Materials

All starting solvents were reagent-grade and were used without further purification. Dimethyl sulfoxide (DMSO) and anhydrous ethanol were obtained from Tianjin BODI chemicals. The 4-aminophenoxyphtalonitrile (APN,  $T_m = 132\text{--}134^\circ\text{C}$ ) was synthesized from 4-nitrophthalonitrile and 4-aminophenol according to Ref. 19. The 2,6-bis(4-diaminobenzoxy) benzonitrile (BDB,  $T_m = 215^\circ\text{C}$ ) was prepared according to the Ref. 9. The 4,4'-diaminediphenyl sulfone (DDS,  $T_m = 174^\circ\text{C}$ ) was purchased from Sichuan Dongcai chemicals. Phthalonitrile oligomer containing biphenyl ether (2PEN-BPh) was prepared according to previous Ref. 16 and was further purified by recrystallization from DMSO/anhydrous ethanol mixed solvents. The structures of the 2PEN-BPh oligomer and curing agents were shown in Figure 1.

### Preparation of phthalonitrile/amine blends, prepolymers, and polymers

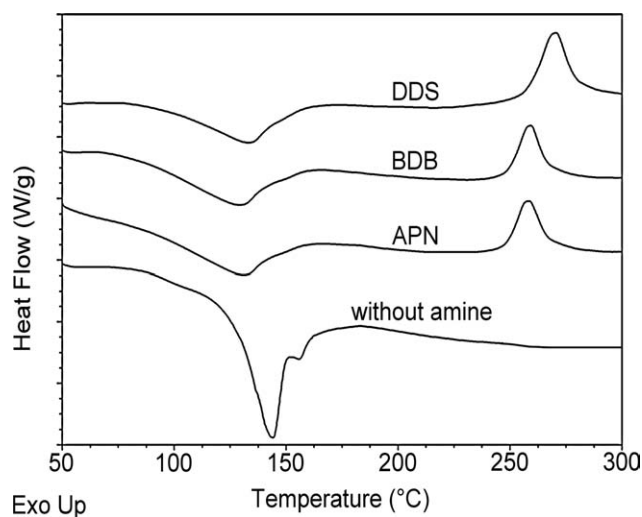
Phthalonitrile/amine blends were prepared by blending 2PEN-BPh oligomer with predetermined concentration (5 wt %) of three aromatic amines (APN, BDB, or DDS) in powdered form under ambient condition.

Phthalonitrile/BDB blends were prepared by blending 2PEN-BPh oligomer with 2, 3, or 5 wt % of BDB as curing agent.

A typical 2PEN-BPh/amine prepolymer preparation was accomplished by adding 5 wt% aromatic amine (APN, BDB, or DDS) or adding BDB of different concentration (2, 3, or 5 wt%) as curing agent to each 2PEN-BPh melt at  $250\text{--}260^\circ\text{C}$ <sup>17</sup> in air, stirring vigorously for about 15 min, then the reaction between the diamine and the phthalonitrile end groups was quenched by rapidly cooling the melt to room temperature.<sup>20</sup> Part of the prepolymers was pulverized for use in viscosity studies.

The 2PEN-BPh/amine polymers were prepared by thermally activated polymerization of the above prepolymers in air-circulation oven in sequence at elevated temperatures. The detailed polymerization procedures of the prepolymers and polymers were according to Ref. 20.

Samples for DMA were made in a mold with cavity dimensions of  $35\text{ mm} \times 10\text{ mm} \times 3.5\text{ mm}$  and sanded to a thickness of 3 mm. The samples were cured by heating according to the above polymerization procedures.



**Figure 2** DSC curves of 2PEN-BPh/amine blends with various amines.

### Measurements

The thermal curing behavior of the 2PEN-BPh oligomer with different curing agents and different concentrations of the same curing agent was studied by TA Instruments Modulated DSC-Q100 with a heating rate of  $10^{\circ}\text{C min}^{-1}$  and a nitrogen flow rate of  $50\text{ mL min}^{-1}$ . The thermal decomposition behavior of the 2PEN-BPh polymers was determined by TA Instruments Q50 thermogravimetric analyzer at a heating rate of  $20^{\circ}\text{C min}^{-1}$  under nitrogen or air atmosphere at a flow rate of  $100\text{ mL min}^{-1}$ . Rheological behavior of curing process was performed using TA Instruments Rheometer AR-G2 at low strain value (0.5%) and with a frequency of 1 Hz at  $250^{\circ}\text{C}$  in air. The glass transition temperatures ( $T_g$ ) of 2PEN-BPh resin formulated with 3 wt % BDB were estimated from the modulus versus temperature plots obtained by DMA. TA Instruments QDMA-800 dynamic mechanical analysis was used to perform the test in the torsional mode at a heating rate of  $3^{\circ}\text{C min}^{-1}$ , 0.5% torque range, and 1 Hz frequency.

## RESULTS AND DISCUSSION

### Crosslinking behavior of 2PEN-BPh/amine blends

DSC was used to monitor the effect of different curing agents on the curing reaction behavior of 2PEN-BPh oligomer, and the DSC curves obtained by heating the phthalonitrile/amine blends to  $300^{\circ}\text{C}$  were presented in Figures 2 and 3.

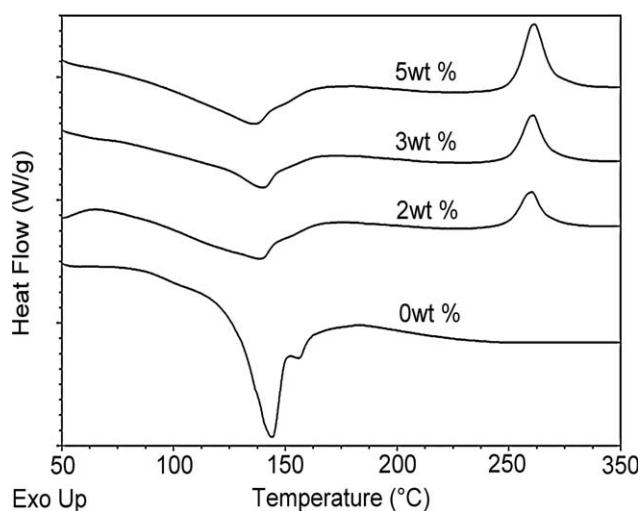
The DSC thermograms of the 2PEN-BPh oligomer with different aromatic amines were compared and the results were shown in Figure 2. It was observed that the 2PEN-BPh oligomer without amine exhibited only two endothermic peaks, and no polymerization peak was found. However, when adding the

same concentration of different aromatic amines, every curve exhibited an exothermic peak which indicated that it was necessary to incorporate aromatic amine as curing agent to accelerate the curing process of 2PEN-BPh effectively.

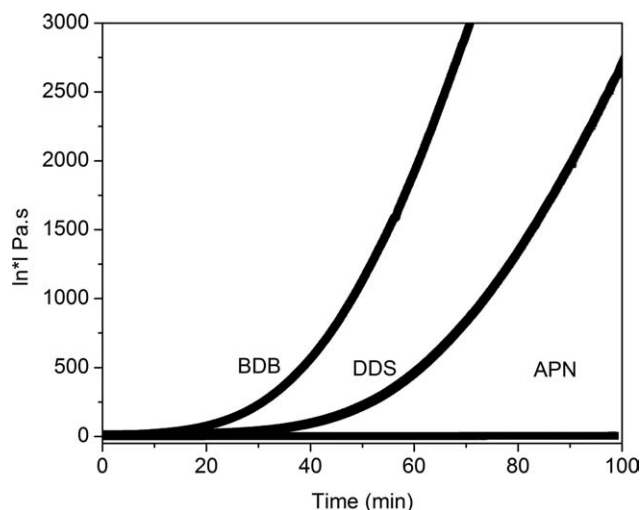
From the DSC results of Figure 3, it was found that no exothermic peak was observed in pure 2PEN-BPh oligomer; whereas when different contents of BDB curing agent were added into the oligomer, an obvious exothermic peak appeared and became larger and larger with the increasing of the concentration of curing agent. The melting endotherms ( $T_{\text{melt}}$ ) were ranged from  $135$  to  $140^{\circ}\text{C}$  and the endothermic heat flows ranged from  $24.54$  to  $32.77\text{ J g}^{-1}$ ; at the same time, the polymerization exotherms were at around  $260^{\circ}\text{C}$  and the exothermic heat flow were in the range of  $9.726$ – $17.70\text{ J g}^{-1}$ . Both of them increased with the increasing of BDB concentration, which indicated that increasing of the concentration of curing agent BDB could make the 2PEN-BPh prepolymerize easier.

### Rheological studies of 2PEN-BPh/amine prepolymers

Rheological studies were performed on the 2PEN-BPh/amine prepolymers to further characterize the curing behavior under isothermal conditions. The variation of the melting viscosity of the prepolymers was determined to study the effect of curing agents and the concentrations of curing agent on the rheological behavior of the 2PEN-BPh/amine prepolymers. The studies were carried out by heating the prepolymers between parallel plates in a rheometer at  $250^{\circ}\text{C}$  and following the complex viscosity,  $G'$  and  $G''$  changed over time as the cure processed. The results were presented in Figures 4–6.



**Figure 3** DSC curves of 2PEN-BPh/BDB blends with various concentrations of BDB.



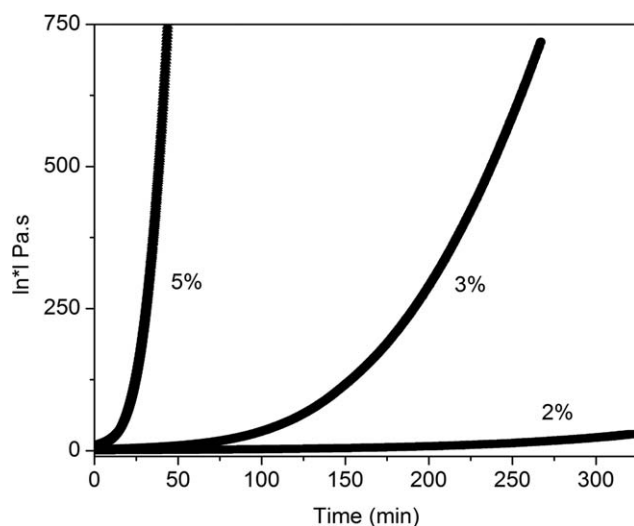
**Figure 4** Time sweep viscosity curves of 2PEN-BPh/amine prepolymers with various amines at 250°C.

Figure 4 compared the complex viscosity changes with cure time at 250°C for the 2PEN-BPh prepolymers with different curing agents. It was observed that the viscosity of 2PEN-BPh prepolymers increased gradually until gelation occurred. With the same concentration of different curing agents (APN, BDB, and DDS), the cure reaction progressed at a different rate. The measurements revealed that among the three aromatic amines, the viscosity of the prepolymer composition containing BDB increased at a faster rate than that of prepolymer composition containing APN or DDS. After measuring for 100 min, the viscosity of the prepolymer composition containing APN only increased to 4 Pa s<sup>-1</sup>, which was probably caused by the low concentration of -NH<sub>2</sub> in APN; however, the viscosity of BDB and DDS increased to over 2500 Pa s<sup>-1</sup>, and the

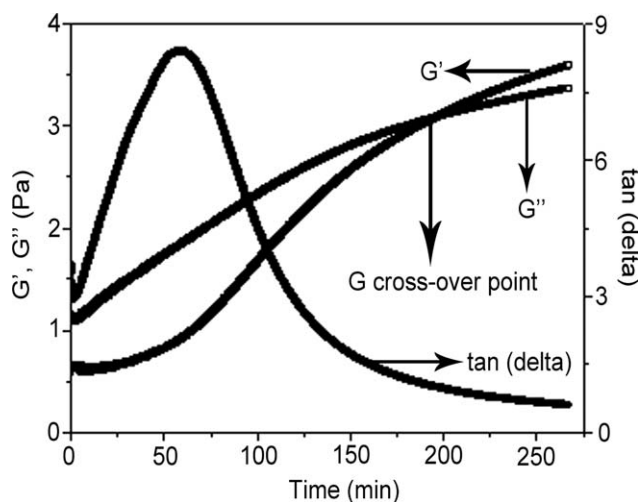
curing rate of the prepolymer composition containing BDB was faster than that of prepolymer composition containing DDS which may be attributed to the lower volatility of the BDB and the presence of the electron-withdrawing sulfone linking group in DDS.<sup>1</sup> Based on these results, BDB was selected as the preferred curing agent in the oligomeric phthalonitrile polymerization studies.

To determine the initial diamine concentration for polymer processing, viscosity measurements were conducted on the oligomeric phthalonitrile prepolymers at 250°C with various concentrations of BDB. A plot of viscosity change versus time at 250°C for phthalonitrile prepolymers containing 2–5 wt % BDB was shown in Figure 5. The measurements revealed that when the prepolymers were held at 250°C, the viscosity of the prepolymer with higher diamine concentration increased more rapidly. Specifically, with diamine concentration of 2 wt %, gradual increase in viscosity was observed over 5 h, which indicated that this concentration may not be high enough to accelerate the curing process; however, with the concentration of BDB increased to 5 wt %, the viscosity increased to 750 Pa s<sup>-1</sup> in less than 45 min. The viscosity studies revealed that the rate of diamine-catalyzed phthalonitrile polymerization could be easily controlled by varying the diamine concentration. In addition, the viscosity measurements demonstrated that higher curing concentration could be used to affect the phthalonitrile oligomer cure.

Control of polymerization rate was necessary for the fabrication of thick composite components where the melt had to impregnate large performs before gelation occurred. Based on the isothermal viscosity data, the concentration of 2 wt % was too low, yet the concentration of 5 wt % was too high which

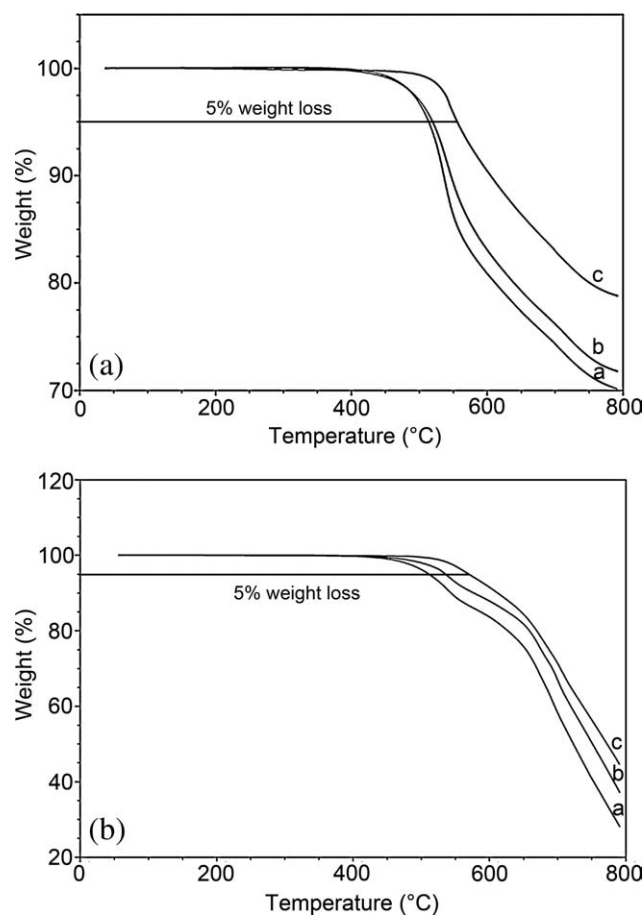


**Figure 5** Time sweep viscosity curves of 2PEN-BPh/BDB prepolymers with various concentrations of BDB at 250°C.



**Figure 6** Time sweep curves of 2PEN-BPh/BDB prepolymer with 3 wt % BDB at 250°C.





**Figure 7** TGA curves of the 2PEN-BPh/BDB prepolymers and polymer with 3 wt % BDB in (A) nitrogen and (B) air.

made the system have not enough time for degassing samples to reduced pressure prior to gelation. The gelation time (determined from the  $G'$  and  $G''$  crossover point)<sup>20</sup> of 2PEN-BPh prepolymer with 3 wt % BDB was observed at 195 min as shown in Figure 6. It showed that this condition allowed approximately a 195-min period for degassing samples to reduced pressure prior to gelation. The degassing was necessary to obtain void-free polymeric samples for dynamic mechanical property measurements.

In conclusion, the aromatic amine BDB was chosen as the preferred curing agent and the preferred concentration of BDB was 3 wt % in the subsequent phthalonitrile polymerization studies.

### Properties of 2PEN-BPh prepolymers and polymers

Thermal properties of 2PEN-BPh polymers with various cure extents

To investigate the effect of various cure extents on the properties of 2PEN-BPh polymers, the thermal stabilities of 2PEN-BPh polymer with 3 wt % of BDB were evaluated. TGA curves obtained by heating the samples with various cure extents to 800°C in nitrogen or air atmosphere were presented in Figure 7(a,b), and a-c (Figure 7) referred to the curing schedules.<sup>16</sup> The results showed the cure extents of 2PEN-BPh polymers and their thermal stabilities as a function of both the heating time and the curing temperature.<sup>20</sup> The data also revealed that the dependence of polymer thermal stabilities on the maximum heat treatment temperature.<sup>20</sup> The sample heat-treated to 250°C for 4 h exhibited 5% weight loss at 514.2, 511.4°C and char yield at 70.2, 28.2% when heated to 800°C in nitrogen and air, respectively. Following the successive heat treatments of the polymer to 325°C for 4 h, 375°C for 8 h, samples showed 5% weight loss at 519.7 and 556.0°C, respectively.

Thermal properties of fully cured 2PEN-BPh polymers

The thermal decomposition of completely cured 2PEN-BPh polymers that had been cured in the presence of the same concentration (5 wt %) of different aromatic amines (APN, BDB, and DDS) and that cured with various concentrations of BDB (2–5 wt %) were also examined by TGA. The results of these studies were summarized in Tables I and II, in which the initial degradation temperature ( $T_i$ ), the temperatures at weight loss 5% ( $T_{5\%}$ ), and the char yields for the polymers heated to 800°C were displayed.

When heated in nitrogen, the polymers started to degrade at temperatures ( $T_{5\%}$ ) of 557.1, 560.1, and 556.2°C when cured with APN, BDB, and DDS, respectively. The residual char yields of these polymers at 800°C were in the range of 76.3–77.7%. Whereas the polymers began to degrade at 569.1, 565.1, and 565.9°C and the char yields were in the range of 21.4–36.8% in air at 800°C when cured with APN, BDB, and DDS, respectively.

**TABLE I**  
Thermal and Thermo-Oxidative Stabilities of 2PEN-BPh Polymers with Various Amines

Samples	N <sub>2</sub>			Air		
	$T_i$ (°C)	$T_{5\%}$ (°C)	Char yield (%)	$T_i$ (°C)	$T_{5\%}$ (°C)	Char yield (%)
APN	506.6	557.1	77.5	517.4	569.1	33.8
BDB	514.4	560.1	77.7	517.9	565.1	36.8
DDS	498.4	556.2	76.3	509.8	565.9	21.4

**TABLE II**  
**Thermal and Thermo-Oxidative Stabilities of 2PEN-BPh Polymers with Various Concentrations of Amines**

Samples	N <sub>2</sub>			Air		
	$T_i$ (°C)	$T_{5\%}$ (°C)	Char yield (%)	$T_i$ (°C)	$T_{5\%}$ (°C)	Char yield (%)
2 wt %	504.8	557.8	78.1	521.3	569.2	44.7
3 wt %	515.7	565.6	79.6	521.2	570.1	48.2
5 wt %	514.4	560.1	77.7	517.9	565.1	36.8

All of the 2PEN-BPh polymers with varying concentrations of BDB (2–5wt %) exhibited thermal stability above 555°C, the initial decomposing temperatures ( $T_i$ ) were above 500°C and the char yields at 800°C were above 77% in nitrogen. Also these polymers had good thermo-oxidative stabilities with the initial decomposition temperatures ( $T_i$ ) above 517°C and the char yield at 800°C above 36% in air.

#### Dynamic mechanical properties of 2PEN-BPh polymers

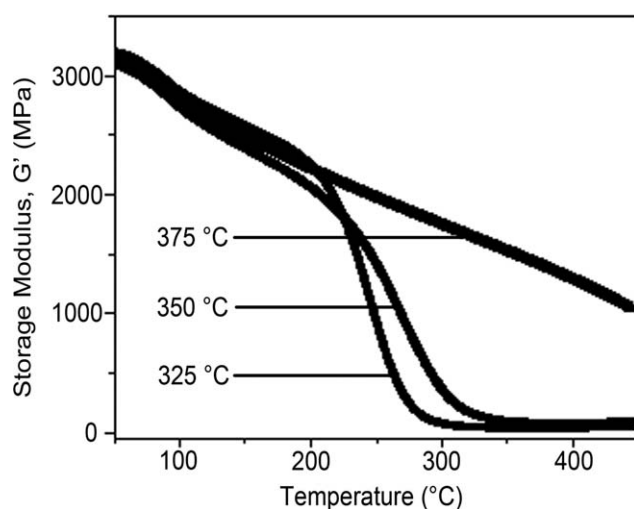
The dynamic mechanical properties of the 3 wt % BDB cured polymers were evaluated to ascertain changes in the sample modulus as a function of postcure time and temperature and to determine the  $T_g$ s of the cured polymers. Plots of the storage modulus ( $G'$ ) and damping factor ( $\tan \delta$ ) versus temperature were presented in Figures 8 and 9, respectively. The  $T_g$  was obtained from the onset of decay in storage modulus in a plot of  $\ln(\text{modulus})$  versus temperature. With 3 wt % BDB as the curing agent, approximate  $T_g$  values of 202, 240°C were observed after the thermal treatment in sequence of 4 h at 325°C, 4 h at 325°C, and 2 h at 350°C, respectively. No  $T_g$  was observed upon thermal treatment at 375°C for 8 h. The  $T_g$  values for the above-mentioned postcure conditions would be higher when estimation was

based on peak maxima in  $\tan \delta$  versus temperature plots which is shown in Figure 9.  $T_g$  values of 284, 310°C were observed after the thermal treatment at maximum temperature for 325 and 350°C, respectively. After thermal treatment at 375°C for 8 h, the  $T_g$  value was not observed before 450°C. These results revealed that postcure at higher temperature increased the cure extent and storage modulus.

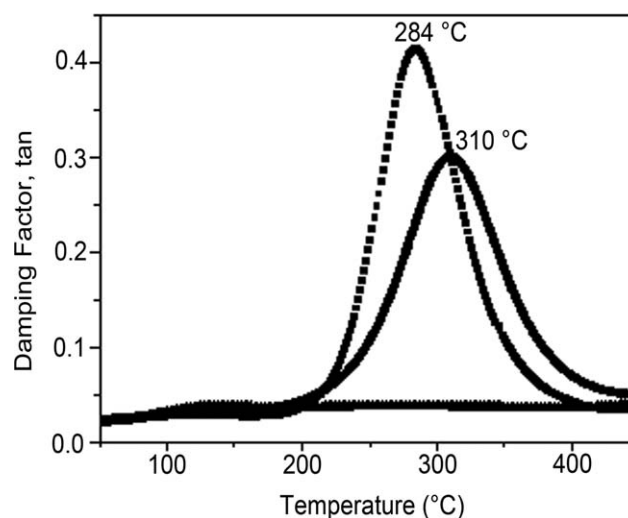
#### CONCLUSIONS

The curing reaction behavior of phthalonitrile oligomer containing biphenyl ether nitrile (2PEN-BPh) had been investigated with three different aromatic amines as curing agents. Cure reaction rates based on viscosity studies indicated that BDB reacted faster with 2PEN-BPh oligomer compared with APN and DDS. The viscosity measurements demonstrated the aromatic amine BDB was the preferred additive and the preferred concentration of BDB was 3 wt %.

The thermal decomposition data showed that all the 2PEN-BPh polymers maintained good structure integrity upon heating to elevated temperatures and exhibited excellent thermal and thermo-oxidative stability with different aromatic amines. Especially, the 2PEN-BPh polymer formulated with 3 wt % BDB could thermally stable up to over 560°C in both air



**Figure 8** Storage modulus ( $G'$ ) as a function of temperature for 3 wt % BDB cured polymers heated in nitrogen.



**Figure 9** Damping factor ( $\tan \delta$ ) as a function of temperature for 3 wt % BDB cured polymers heated in nitrogen.

and nitrogen atmospheres, and could achieve char yield above 79% in nitrogen and above 48% in air at 800°C. The dynamic mechanical analysis showed that postcure at higher temperature increased the cure extent and storage modulus. The glass transition temperature ( $T_g$ ) was improved with increase in the curing temperature and curing time.

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