

# Curing Behaviors and Properties of Novolac/Bisphthalonitrile Blends

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**ABSTRACT:** Bisphthalonitrile (BAPh) monomer was blended with novolac resins to achieve good processing resin blends. The curing behaviors of the novolac/BAPh (novolac/BAPh) blends were studied by differential scanning calorimetry (DSC) and dynamic rheological analysis. The results indicated that the blends had large processing windows (98–118°C), and they can copolymerize without any other curing additives. The novolac/BAPh copolymers were obtained by short curing times and low curing temperatures. Thermal and thermal-oxidative stabilities of the copolymers were investigated by thermal gravimetric analysis, and the char yields up to 74 and 35% by weight at 800°C were achieved under nitrogen and air atmosphere, respectively. These postcured copolymers exhibited a 5% weight loss temperature of 502°C in air. These results

revealed that the copolymers exhibited excellent thermal and thermal-oxidative stabilities. Dynamic mechanical properties of the copolymers were systematically evaluated by dynamic mechanical analysis. The copolymers exhibited higher glass transition temperatures ( $T_g$ ) as the BAPh content increased. Mechanical properties of the copolymers were investigated, and these data showed that flexural strength and flexural modulus of the 50 : 50 novolac/BAPh copolymers were 91 MPa and 5.78 GPa, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 649–656, 2012

**Key words:** differential scanning calorimetric; rheology; thermal properties; mechanical properties

## INTRODUCTION

Phthalonitrile resins exhibit excellent mechanical properties, high glass temperatures, superior moisture resistance, and outstanding thermal stability due to their highly aromatic character and heterocyclic ring structures. During the last four decades, phthalonitrile resins are extensively used to fabricate advanced polymeric composites in marine, aerospace, and electronic fields.<sup>1–3</sup> However, further applications of phthalonitrile resins are greatly limited by high cure temperature and narrow processing window (temperature between the melting point and the polymerization temperature).<sup>4,5</sup> Previous researches showed that a series of low-melting phthalonitrile monomers had been designed and synthesized.<sup>6–10</sup> These phthalonitrile monomers can be initiated to obtain phthalonitrile polymers in the presence of various curing agents such as metallic salts,<sup>11</sup> organic amines,<sup>10,12</sup> and phenols.<sup>13</sup> Therefore, a small quantity of curing agents are needed to improve the reactivity of phthalonitrile resins while retaining high thermal stability.<sup>14</sup> However, phenols

have not been thoroughly studied as curing agents of phthalonitrile resins and the polymerization reaction occurs between the nitrile groups of phthalonitriles and phenol groups.

It is well known that novolac resins are versatile thermosetting polymers, which are a mixture of linear oligomers commonly obtained in the phenol/formaldehyde reaction under acidic conditions. Curing with reagents such as hexamethylenetetramine, the commercial novolac resins could be found in many industrial applications owing to their low cost, good flame resistance, and excellent insulating properties.<sup>15,16</sup> Recently, there is growing interest in curing novolac resins with phthalonitriles as curing agents where novolac resins are the major component.<sup>13</sup> The results indicated clearly that the reaction between the phenolic hydroxyl groups of novolac resins as a phenolic catalyst and the nitrile groups of phthalonitriles can be catalyzed because novolac resins offered a rapid proton from the hydroxyl group of nucleophilic phenol groups.

In this article, we report that the bisphthalonitrile (BAPh) and novolac resins as a curing agent were blended and polymerized thermally with short curing times and low curing temperatures without addition of any other curing agents. It is an effective approach for tailoring thermal and mechanical properties of the copolymers by varying the content of

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**TABLE I**  
**The Curing Schedule of the Novolac/BAPh Copolymers**

Samples	Time and temperature
A	200°C and 1 h; 230°C and 3 h; 260°C and 2 h; 290°C and 1 h
B	200°C and 1 h; 230°C and 3 h; 260°C and 2 h; 290°C and 1 h; 330°C and 2 h

BAPh. The as-prepared novolac/BAPh blends possessed high thermal stability, desirable processing temperature, and gelation time for processability, which exhibited promising applications in engineering industry.

## EXPERIMENTAL

### Materials

All the materials were used as received. The commercial novolac resins were supplied by Shenzheng Beier Co. Ltd. Anhydrous potassium carbonate ( $K_2CO_3$ ), 4-nitrophthalonitrile, and bisphenol A were obtained from Tianjin BODI Chemicals. Dimethyl sulfoxide (DMSO) was received from Tianjin Guangfu Fine Chemical Research Institute.

### Preparation of BAPh monomer

The BAPh monomer was synthesized via the reaction of 4-nitrophthalonitrile and bisphenol A. The typical procedure of the synthesis of BAPh was as follows: In a 100-mL three-neck round bottle flask equipped with a mechanical stirrer and refluxing condenser, 4-nitrophthalonitrile (17.3 g), bisphenol A (11.4 g), and DMSO (50 mL) were taken. Then, the powdered anhydrous  $K_2CO_3$  (15 g) was added into the solution in three portions at 1 h intervals. After refluxing at 80°C for 24 h, the reaction mixture was poured into a cold 10% aqueous HCl solution in the formation of a solid. The product was filtered and washed several times with distilled water until pH value reached 7. Then, the light orange solid was dried at 80°C over night after recrystallization.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm): 1.691 ( $-CH_3$ ), 7.136, 7.353, 7.787, 8.082, 8.109 (Ar-H). Typical IR data: 2231  $cm^{-1}$  (stretch,  $-CN$ ), 1248  $cm^{-1}$  (stretch,  $C-O-C$ ), 889  $cm^{-1}$  (bend, 1, 2, and 4 substitution of benzene ring), 835  $cm^{-1}$  (bend, 1, 4 substitution of benzene ring), 777, 717  $cm^{-1}$  (bend, benzene).

### Preparation of novolac/BAPh blends

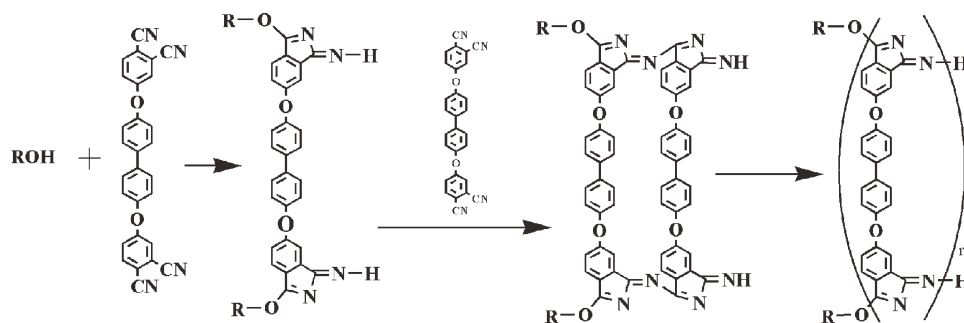
The novolac/BAPh blends were prepared by powder-stirring the BAPh monomer and novolac resins to form a homogeneous mixture at room temperature. The novolac/BAPh blends were formulated with 80 : 20, 60 : 40, 50 : 50, 40 : 60, and 20 : 80 in which the numbers represented the weight percentages of novolac resins and the BAPh monomer, respectively.

### Preparation of novolac/BAPh prepolymers and copolymers

In a three-neck, round bottom flask equipped with a mechanical stirrer, novolac resins were heated into reddish brown viscous liquid at 120–170°C, and then the BAPh monomer was added to achieve a homogeneous melt until dark green. After stirring for 10 min, the viscous melt was cooled rapidly to room temperature. The prepolymers were pulverized for use in DSC and viscosity studies. Meanwhile, the same viscous melt was poured into a preheated polytetrafluoroethylene mold with cavity dimensions 65 mm  $\times$  15 mm  $\times$  5 mm. Then, the gelled samples were thermally cured in an oven under ambient conditions. The detailed curing procedures of the novolac/BAPh copolymers were described in Table I. The cured novolac/BAPh copolymers were sanded to a thickness of 2 mm for the dynamic mechanical measurements and mechanical tests and pulverized for thermal gravimetric analysis (TGA).

### Characterizations

$^1H$ -NMR spectra were taken on a Bruker AV400 nuclear magnetic resonance spectrometer (NMR) with a proton frequency of 400 MHz and the solvent was  $CDCl_3$ . FTIR spectra were recorded with Shimadzu FTIR8400S Fourier Transform Infrared spectrometer in KBr pellets between 4000 and 400  $cm^{-1}$  in air. Differential scanning calorimetric (DSC) analysis was performed by TA Instruments Modulated DSC-Q100 at a heating rate of 10°C/min and a nitrogen flow rate of 50 mL/min. Viscosity studies and curing process of the blends and prepolymers were conducted using TA Instruments Rheometer AR-G2 with a heating rate of 3°C/min and a frequency of 1 Hz. The samples (0.5–1 g) were melted between 25 mm diameter parallel plates with an environmental testing chamber of the rheometer. TGA on the copolymers were determined by TA Instruments Q50 with a heating rate of 20°C/min under nitrogen or air with a purge of 40 mL/min. Dynamic mechanical analysis (DMA) in a three-point-blend mode was used to determine the glass transition temperature ( $T_g$ ). Dynamic viscosity measurements were performed on a TA Instruments QDMA-800 dynamic mechanical analyzer. The rheometer was used to measure the storage modulus ( $G'$ ) and damping factor ( $\tan \delta$ ) at a frequency of 1 Hz, and the samples (dimensions 30 mm  $\times$  10 mm  $\times$  2 mm) were heated from 0 to 350°C at a temperature ramp of 3°C/min.



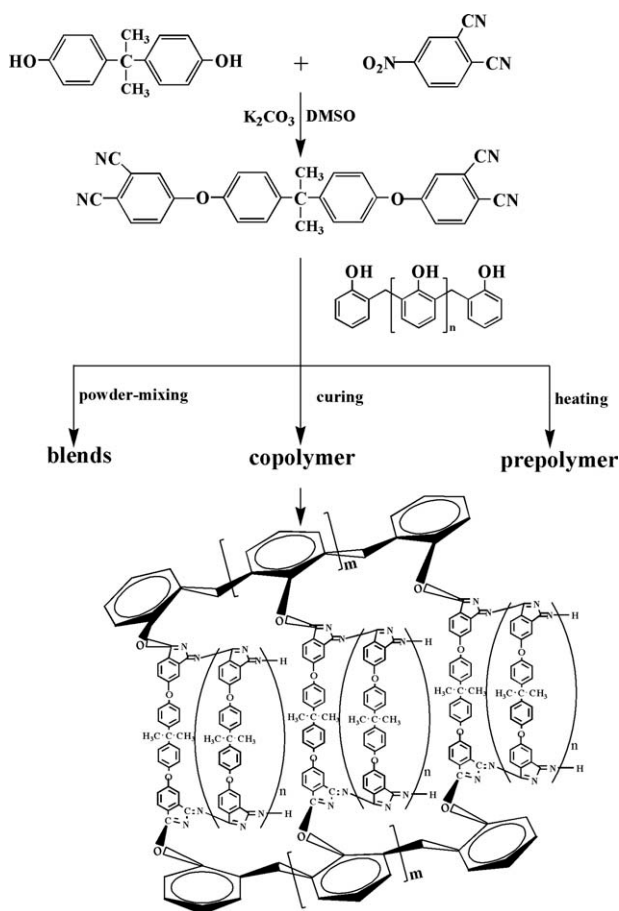
**Scheme 1** Reaction mechanism of the phthalonitrile monomer and phenolic catalysts.

Flexure tests were performed with an Electronic universal testing machine CM T6104 at room temperature with a crosshead displacement speed of 10 mm/min, and the test fixture was mounted in a 10 kN capacity. The samples (dimensions 60 mm × 12 mm × 2 mm) were tested with a support span/sample thickness ratio of 15 : 1.

## RESULTS AND DISCUSSION

### Curing studies on novolac/BAPh blends

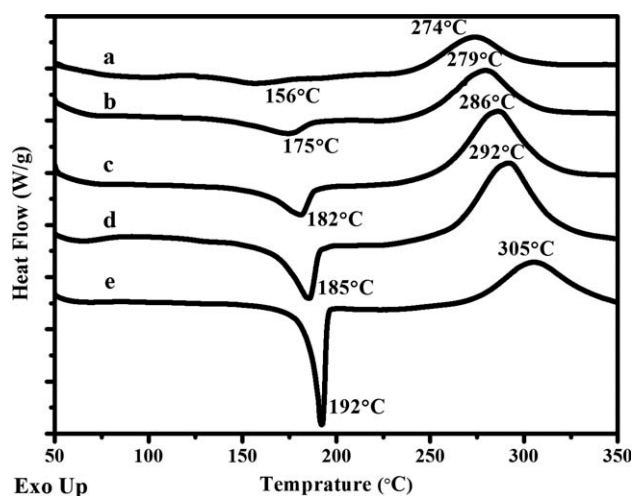
Model curing studies were conducted to characterize the curing behavior of the phthalonitrile monomer



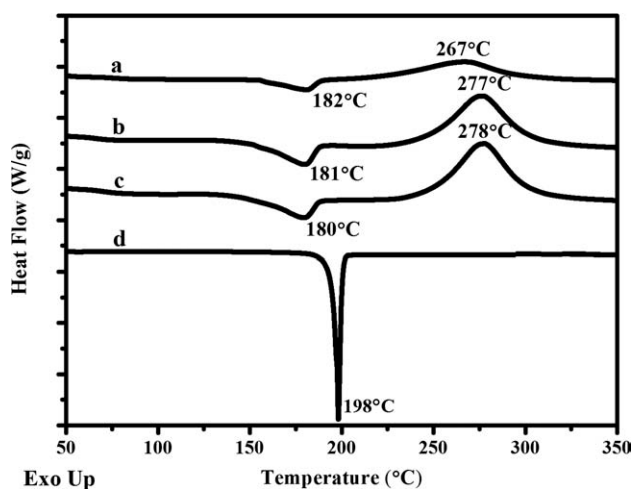
**Scheme 2** Synthesis of the BAPh monomer and novolac/BAPh copolymers.

(BPh, 4,4'-bis(3,4-dicyanophenoxy)biphenyl) with the curing agent of 2-hydroxydiphenylmethane.<sup>17</sup> Detailed reaction mechanism was shown in scheme 1. It was demonstrated that phenolic compounds as curing agents had been used to catalyze the crosslinking reaction of the nitrile groups. Phenolic compounds were used as a nucleophilic initiator to catalyze the reaction between the nitrile groups of the phthalonitrile monomer and phenol hydroxyl groups. This has been driven by the fact that the nitrile groups can readily form isoindoline, diimino, triazine, and phthalocyanine with nucleophilic phenol groups of novolac resins.<sup>13</sup>

The curing behaviors of the novolac/BAPh blends and prepolymers (scheme 2) were studied by DSC. As shown in Figure 1, the peak melting temperatures for the blends were observed (156–192°C), and only one melting peak was evident for each blend. Then, the melting peaks of the transitions were dependent on the blend compositions. Obviously, neat BAPh monomer exhibits a single characteristic melting transition. However, novolac resins are a mixture of linear oligomers in the amorphous phase



**Figure 1** DSC curves of novolac/BAPh blends. The samples are as follows: (a) 80 : 20 novolac/BAPh, (b) 60 : 40 novolac/BAPh, (c) 50 : 50 novolac/BAPh, (d) 40 : 60 novolac/BAPh, and (e) 20 : 80 novolac/BAPh.

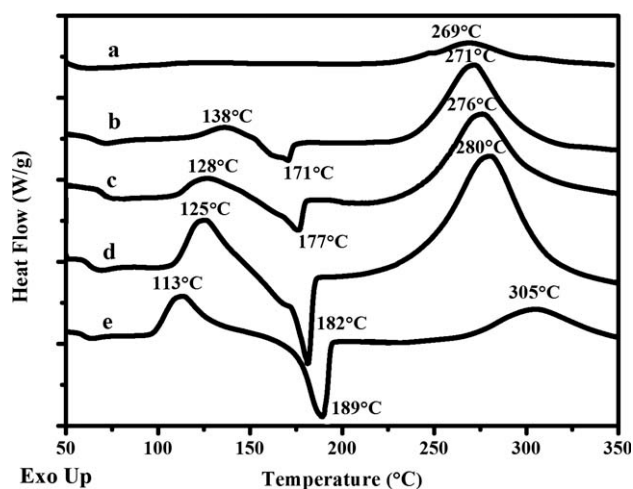


**Figure 2** DSC curves of BAPh monomer and the 50 : 50 novolac/BAPh blend acquired after heating at 150°C for (a) 2 h; (b) 1 h; (c) 10 min; (d) BAPh monomer.

without a single melting peak. Instead, a softening temperature range (110–180°C) was apparent. Importantly, it is evident from the curves that the novolac/BAPh blends exhibited one melting peak, indicating the existence of one predominant component. For these blends, the peaks of the exothermic transitions were centered at 274–305°C, moreover the exotherms shifted to higher temperatures with an increasing BAPh content. In this case, the temperature exotherms were attributed to the copolymerization reaction between the nitrile groups of the BAPh and novolac resins.

The blends with a 50 : 50 weight ratio of novolac resins and the BAPh monomer were treated at 150°C for different times, and the DSC thermograms were depicted in Figure 2. As noted in Figure 2, these exothermic transitions were centered at 278, 277, and 267°C, respectively. It is obvious that the peak temperature of the copolymerization exotherm gradually decreased as the time of heat treatment increased. The enthalpy of cure for the 50 : 50 novolac/BAPh blend decreased from 171.5 to 160.3 and 145.6 J/g. This was related to the fact that the nitrile groups were more easily to form heterocyclic rings,<sup>17</sup> as the treated time increased. Additionally, the peaks of the melting transitions occurred at 180, 181, and 182°C, respectively. It indicated that the melting temperature shifted to higher temperature may be suggestive of the concentration of these crosslinked structures.

The DSC thermograms of the novolac/BAPh prepolymers were shown in Figure 3. The peaks of the endothermic transitions for the novolac/BAPh prepolymers occurred at 171–189°C ( $T_{\text{melt}}$ ), which were lower than that of novolac/BAPh blends observed in Figure 1. Clearly, there are no endotherm and exo-



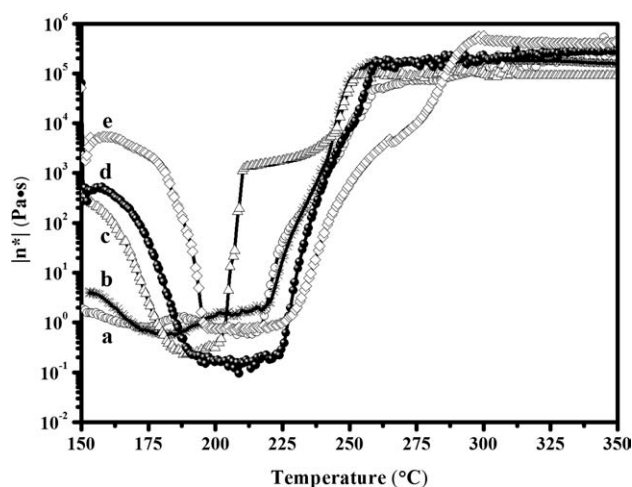
**Figure 3** DSC curves of novolac/BAPh prepolymers. The samples are as follows: (a) 80 : 20 novolac/BAPh, (b) 60 : 40 novolac/BAPh, (c) 50 : 50 novolac/BAPh, (d) 40 : 60 novolac/BAPh, and (e) 20 : 80 novolac/BAPh.

therm for sample observed between 50 and 200°C in Figure 3. However, two endothermic peaks or shoulders for samples b, c, and d were apparent, which indicated that novolac resins remained in the amorphous phase and phase separation had occurred. Additionally, the step transitions at temperature range of 50–75°C revealed that novolac resins possessed  $T_g$ s. When comparison with Figure 1, the appearance of the additional exotherms ( $T_{\text{top1}}$ , 113–138°C) indicated that the polymerization reaction of novolac resins occurred in the present of the nitrile groups. It was observed that the exothermic heat flows ( $\Delta H_{\text{curing1}}$ ) were in the range of 8.44–54.96 J/g. Furthermore, the exotherms and endotherms gradually separated from each other, implying that the nitrile groups concentration was determined to be a major factor in the curing temperature of novolac resins. As shown in Figure 3, these exotherms ( $T_{\text{top2}}$ ) were observed (269–305°C) and the peak temperatures appeared to be related to the BAPh content. Meanwhile, the enthalpy ( $\Delta H_{\text{curing2}}$ ) of reaction for novolac resins and the BAPh monomer was summarized in Table II. As expected, the novolac/BAPh blends and prepolymers showed

**TABLE II**  
The Thermal Properties of Novolac/BAPh Prepolymers

Samples	$T_{\text{melt}}$ (°C)	$T_{\text{top1}}$ (°C)	$T_{\text{top2}}$ (°C)	$\Delta H_{\text{curing1}}$ (J/g)	$\Delta H_{\text{curing2}}$ (J/g)	Gelation time at 200°C (min)
80 : 20	–	–	269	–	84.00	11
60 : 40	171	138	271	8.44	118.50	9
50 : 50	177	128	276	25.11	187.20	8
40 : 60	182	125	280	32.84	163.00	13
20 : 80	189	113	305	54.96	75.74	35





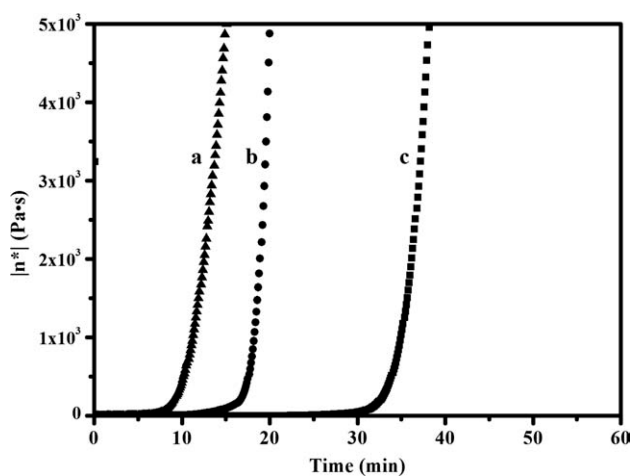
**Figure 4** Complex viscosity ( $\eta^*$ ) as a function of temperature for novolac/BAPh blends. The samples are as follows: (a) 80 : 20 novolac/BAPh, (b) 60 : 40 novolac/BAPh, (c) 50 : 50 novolac/BAPh, (d) 40 : 60 novolac/BAPh, and (e) 20 : 80 novolac/BAPh.

large processing window (98–118°C), which revealed that it was useful to control the reaction of phthalonitrile resins with novolac resins and improve enhanced processability of the system.

#### Dynamic rheological analysis on novolac/BAPh blends

The rheological behavior, a key factor in predicting processability, was performed on viscosity changes accompanying the cure reaction of the novolac/BAPh blends. In Figure 4, the complex viscosity of the novolac/BAPh blends was shown as a function of temperature from 150 to 350°C. The data revealed that the complex viscosity of the blends decreased in the temperature range from 175°C up to 190°C. Moreover, the viscosity (0.1–1 Pa s) was observed for the blends while the temperature increased from 190 to 225°C for  $\sim 7$  min. Up to 225°C, abrupt complex viscosity increases were shown, which indicated that the curing reaction of the novolac/BAPh was progressing. Therefore, the low complex viscosity of the blends at moderate temperature is evidence of good processability. However, the 50 : 50 novolac/BAPh blends appeared to melt in a two-step procedure (200°C and 225°C).

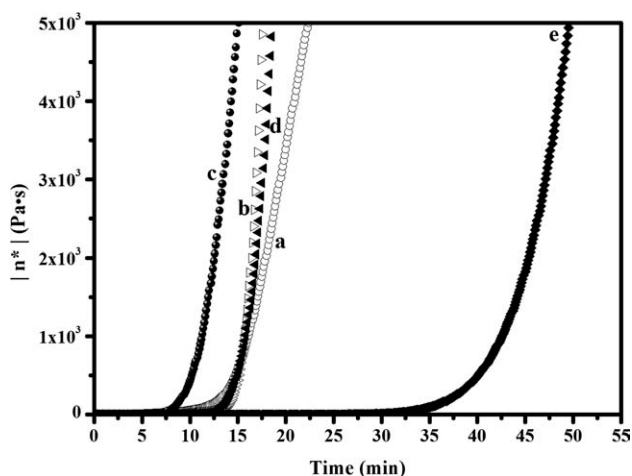
Complex viscosity changes of the 50 : 50 novolac/BAPh prepolymers were noted as a function of time at various temperatures. The curves, shown in Figure 5, indicated that the higher the curing temperature, the faster the viscosity increase. This result demonstrated that high curing temperature had a great tendency to accelerate the crosslink reaction of novolac/BAPh. For comparison, the complex viscosity increase of the novolac/BAPh prepolymers as a function of time at 200°C was depicted in Figure 6. It can be seen that the viscosity of the prepolymers



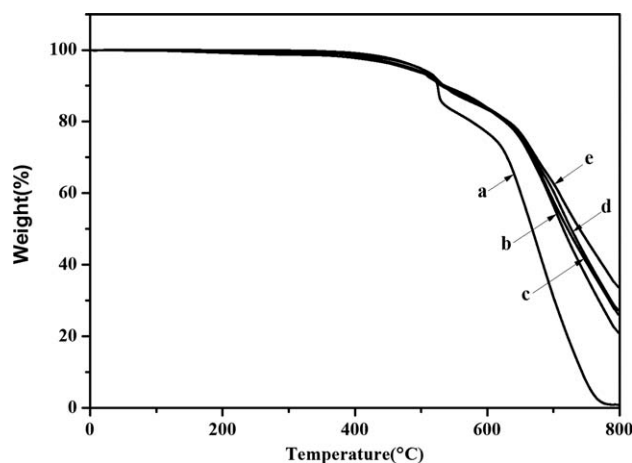
**Figure 5** Complex viscosity ( $\eta^*$ ) as a function of time for the 50 : 50 novolac/BAPh prepolymer at various temperatures. The temperatures were (a) 220°C, (b) 200°C, and (c) 180°C.

increased gradually until gelation (defined as the  $G'$ ,  $G''$  crossover points<sup>18</sup>) occurred. The gelation times for the novolac/BAPh prepolymers were summarized in Table II. As Figure 6 showed, the influence of the BAPh content on the gelation time is evident. Therefore, these data revealed that the gelation time of the 80 : 20, 60 : 40, and 50 : 50 novolac/BAPh prepolymers decreased as the BAPh content of the sample increased. However, the gelation time of the 50 : 50, 40 : 60, and 20 : 80 novolac/BAPh prepolymers increased with the BAPh content increased.

The rheological behavior of the prepolymers demonstrated that it was easy to control the novolac/BAPh polymerization by varying the BAPh concentration. Furthermore, the novolac/BAPh prepolymers had the desirable processing temperature and



**Figure 6** Complex viscosity ( $\eta^*$ ) as a function of time at 200°C for novolac/BAPh prepolymers. The samples are as follows: (a) 80 : 20 novolac/BAPh, (b) 60 : 40 novolac/BAPh, (c) 50 : 50 novolac/BAPh, (d) 40 : 60 novolac/BAPh, and (e) 20 : 80 novolac/BAPh.

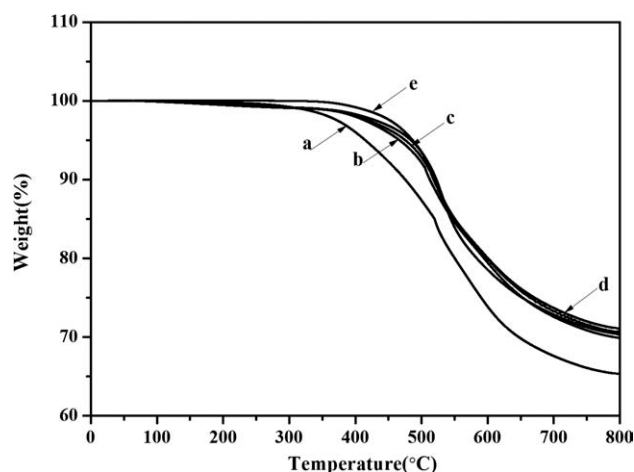


**Figure 7** TGA curves of novolac/BAPh copolymers in air. The samples cured up to a maximum temperature of 290°C are as follows: (a) 80 : 20 novolac/BAPh, (b) 60 : 40 novolac/BAPh, (c) 50 : 50 novolac/BAPh, (d) 40 : 60 novolac/BAPh, and (e) 20 : 80 novolac/BAPh.

gelation time, which exhibited promising applications in engineering industry.

### Thermal properties of novolac/BAPh copolymers

The novolac/BAPh copolymers cured up to maximum temperatures of 290 and 330°C were analyzed using TGA to evaluate their thermal and thermal-oxidative stabilities. Results of these studies were shown in Figures 7 and 8. Tables III and IV presented the residue remaining (char yield %) after heating the copolymers samples to 800°C in nitrogen and air atmosphere and the letters A and B referred to the curing schedules listed in Table I. The 5% and



**Figure 8** TGA curves of novolac/BAPh copolymers in nitrogen. The samples cured up to a maximum temperature of 290°C are as follows: (a) 80 : 20 novolac/BAPh, (b) 60 : 40 novolac/BAPh, (c) 50 : 50 novolac/BAPh, (d) 40 : 60 novolac/BAPh, and (e) 20 : 80 novolac/BAPh.

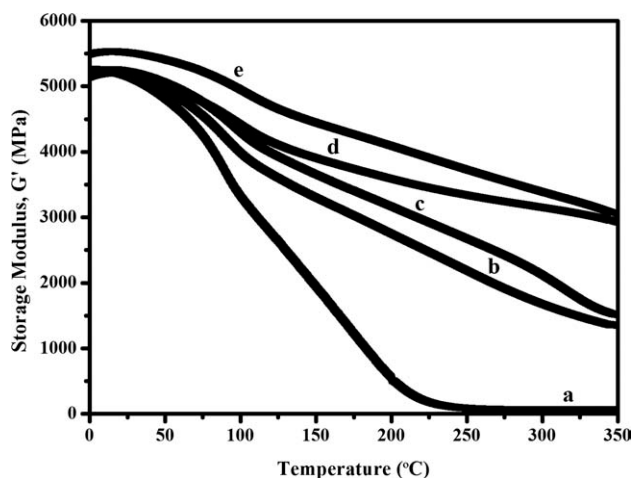
**TABLE III**  
Thermal and Thermo-oxidative of Novolac/BAPh Copolymers (Sample A) in Air and Nitrogen

Samples	Nitrogen			Air		
	$T_{5\%}$ (°C)	$T_{30\%}$ (°C)	Char yield (%) at 800°C	$T_{5\%}$ (°C)	$T_{30\%}$ (°C)	Char yield (%) at 800°C
80 : 20	415	647	65	477	630	1
60 : 40	467	789	70	480	666	23
50 : 50	470	790	70	484	668	27
40 : 60	484	791	71	497	670	29
20 : 80	487	789	71	497	674	35

30% weight loss decomposition temperatures ( $T_{5\%}$  and  $T_{30\%}$ ) in nitrogen and air were also shown in the tables. After curing up to 290°C, the copolymers started to degrade at temperatures ( $T_{5\%}$ ) of 415, 467, 470, 484, and 487°C, respectively, when heated in a nitrogen atmosphere. In air, these samples demonstrated  $T_{5\%}$  at 477, 480, 484, 497, and 497°C, respectively. According to these results,  $T_{5\%}$  is somewhat higher with air atmosphere relative to nitrogen, which may be ascribed to heterogeneity of the crosslink density. Obviously, the decomposition temperatures for the novolac/BAPh copolymers were greatly improved compared with that of the neat novolac resin. The 65–71% and 1–35% char yields remained at 800°C under nitrogen and air, respectively. The resulting char was observed to be a fine orange powder, which was relative to the cured novolac resins. Then, the novolac/BAPh copolymers exhibited good thermal and thermal-oxidative stabilities, owing to the high aromatic nature of the system and the crosslinking density after cured. On the other hand, after curing to the maximum temperature of 330°C, the copolymers improved the residual char yields and thermal decomposition temperatures. Therefore, these data revealed that high thermal and thermal-oxidative stabilities of the copolymers were determined from the maximum processing temperature and appeared to be related to the BAPh content.

**TABLE IV**  
Thermal and Thermo-oxidative of Novolac/BAPh Copolymers (Sample B) in Air and Nitrogen

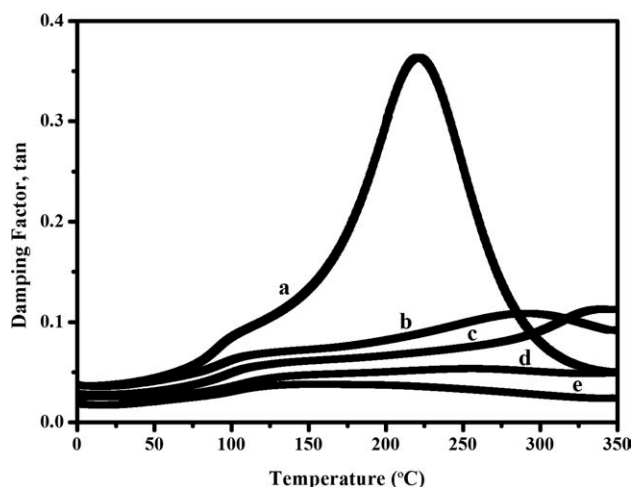
Samples	Nitrogen			Air		
	$T_{5\%}$ (°C)	$T_{30\%}$ (°C)	Char yield (%) at 800°C	$T_{5\%}$ (°C)	$T_{30\%}$ (°C)	Char yield (%) at 800°C
80 : 20	447	700	67	490	631	3
60 : 40	473	800	70	482	660	10
50 : 50	489	800	74	494	663	26
40 : 60	491	800	72	498	668	26
20 : 80	495	800	71	502	669	27



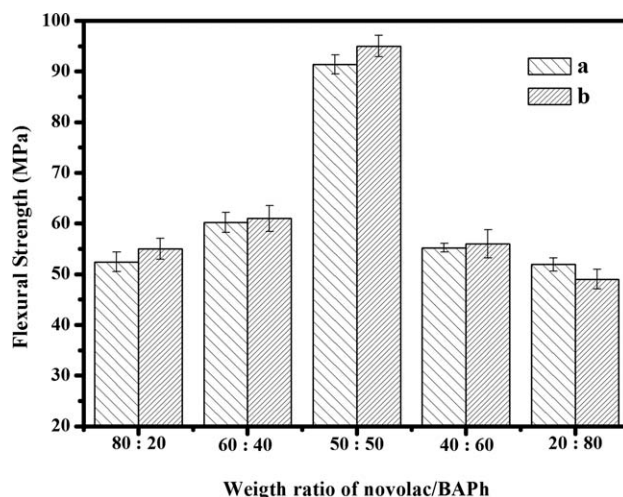
**Figure 9** Storage modulus ( $G'$ ) as a function of temperature for the copolymers heated in nitrogen: (a) 80 : 20 novolac/BAPH, (b) 60 : 40 novolac/BAPH, (c) 50 : 50 novolac/BAPH, (d) 40 : 60 novolac/BAPH, and (e) 20 : 80 novolac/BAPH.

#### Dynamic mechanical properties of novolac/BAPH copolymers

Rheometric studies were conducted to evaluate the changes in the sample modulus as a function of temperature and determinate the  $T_g$ s of the copolymers. From these studies, storage modulus ( $G'$ ) and damping factor ( $\tan \delta$ ) plots generated on novolac/BAPH copolymers cured up to maximum temperatures of 290°C were presented in Figures 9 and 10, respectively. In Figure 9, the  $G'$  for sample a changed from 5050 to 40 MPa when heated from 0 to 350°C. For samples b, c, d and e, large modulus changes were observed gradually from 220 to 350°C. The data showed that the extent of the moduli changes



**Figure 10** Damping factor ( $\tan \delta$ ) as a function of temperature for the copolymers heated in nitrogen: (a) 80 : 20 novolac/BAPH, (b) 60 : 40 novolac/BAPH, (c) 50 : 50 novolac/BAPH, (d) 40 : 60 novolac/BAPH, and (e) 20 : 80 novolac/BAPH.

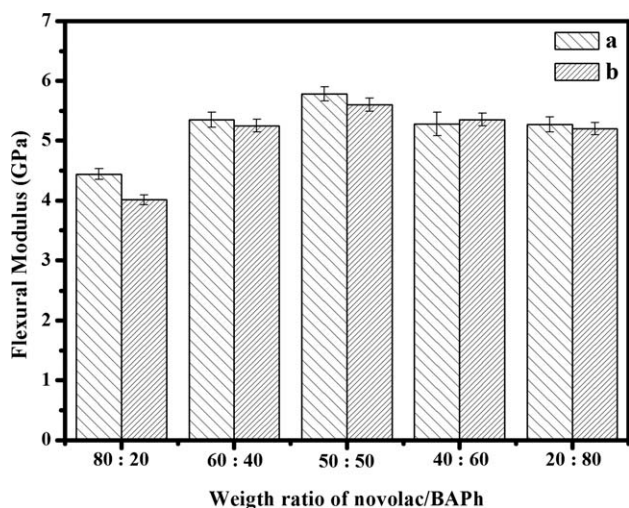


**Figure 11** Flexural strength of novolac/BAPH copolymers as a function of maximum cure temperature: (a) 290°C and (b) 330°C.

decreased as the BAPH content increased, and the decreases in the storage moduli were attributed to stress relaxation of the copolymers. Thus, the  $T_g$  was defined as the peak temperature of the  $\tan \delta$  versus temperature plots. As noted in Figure 10, one or two relaxation peaks were observed in each plot. The  $\tan \delta$  peaks (100–150°C) of all the novolac/BAPH copolymers were attributed to novolac resins. On heating to 350°C, the  $\tan \delta$  peaks of the 80 : 20, 60 : 40, and 50 : 50 novolac/BAPH copolymers increased from 221 to 289°C and 330°C, respectively. The data indicated that the  $\tan \delta$  peak height decreased and shifted to higher temperatures as the BAPH content of the copolymers increased. However, no viscoelastic transition characteristic of the  $T_g$  was observed for the 40 : 60 and 20 : 80 novolac/BAPH copolymers before 350°C. These results revealed that the novolac/BAPH copolymers had formed during the curing reaction and remained in the glassy state to at least 350°C.

#### Mechanical properties of novolac/BAPH copolymers

The mechanical properties of the copolymers were evaluated by using the Electronic universal testing machine (CMT6104) at room temperature. As shown in Figures 11 and 12, the samples for the novolac/BAPH copolymers cured up to maximum temperature of 290 and 330°C displayed the flexural strength (49.0–91.4 MPa) and flexural modulus (4.01–5.78 GPa), which indicated that the mechanical properties of the novolac/BAPH copolymers were affected by the BAPH content. Moreover, there is a mechanical advantage for the 50 : 50 novolac/BAPH copolymers cured up to maximum temperature of 290 and 330°C over that of the neat BAPH<sup>12</sup> or the neat



**Figure 12** Flexural modulus of novolac/BAPh copolymers as a function of maximum cure temperature: (a) 290°C and (b) 330°C.

phenolic resins.<sup>19</sup> However, these data indicated that the mechanical properties of the copolymers show no dependence on the maximum curing temperature.

### CONCLUSIONS

The novolac/BAPh blends, prepolymers and copolymers were prepared and characterized. The curing and rheological behaviors of the novolac/BAPh blends and prepolymers with varying BAPh contents were studied without addition of any other curing additives. The results revealed that the novolac/BAPh blends had large processing windows with low melt viscosity and that the size of the processing windows was related to the BAPh content.

TGA results showed that the copolymers cured by short curing times and low curing temperatures exhibited excellent performance such as high thermal stability, thermal-oxidative stability and high char yield. It is believed that the novolac/BAPh copolymer can be used as a matrix of advanced composites with good processability.

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