

Blended Resins Based on a New Propargyl-Functional Resin: Synthesis, Cure, and Thermal Properties

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ABSTRACT: A new propargyl-functional resin, propargyl ether bisphenol A novolac (PBPB), was synthesized, and the structure of PBPB was characterized using ¹H NMR and FTIR spectra. The PBPB was blended with 4,4'-bismaleimide diphenyl methane (BDM) at different molar ratio to obtain the blends. Differential scanning calorimetry (DSC) was used to characterize the cure behavior of PBPB and the blends. Thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA) were performed, respectively, to evaluate thermal stability and dynamic

mechanical properties of the cured resins. The results indicate that the PBPB presented better cure and thermal properties than do traditional propargyl resins; furthermore, the cure behavior and thermal properties of PBPB could be improved remarkably by blending with BDM. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4207–4212, 2006

Key words: propargyl ether bisphenol A novolac; bismaleimide; thermal stable polymer; addition polymerization

INTRODUCTION

Propargyl-functional resins are novel class of thermally stable composite matrix resins. There have been growing interests in this kind of resins because of their excellent properties such as good thermal stability, low moisture absorption, and low dielectric constant.¹ In addition, they could cure via addition reaction to avoid the evacuation of volatiles, which makes it possible to get void-free materials without high pressure. A series of propargyl-functional resins, such as bis propargyl ether bisphenol A (PBPA) and propargyl ether benzoxazine, have been synthesized, and the cure and thermal properties have also been studied.^{2–4} Although the resins mentioned above are thermally stable, their properties need further improvement to meet the ever-increasing performance requirements.

In general, an effective way to improve the properties of the resins is to blend with other high performance resins. In our early work, PBPA has been investigated to blend with 4,4'-bismaleimide diphenyl methane (BDM) resins and a high thermal stability resin system was obtained. The results indicate that the blended resins presented better thermal properties than do pure PBPA and BDM.⁵

In this paper, we prepared a new propargyl-functional resin, propargyl ether bisphenol A novolac

(PBPB). It was different from PBPA monomer that PBPB was oligomer and based on bisphenol A novolac resin. The synthetic routes are shown in Scheme 1. PBPB was blended with BDM at different stoichiometry to obtain the blends. The cure behavior and the thermal properties of PBPB and the blends were studied in detail. We expected that the blends based on PBPB (oligomer) could present better performance than do the blends based on PBPA (monomer).

EXPERIMENTAL

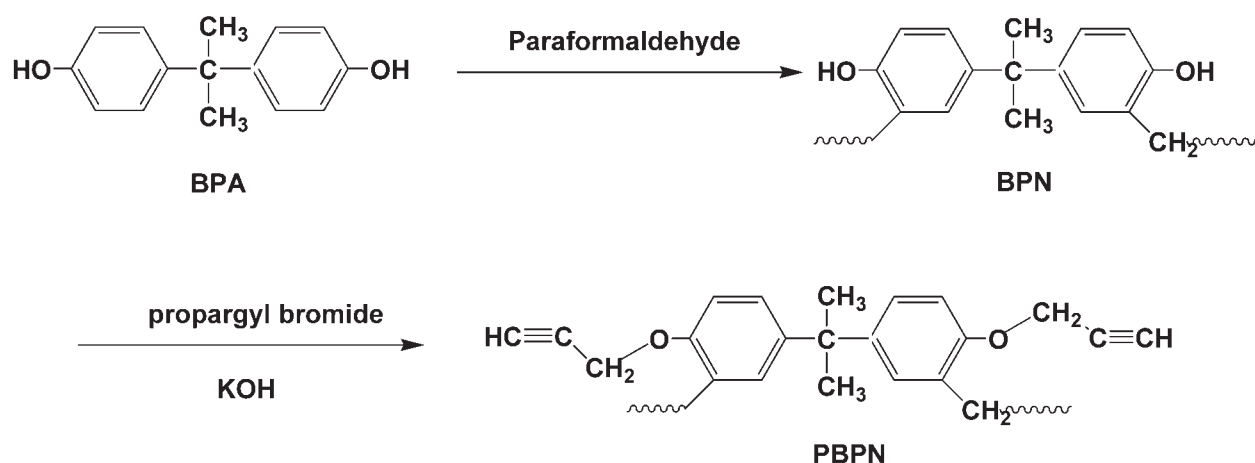
Materials

4,4'-Bismaleimide diphenyl methane (BDM) (CP, Feng Guang Chemical, China), bisphenol A (BPA) (AR, Xin Xing Reagent, China) were used as received. Propargyl bromide (CP, Yang Nong Chemical China) was distilled before use. Paraformaldehyde (AR, Beijing Regent, China) was used without further purification. Bispropargyl ether bisphenol A (PBPA) was prepared in our laboratory by a procedure reported in an early publication.⁵ Other reagents were used as received.

Instruments

FTIR spectra were obtained from Bruker Tensor 27. ¹H NMR spectra were recorded on a Bruker DMX-300 (300 MHz) with DMSO-*d*₆ as solvent. Gel permeation chromatography (GPC) was carried on Waters 1515 equipped with HR1, HR0.5 Waters Styragel

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Scheme 1 The synthesis of PBPN.

columns, using tetrahydrofuran (THF) as eluent. Differential scanning calorimetry (DSC) was recorded with a Mettler thermal analysis DSC-822e, at a heating rate of 10°C/min under nitrogen atmosphere. Thermal gravimetric analysis (TGA) was performed by a Netsch STA 409PC, at a heating rate of 10°C/min under nitrogen atmosphere. The dynamic mechanical properties were carried out on Netsch DMA242 using a dual-cantilever mode under nitrogen atmosphere at a heating rate of 3°C/min in a frequency of 1 Hz.

Synthesis of bisphenol A novolac (BPN) resin

In a typical synthesis, BPA (22.8 g, 0.1 mol) was mixed intensively with paraformaldehyde (3.0 g, 0.1 mol) and heated to 180°C in a one-necked flask with a reflux condenser and a drying tube filled with glass wool. The reflux condenser was removed after 30 min, and the formed water was distilled. When no more water could be distilled, the temperature of the reaction mixture was quickly (about 5 min) raised up to 200°C. Then the BPN was removed from the flask and cooled to the room temperature. The yield of the yellow to amber-colored BPN was 85–90%. BPN was characterized using ¹H NMR and GPC.

Synthesis of propargyl ether bisphenol A novolac (PBPN) resin

In a typical synthesis, BPN (22.8 g, about 0.1 mol), potassium hydroxide (11.2 g, 0.2 mol), and ethanol were placed in a three-necked flask equipped with a mechanical stirrer, a thermometer, and a condenser. The mixture was stirred to form a solution, and propargyl bromide (26.2 g, 0.22 mol) was added dropwise under agitation at room temperature. The reaction mixture was heated to 75–80°C and kept for 4 h. The salt formed in the reaction was removed by

filtration. The solvent in the filtrate was removed by distillation and brown oily liquid was obtained. The crude product was dissolved in ethyl acetate and washed thrice with distilled water, then ethyl acetate was removed and PBPN was obtained (yield 80%). The as-prepared PBPN was characterized using FTIR and ¹H NMR.

Preparation and cure of the blended resins based on PBPN

PBPN was reactively blended with BDM at varying propargyl to maleimide stoichiometry at 150°C to give transparent liquid resins. The blended resins of PBPN and BDM were designated as PBPN-BDM (1.0 : 0.5), PBPN-BDM (1.0 : 1.0), and PBPN-BDM (1.0 : 2.0) respectively, according to the molar ratio of propargyl and maleimide groups. The blended resins were cured in air oven by the following gradual heating procedure: 170°C/4 h + 200°C/4 h + 250°C/6 h. The pure PBPN, PBPA, and BDM were also cured following the same procedure for comparison.

RESULTS AND DISCUSSION

Synthesis and characterization

Synthesis of bisphenol A novolac (BPN) resin

The synthesis of BPN was conducted under melt conditions according to the literature,⁶ and the synthetic routes are shown in Scheme 1. By regulating the molar ratios of the reactants, the number average molecular weight (M_n) of BPN was controlled. The chemical shifts in ¹H NMR spectra were assigned as follows: δ (ppm) 1.32 (s, isopropyl), 3.70 (s, —CH₂—), 6.56–6.99 (d, aromatic) 9.00–9.40 (d, —OH). The number average molecular weight (M_n) of novolac could be calculated according to the integral intensity of the proton of methylene (H_M) and

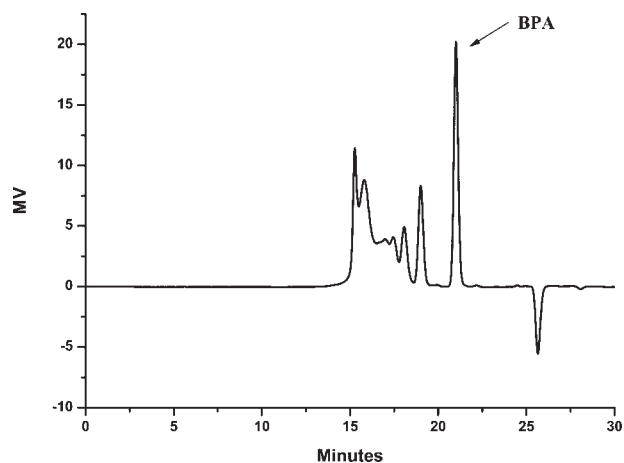


Figure 1 The GPC profile of BPN resin.

aromatic (H_{Ar}).⁷ In the present work, the M_n of BPN was calculated using the following equation:

$$\frac{6n + 14}{2n + 2} = \frac{H_{Ar}}{H_{Mt}}$$

$$M_n = 468 + 240n$$

where n is number of the repeat unit. The M_n of as-prepared BPN, using the formula, was found to be 559.

GPC was also used to characterize the BPN and the profile was shown in Figure 1. Because of the absence of model compounds, the absolute molecular weight could not be obtained by GPC. The peak at 21 min was ascribed to the presence to BPA monomer (the area % of the BPA peak was 22.85%), which indicated that the as-prepared BPN contained unreacted BPA monomer.

Synthesis of PBPn resin

The propargylation of BPN was attained via Willmson reaction to obtain PBPn as shown in Scheme 1,⁸ and the as-prepared PBPn was a viscous liquid at room temperature. The product was characterized by IR and ¹H NMR. The chemical shifts were assigned as follows: δ (ppm) 1.37–1.59 (broad, isopropyl), 3.59 (s, $\equiv C-H$), 3.75–3.86 (m, $-CH_2-$), 4.66–4.74 (s, $-CH_2-$), 6.78–7.14 (m, aromatic). FTIR spectrum of PBPn is shown in Figure 2. The characteristic absorption peaks of $\equiv C-H$ and $C\equiv C$ were at 3263 and 2119 cm^{-1} , respectively. The ether bond absorption peak of $Ar-O-CH_2$ was at 1019 cm^{-1} , and the $-OH$ absorption of the precursor BPN was absent. These results confirmed the structure of PBPn.

Cure behavior of PBPn and its blends

Many studies had already reported the cure reaction mechanism of propargyl-functional resins, and phenyl

propargyl ether was used as model compound to investigate the cure reaction mechanism.^{9–11} Phenyl propargyl ether could undergo Claisen-type sigmatropic rearrangement to 2H-chromenes, and then the 2H-chromenes can be thermally polymerized to form macromolecules. Owing to the strong electron-withdrawing property of the maleimide group, it could react with electron-supplying propargyl group via addition reactions. It was reported that acetylene compounds could copolymerize with maleimide groups via Diels–Alder reactions.¹² The possible cure reactions of the blends of PBPn with BDM are shown in Scheme 2.

DSC was performed to evaluate the cure behavior of the PBPn and the blended resins. Figure 3 showed the DSC profile of PBPn, and DSC curve of pure PBPA was also given for comparison. It could be seen that both resins presented a sharp exotherm above 200°C, corresponding to the rearrangement and polymerization of propargyl groups. However, the onset cure temperature and peak temperature of PBPA were 248 and 286°C, respectively, while the onset cure temperature and peak temperature of PBPn were 223 and 273°C, which were much lower than that of PBPA. In other words, the cure temperature of PBPn was about 13–25°C lower than that of PBPA. The difference of cure temperature might be caused by the methylene between two aromatic rings of PBPn. Because of the electron-supplying property of methylene, the electronegativity of conjugated system would be enhanced, which rendered the propargyl group more reactive. For the thermosetting resins, the low cure temperature was much favorable for the cure process. Therefore, PBPn presented better processability than did PBPA.

Figure 4 shows the DSC profiles of the blends at different PBPn to BDM ratio; the DSC profiles of pure PBPn and BDM were also given for comparison. A sharp exotherm was observed for PBPn

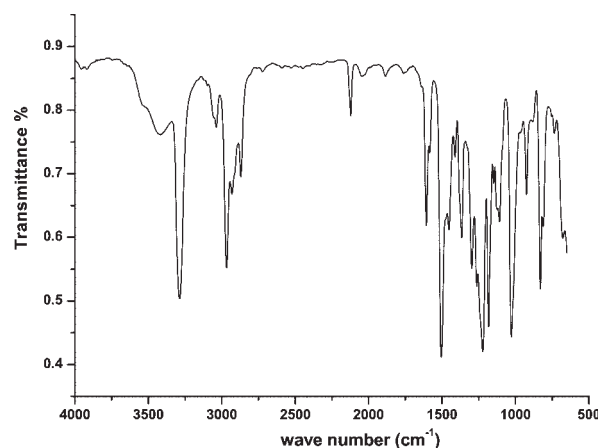
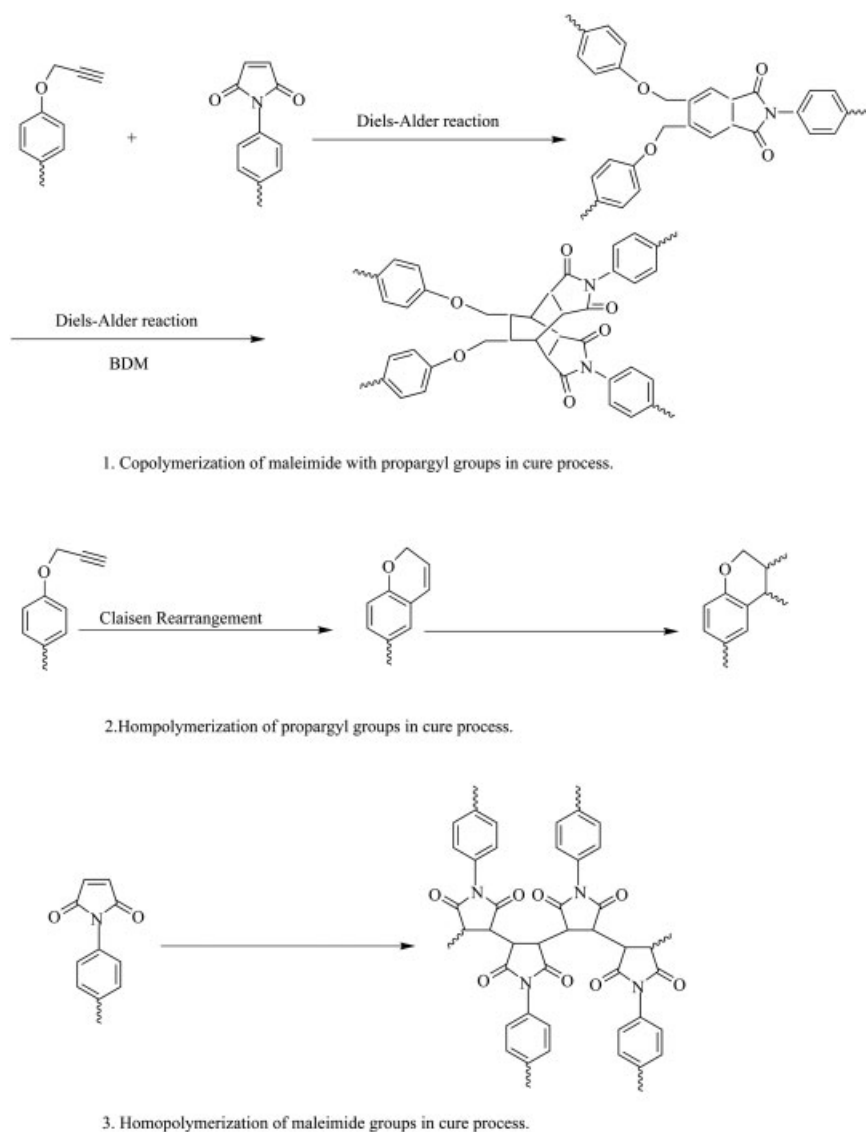


Figure 2 The FTIR spectrum for PBPn.



Scheme 2 The possible cure reactions of PBPN with BDM in cure process.

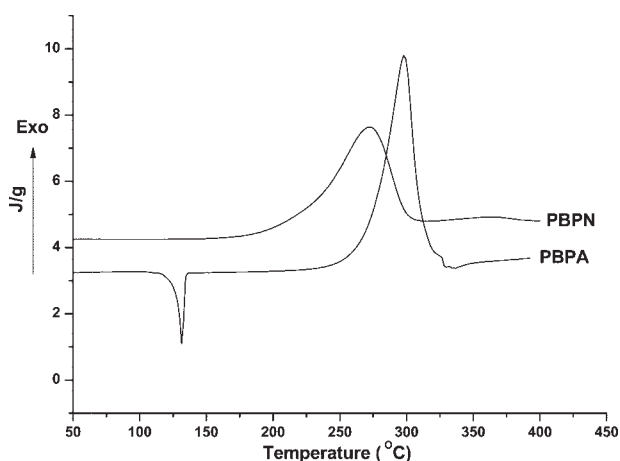


Figure 3 The DSC profiles of PBPN and PBPA (heating rate 10°C/min, N₂ 50 mL/min).

corresponding to the rearrangement and polymerization. For BDM, a broad and small exotherm observed, which was attributed to the double bond self-polymerization. On the other hand, the blends of PBPN with BDM showed a broad exotherm at a lower temperature range, and the onset cure temperature and the peak temperature of the blends were about 10–20°C lower than that of pure PBPN, which revealed that the cocure reactions between PBPN and BDM took place more easily than the self-cure reactions of PBPN. With the increase in BDM content, the cure exothermic enthalpy of the blend decreased from 1194 J/g for PBPN to 518 J/g for PBPN–BDM (1.0 : 2.0), and the small cure exothermic made the cure process more moderate. In conclusion, the processability of PBPN improved markedly by addition of BDM because of the lower cure temperature and moderate cure reactions.

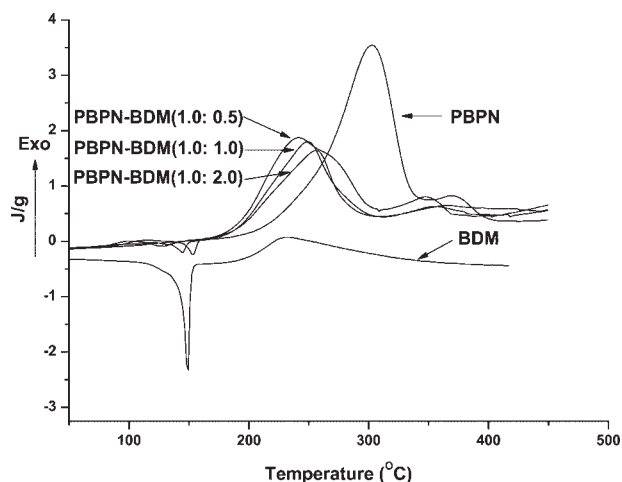


Figure 4 The DSC profiles of PBPN, BDM, and their blends (heating rate 10°C/min, N₂ 50 mL/min).

Thermal stability of cured PBPN and its blends

In the cure process, it was very important to control the rate of cure reactions because the fast cure reactions often produce more deficiency in the cured resins. Therefore, to control the cure reactions rate, the gradual heating cure process was adopted to obtain compact resin cast. All the resins were cured in air oven according to the following procedure: 170°C/4 h + 200°C/4 h + 250°C/6 h. The DSC curves of the cured resin exhibited no exothermic peak in the cure temperature range (the curves were not shown), indicating that the cure reactions were complete. The thermal stability of the cured resins was characterized by TGA.

Figure 5 showed the TGA profiles of cured PBPN, the TGA curves of cured PBPA also given for comparison. It could be seen that both resins showed similar decomposition curves, but the difference was that the 5% mass loss temperature ($T_{5\%}$) of PBPN was

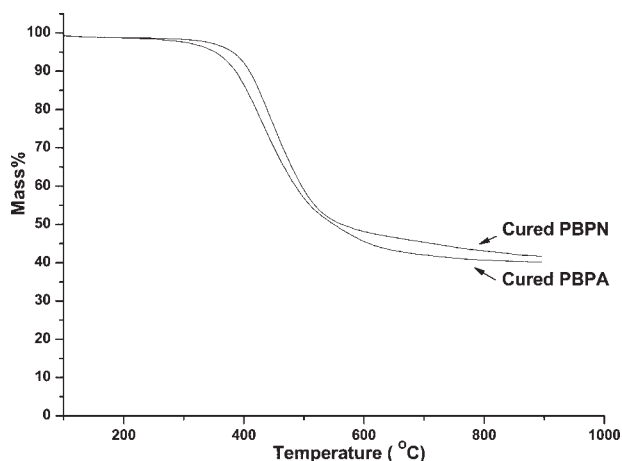


Figure 5 The TGA profiles of cured PBPN and cured PBPA (heating rate 10°C/min, N₂ 50 mL/min).

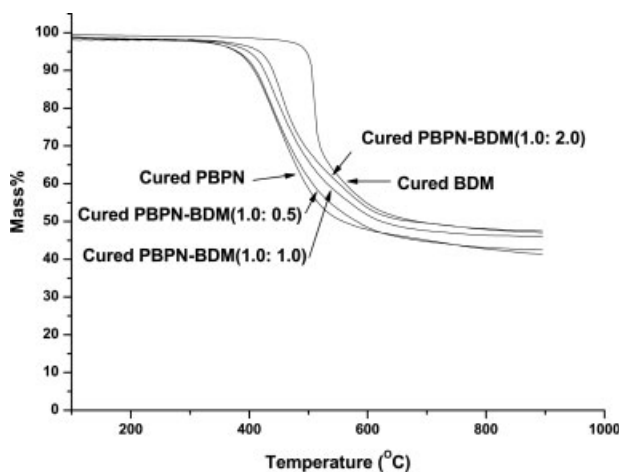


Figure 6 The TGA profiles of cured PBPN, BDM, and their blends (heating rate 10°C/min, N₂ 50 mL/min).

378°C, which was much higher than that of cured PBPA (353°C). The result revealed the cured PBPN presented better thermal stability than cured PBPA has. Owing to the linkage of methylene between two aromatic rings, the cured PBPN would possess higher crosslinked density than cured PBPA, which attributed to better thermal stability of the cured PBPN.

Figure 6 shows the TGA curves of cured blended resins of PBPN with BDM at different stoichiometry. As seen from the TGA thermograms, cured BDM exhibited excellent thermal stability, and $T_{5\%}$ was as high as 496°C, which was much higher than that for cured PBPN. Also, the residue in 900°C (R_{900}) for cured BDM was 47.0%, which was higher than that for cured PBPN. On the other hand, for cured blends of PBPN with BDM, $T_{5\%}$ and R_{900} were between that for cured PBPN and cured BDM. With the increase in BDM content, $T_{5\%}$ for the cured blends improved markedly from 383°C [cured PBPN-BDM (1.0 : 0.5)]

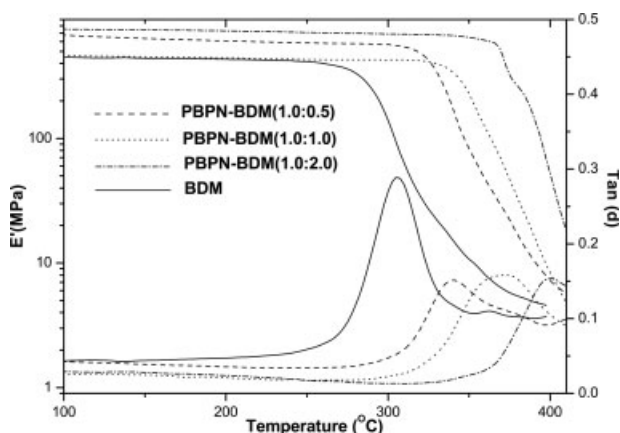


Figure 7 The DMA profiles of the cured blends of PBPN with BDM (heating rate 3°C/min, N₂ 50 mL/min, frequency 1 Hz).

TABLE I
 T_g of Cured BDM and the Blends of BDM with PBPA and PBPN

Resins	T_g (°C)
PBPA-BDM (1.0 : 0.5)	306
PBPA-BDM (1.0 : 1.0)	324
PBPA-BDM (1.0 : 2.0)	358
Pure BDM	216
PBPN-BDM (1.0 : 0.5)	344
PBPN-BDM (1.0 : 1.0)	371
PBPN-BDM (1.0 : 2.0)	399

to 421°C [cured PBPN-BDM (1.0 : 2.0)], and R_{900} increased correspondingly. Therefore, owing to the excellent thermal stability of BDM, the cured blends showed better thermal stability than cured did PBPA. The stability of the blends depended on the content of BDM, and higher BDM content for blends resulted better thermal stability.

The dynamic mechanical properties of the cured blends

In the cured experiment to prepare casting matrix, it was unable to form a compact sample of PBPN because of its large cure exothermic enthalpy. However, when BDM was added, the compact sample could be obtained easily. Therefore, only the cured BDM and the cured blends were measured by DMA. The storage modulus (E') and the loss factor ($\tan(\delta)$) are shown as a function of temperature in Figure 7.

It could be seen that the E' of the blends were decreasing between 300 and 400°C, and the retention rate of E' at 350°C for cured PBPN-BDM (1.0 : 0.5), PBPN-BDM (1.0 : 1.0), and PBPN-BDM (1.0 : 2.0) were 10.3%, 35.4% and 75.3%, respectively. In other words, the retention rates of E' at 350°C were increasing with the increase in BDM content. On the other hand, the glass transition temperature (T_g) was defined as the peak temperature of $\tan(\delta)$. T_g of the cured blends were depicted in Table I, and the T_g of the cured blended resins of PBPA with BDM were also shown for comparison. Obviously, with the same BDM content, the cured blends of PBPN presented higher T_g than did the cured blends of PBPA because the methylene-bridge of PBPN provided higher crosslinked density. On the other hand, with the increase in BDM content, the T_g of the cured blends were increasing, but the T_g of the cured blends were much higher than that of BDM. According to the literature, the crosslinked structures would highly depend on the content of BDM. At low BDM

content, the linear structures would be predominant in cure process, whereas, the more crosslinked structures would form at high BDM content.¹³ Also, for cured BDM, the thermal initial self-polymerization of maleimide group produced more linear structures, and more linear structures would result in lower T_g .

CONCLUSIONS

A new propargyl-functional resin, propargyl ether bisphenol A novolac (PBPN), was successfully prepared, and the PBPN was blended with BDM at different molar ratio to obtain the blended resins. The cure behavior studies showed that the PBPN presented lower cure temperature than PBPA, and the cure behavior of PBPN could be improved markedly by blending with BDM. The TGA results indicated that cured PBPN possessed better thermal stability than have traditional cured PBPA resins, and the thermal stability of the cured blends of PBPN and BDM were enhanced with the increase of BDM content. Also, DMA results revealed that the T_g of the blends of PBPN and BDM improved with the increase in BDM content. At fixed BDM content, the cured blends based on PBPN exhibited a higher T_g than that based on PBPA. In conclusions, owing to their excellent cure and thermal properties, PBPN and the blends of PBPN with BDM were among ideal candidates for matrices of high temperature materials.

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