

Bismaleimide Modified Bis Propargyl Ether Bisphenol A Resin: Synthesis, Cure, and Thermal Properties

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ABSTRACT: Bis propargyl ether bisphenol A (PBPA) was synthesized and blended with 4,4'-bismaleimide diphenyl methane (BDM) at different molar ratios. The cure behavior of the blend resins was measured by DSC and FTIR spectra. The results indicated that the onset cure temperatures of the blend resins were about 20–30°C lower than that of pure PBPA, and the cure exothermic enthalpy of the resins also significantly reduced from 1320 (PBPA) to 493 J/g (PBPA–BDM (1.0:2.0)). The thermal stabilities and dynamic mechanical properties of the cured resins were characterized by

TGA and DMA, respectively. The thermal stability of the resins improved markedly with the increase in BDM content, and the glass transition temperature increased from 306°C for PBPA–BDM (1.0:0.5) to 358°C for PBPA–BDM (1.0:2.0). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3610–3615, 2006

Key words: bis propargyl ether bisphenol A; bismaleimide; modification; addition polymerization; thermal properties

INTRODUCTION

Propargyl ether resins are a novel class of thermal stable composite matrix resins. There has been growing interests in this kind of resins due to their excellent properties, such as good thermal stability, low moisture absorption, and low dielectric constant.¹ In addition, they could be cured via addition reaction to avoid producing volatiles, which makes it possible to get void-free materials without high pressure. A series of propargyl resins, such as bis propargyl ether bisphenol A (PBPA),² propargyl ether novolak,^{3,4} and propargyl ether benzoxazine,⁵ have been synthesized. Moreover, the cure behavior and thermal properties of the resins have been also studied.

Among the resins mentioned before, PBPA has attracted much attention in recent years because of easy synthesis and good thermal stability. Many studies have reported on its rearrangement and thermal polymerization with and without catalyst, and the thermal properties of the cured PBPA have been also investigated.^{6,7} However, the large cure exothermic enthalpy and the high cure temperature of PBPA make it unsuitable to be matrix to fabricate high performance fiber-reinforced composites. Furthermore, the mechanical properties of the cured PBPA and its

composite are poor. In general, an effective way to improve the properties of the resin is needed.

The bismaleimide resin, owing to its excellent thermal-oxidative stability and outstanding mechanical properties, has been successfully used for aerospace structure composites.⁸ Since maleimide group of bismaleimide is capable of reacting with allyl group through the addition reaction, many studies have devoted to blend bismaleimide with allyl derivatives of phenols, such as 2,2'-diallyl-bisphenol A (DABA), allyl ether novolak. The results indicated that the blend resins exhibited better toughness and high heat resistance.^{1,9} Owing to the similar chemical property of allyl with propargyl, we expected to improve the processability and thermal properties of PBPA by blending it with 4,4'-bismaleimide diphenyl methane (BDM).

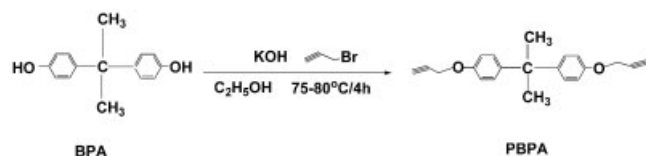
In this study, we first blended and co-cured PBPA with BDM to improve the cure behavior and thermal properties of PBPA. The effects of BDM content on the cure behavior and thermal properties were studied. The results indicate that the blend resins present better processability and thermal properties.

EXPERIMENTAL

Materials

4,4'-Bismaleimide diphenyl methane (BDM) (Feng Guang Chemical Co. Honghu, China), bisphenol A (BPA) (Xin Xing Reagent Co., China) were used as received. Propargyl bromide (Yang Nong Chemical

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Scheme 1 Synthesis of bis propargyl ether bisphenol A (PBPA).

Co., China) was distilled before use. Other reagents were used as received.

Instruments

Fourier transform infrared (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. The cure characteristics of the resins were studied by differential scanning calorimetry (DSC) using a Mettler thermal analysis DSC-822e at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Thermal gravimetric analysis (TGA) was performed by a Netch STA 409PC at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Dynamic mechanical analysis (DMA) was carried out on Netch DMA242 under nitrogen atmosphere at a heating rate of $3^\circ\text{C}/\text{min}$, and the test frequency was 1 Hz.

Synthesis of bis propargyl ether bisphenol A

PBPA were synthesized via Williamson reaction between BPA and propargyl bromide in the presence of potassium hydroxide in ethanol solution. In a typical synthesis, BPA (22.8 g, 0.1M), potassium hydroxide (11.2 g, 0.2M), 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, 0.22M) was added dropwise under agitation at room temperature. The reaction mixture was heated to $75\text{--}80^\circ\text{C}$ 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 a white solid was obtained. The crude product was recrystallized from 2-propanol to obtain a white crystal in 80% yield. The product was characterized by FTIR and ^1H NMR.

Preparation and cure of the blend resins of PBPA and BDM

PBPA was blended with BDM at different molar ratios at 150°C to give brown-red transparent liquid resins. The blend resins were designated as PBPA-BDM (1.0 : 0.5), PBPA-BDM (1.0 : 1.0), and PBPA-BDM (1.0 : 2.0), respectively, according to molar ratio of PBPA : BDM. They were cured as the following procedure: $170^\circ\text{C}/4$

h + $200^\circ\text{C}/4$ h + $250^\circ\text{C}/6$ h. The pure PBPA and BDM were also cured in the same procedure for comparison.

RESULTS AND DISCUSSION

Synthesis and characterization of PBPA

PBPA was synthesized according to the method for synthesis of allyl ether novolak described in our previous paper,⁹ and the route is illustrated in Scheme 1. To easily maintain the reaction temperature at proper temperature, ethanol was used as solvent instead of butanol for its low boiling-point (78°C), and furthermore, ethanol is also a good solvent for PBPA and can be removed easily.

The product PBPA was characterized by FTIR and ^1H NMR. In ^1H NMR spectrum, the chemical shifts were assigned as follows: δ (ppm): 1.65 (s, 6H, isopropyl), 3.59 (s, 2H, $\equiv\text{C-H}$), 4.80 (s, 4H, $-\text{CH}_2-$), 6.92–7.20 (d, 8H, aromatic). FTIR spectrum of PBPA is shown in Figure 1. The characteristic absorption peaks of $\equiv\text{C-H}$ and $\text{C}\equiv\text{C}$ 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 $-\text{OH}$ absorption of the precursor BPA was absent. The above results confirmed the structure of PBPA.

Cure behavior of the blend resins of PBPA with BDM

Both PBPA and BDM could self-cure at certain temperature. It is well known that phenyl propargyl ethers could undergo Claisen type sigmatropic rearrangement to 2H-chromenes. Then the 2H-chromenes thermally polymerized to form macromolecule.¹⁰ For PBPA the same cure reactions occurred, and are shown in Scheme 2. At the same time, BDM could also be thermally polymerized to form crosslinked net-

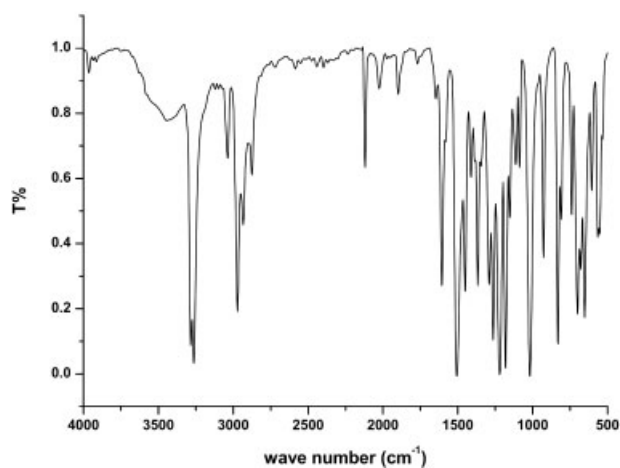
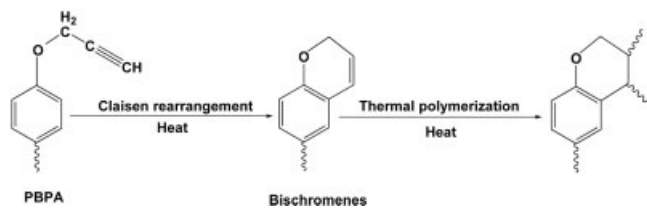


Figure 1 FTIR spectrum for PBPA.



Scheme 2 The cure reactions of PBPA.

works.¹¹ Furthermore, owing to the strong electron-withdrawing property, maleimide group could react with many unsaturated groups (vinyl, allyl, acetylene, propargyl, etc.) in different ways.¹² In literatures, the co-cure reactions of BDM and allyl derivate of phenols have been studied widely. In cure process, the ene-reaction between allyl and maleimide groups occurs first, and then the Diels–Alder reaction of residue maleimide groups with the product of ene-reaction take place, which leads to the formation of the crosslinked network.^{13,14} Owing to the similar chemical property of propargyl with allyl groups, we suppose that the same cure reactions may occur in the cure process of the blend resins (PBPA and BDM). However, there were not adequate proofs to provide the cure reaction mechanisms because of few techniques available to characterize the crosslinked structure of the products. In this paper, the cure behavior of the blend resins was characterized by DSC and FTIR.

DSC measurement

Figure 2 showed the DSC curves of the blend resins, and curves of pure PBPA and BDM were also given for comparison. The corresponding DSC data were shown in Table I. It could be known from the DSC data that the cure reactions of the resins occurred at temperatures above 200°C. A sharp exotherm was observed for PBPA corresponding to the rearrangement and polymerization. For BDM, a broad and small exotherm was observed, which was attributed to the double bond self-polymerization. Among the resins shown in Figure 2, the PBPA presented the highest cure temperature (T_{onset} and T_{peak}) and largest cure exothermic enthalpy (ΔH), while the BDM showed the lowest cure temperature and smallest exothermic enthalpy. On the other hand, the blend resins showed single exotherm and their cure temperatures and exothermic enthalpy were between that of PBPA and BDM. With the increase in BDM content, the cure temperatures and exothermic enthalpy of the blend resins decreased. In other words, the addition of BDM significantly decreased the cure temperature and exothermic enthalpy of the blend resins. As a result, the blend resins could cure in lower temperature range, and their cure reaction were more moderate due to

lower exothermic enthalpy, which made them exhibit better processability than PBPA resin.

DSC technique has been performed to investigate the curing kinetics of thermosetting resins, and there are many methodologies used to calculate the kinetic parameters. In this paper, Coats–Redfern (C–R) equation^{15,16} was chosen to obtain kinetic parameters for PBPA–BDM systems.

The Coats–Redfern equation can be written as

$$\ln\{g(\alpha)/T^2\} = \ln\{AR/\Phi E(1 - 2RT/E)\} - E/RT$$

where $g(\alpha) = \{1 - (1 - \alpha)^{1-n}\}/(1-n)$, for $n = 1$ and $g(\alpha) = -\ln(1 - \alpha)$; R is the universal gas constant; n is the reaction order; A is Arrhenius frequency factor; E is the apparent activation energy; and T is the absolute temperature. α is estimated from the fractional enthalpy of reaction. Kinetic plots were made by assuming different reaction order according to the C–R equation, and the one which fit best furnished the value of n . The fit plots of PBPA–BDM system were shown in Figure 3, and the as-calculated kinetic data are compiled in Table I.

The fit results showed that the cure reaction followed mostly the first order. The cure apparent activation energy (E_c) value was in the range 150–200 kJ/mol. E_c for the blend resins was lower than that for BDM and PBPA, and decreased with the increase in BDM content. It implied that the co-cure reactivity between PBPA and BDM was higher than self-cure reactivity of PBPA and BDM, which might be the reason that the blend resins presented lower cure temperatures.

FTIR measurement

FTIR spectra were used to follow the cure process. PBPA–BDM (1.0:1.0) was chosen as an example, and

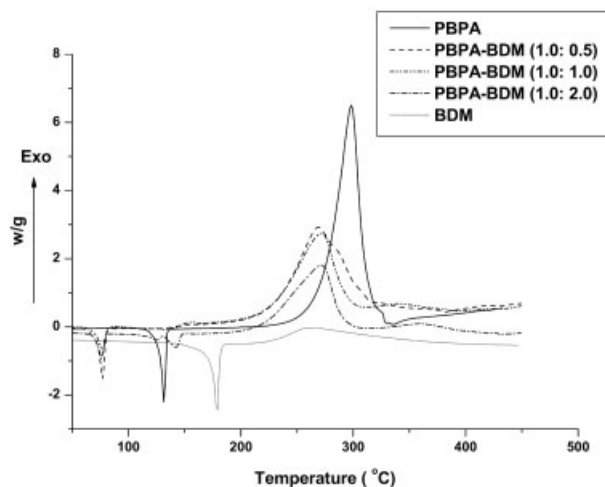


Figure 2 DSC curves of PBPA, BDM, and the blend resins of them.

TABLE I
DSC and Kinetic Parameters of Cure Reaction for PBPA, BDM, and the Blend Resins of Them

Sample name	T_{onset}^a (°C)	T_{peak}^b (°C)	ΔH^c (J/g)	Cure temperature (°C)	n	E_c (KJ/mol)	A_c (s^{-1})
PBPA	253	286	1320	210–310	1	164.8	1.48×10^{12}
PBPA-BDM (1.0 : 0.5)	229	271	837	210–310	1	158.9	0.9×10^{12}
PBPA-BDM (1.0 : 1.0)	226	271	630	210–310	1	150.7	1.61×10^{11}
PBPA-BDM (1.0 : 2.0)	217	271	493	210–310	1	143.1	3.71×10^{10}
BDM	205	241	212	205–310	1	199.2	1.06×10^{17}

^a T_{onset} is the onset temperature in the exotherm.

^b T_{peak} is the peak temperature in the exotherm.

^c ΔH is the exothermic enthalpy in the exotherm.

the FTIR spectra of uncured resin, cured resins after 170°C/4 h, and 170°C/4 h + 200°C/4 h + 250°C/6 h are shown in Figure 4. In the cure process, after the resin was cured at 170°C/4 h, the absorption peak of $\equiv\text{C}-\text{H}$ at 3263 cm^{-1} and the absorption peak of $\text{C}\equiv\text{C}$ at 2119 cm^{-1} were decreased remarkably, while the absorption peak of $\text{C}-\text{N}-\text{C}$ of maleimide at 1149 cm^{-1} changed slightly. This indicated that more propargyl groups were consumed than maleimide groups in co-cure reactions. After the resin was cured at 170°C/4 h + 200°C/4 h + 250°C/6 h, the absorption of maleimide and propargyl groups both disappeared, which suggested that the resin could cure completely under such conditions.

Thermal properties of the cured blend resins of PBPA with BDM

TGA measurement

Thermal stability of the cured blend resins were evaluated by TGA. Figure 5 shows the TGA curves

of cured PBPA, cured BDM, and the cured blend resins recorded under nitrogen atmosphere. The 5% mass loss temperature ($T_{5\%}$) and char residue at 900°C (R_{900}) were chosen as the thermal stability parameters and are compiled in Table II. As seen from 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 PBPA (353°C). Also, the R_{900} for cured BDM was 47% and higher than that for cured PBPA (41%). On the other hand, for the cured blend resins, $T_{5\%}$ and R_{900} were between that for cured PBPA and cured BDM. With the increase in BDM content, $T_{5\%}$ for the cured blend resins improved from 354°C (cured PBPA-BDM (1.0:0.5)) to 396°C (cured PBPA-BDM (1.0:2.0)), and R_{900} for that also increased from 40% (cured PBPA-BDM (1.0:0.5)) to 46% (cured PBPA-BDM (1.0:2.0)). So the cured blend resins presented much better thermal stability than cured PBPA, which were beneficial from the addition of the BDM.

The kinetics of decomposition of the major step were analyzed using the C-R method, and a first

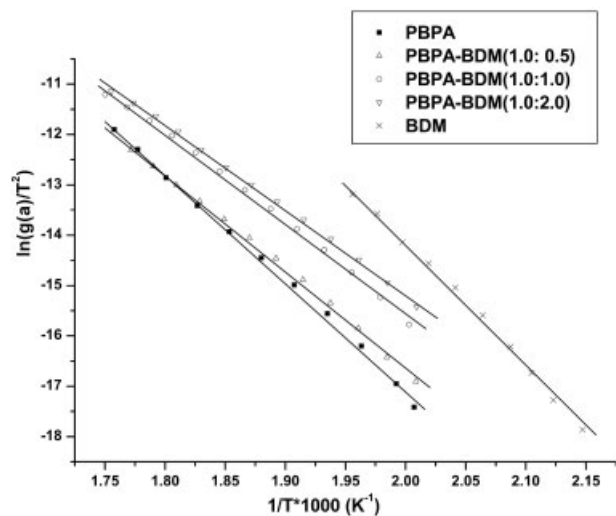


Figure 3 Cure kinetic plots for PBPA, BDM, and the blend resins of them calculated by C-R method.

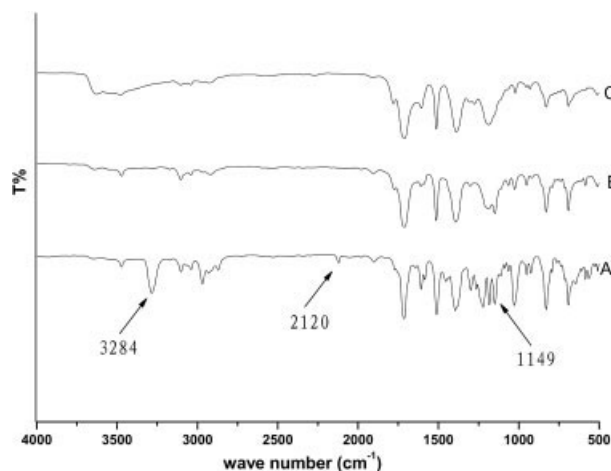


Figure 4 FTIR spectra for PBPA-BDM (1.0:1.0) following the cure process. (A) uncured resin, (B) cured after 170°C/4 h, and (C) cured after 170°C/4 h + 200°C/4 h + 250°C/6 h.

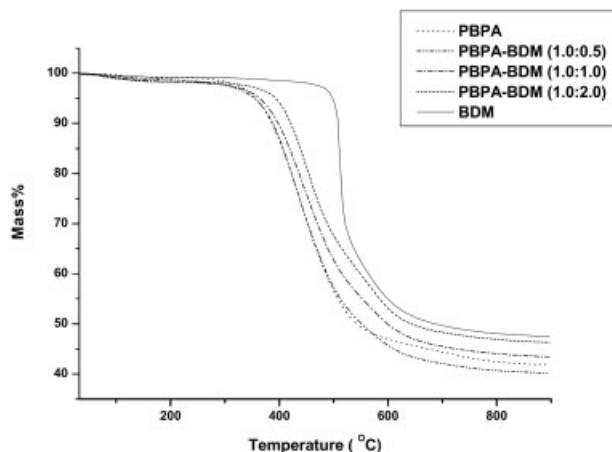


Figure 5 TGA curves for cured PBPA, BDM, and the cured blend resins of them.

order ($n = 1$) kinetics was assigned for the degradation of the cured resins under nitrogen atmosphere. The fit kinetic plots are shown in Figure 6 and the calculated parameters are depicted in Table II. The cured resins showed two-stage decomposition reaction and the inflection temperatures of the two stages were in the range of 430–452°C, except that the inflection temperature of BDM was 510°C. The first stage could be attributed to the degradation of methylene and the structures derived from propargyl group, and the second stage should be attributed to the aryl and the structures derived from maleimide in the cured resins. With the increase in BDM content, the computed decomposition apparent activation energy (E_d) and decomposition frequency factor (A_d) were both increased, and the increase in E_d implied indirectly that the thermal stabilities of the blend resins improved.

DMA measurement

In the cured experiment to prepare casting matrix, PBPA was unable to form a compact sample because of its large cure exothermic enthalpy. However, when

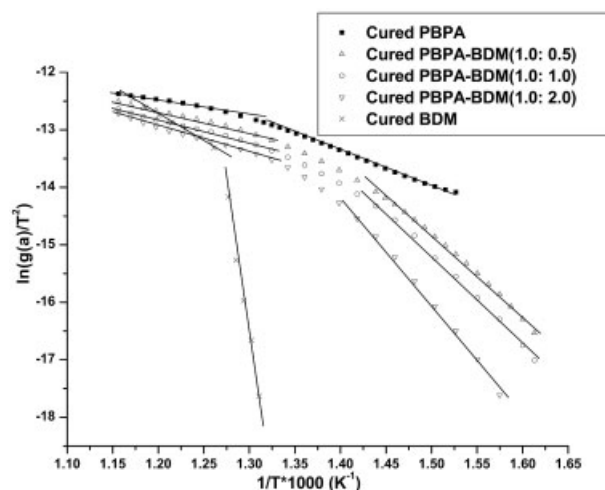


Figure 6 Degradation kinetic plots for cured PBPA, BDM, and the cured blend resins of them calculated by C–R method.

BDM was added, the compact sample could be obtained easily. Therefore, only the cured BDM and the cured blend resins were measured by DMA, and the storage modulus (E') and the loss factor ($\tan(\delta)$) are shown as a function of temperature in Figure 7. The corresponding analysis data are compiled in Table III. The glass transition temperature (T_g) was defined as the peak temperature of $\tan(\delta)$. The T_g of cured PBPA–BDM (1.0:0.5), PBPA–BDM (1.0:1.0), and PBPA–BDM (1.0:2.0) were 306, 324, and 358°C, respectively. It was obvious that the T_g increased markedly with increase in BDM content, and the T_g of the cured blend resins was much higher than that of cured BDM (216°C), which was cured by the same cure procedure as the blend resins.

From the rubber elasticity theory,¹⁷ the variation in the rubbery storage modulus (E') can be expressed as a function of crosslink density by the following relationship:

$$E' = 3\theta\rho RT/M_c$$

TABLE II
TGA Data and Degradation Kinetic Parameters for Cured PBPA, BDM and the Cured Blend Resins of Them

Sample name	$T_{5\%}^a$ (°C)	R_{900}^b (%)	Inflection temperature (°C)	First stage		Second stage	
				A_d (S^{-1})	E_d (kJ/mol)	A_d (S^{-1})	E_d (kJ/mol)
PBPA	353	41	432	12.6	69.7	2.48×10^{-5}	4.6
PBPA-BDM (1.0 : 0.5)	354	40	433	4.47×10^4	114.0	7.15×10^{-3}	29.0
PBPA-BDM (1.0 : 1.0)	364	43	445	1.74×10^6	135.3	3.10×10^{-2}	34.0
PBPA-BDM (1.0 : 2.0)	393	46	452	2.29×10^7	154.2	5.50×10^{-2}	42.1
BDM	496	47	510	2.63×10^{51}	819.0	15.46	75.9

^a $T_{5\%}$ is the 5% mass loss temperature.

^b R_{900} is the char residue at 900°C.

where E' is the storage modulus of the cured resins in the rubbery plateau region above T_g ($T_g + 40^\circ\text{C}$), R is the gas content, T is the absolute temperature, ρ is the density of the crosslinked network, θ is the front factor, and M_c is the average molecular weight between entanglements. The aforementioned equation shows that E' is proportional to $1/M_c$; in other words, an increase in E' will reveal an increase in the crosslink density.

Consequently, for the cured blend resins, the data in Table III revealed that the plateau E' increased with increase in BDM content, and the cured BDM presented lowest plateau E' . As a result, the cured blend resins possessed higher crosslink density (or smaller M_c) than cured BDM. As discussed in DSC section, the blend resins presented higher cure reactivity than pure PBPA and BDM, which might make the blend resins react completely and possess high crosslink density in the cure process, and the high crosslink density resulted in high T_g of the cured blend resins.

The TGA and DMA results indicated that the thermal stability and thermal mechanical properties of PBPA resins evidently improved with the addition of BDM. On the other hand, too much addition of BDM might make the cured blend resins more brittle because of the inherent brittleness of BDM. So a proper content of BDM should be chosen in applications, which not only improves the processability and thermal properties of the blend resins, but also keeps enough toughness. For example, for the blend resins of BDM and diallyl bisphenol A, approximately equivalent molar of BDM and diallyl bisphenol A presented better comprehensive properties.¹⁸

CONCLUSIONS

PBPA was blended with different molar ratios of BDM. The blend resins presented better processability

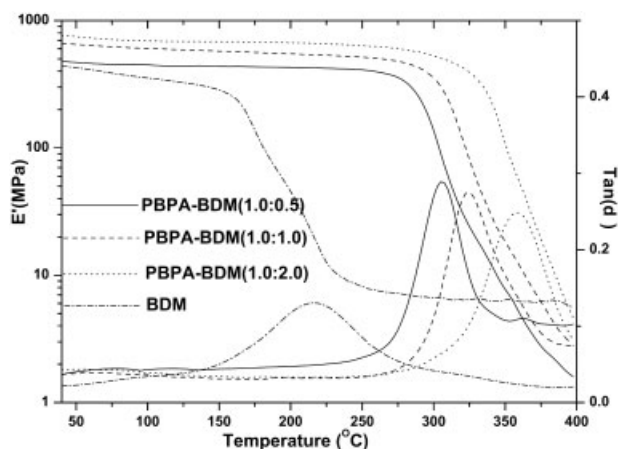


Figure 7 DMA curves for cured BDM and the cured blend resins of PBPA with BDM.

TABLE III
DMA Analysis Data for Cured BDM and the Cured Blend Resins of PBPA and BDM

Sample name	Initial E' (MPa)	Plateau E' (MPa) ^a	T_g ($^\circ\text{C}$)
PBPA-BDM (1.0 : 0.5)	482	12	306
PBPA-BDM (1.0 : 1.0)	681	28	324
PBPA-BDM (1.0 : 2.0)	784	32	358
BDM	439	8	216

^a The plateau E' is taken at $T_g + 40^\circ\text{C}$.

and thermal properties. DSC analysis revealed that the cure exothermic enthalpy and temperature of the blend resins decreased with the increase in BDM content, and so the blend resins could cure at lower temperature and the cure process was more moderate. Kinetic analysis further confirmed the aforementioned conclusion. The TGA results indicated that the thermal stability of the cured blend resins improved with the increase in BDM content due to the excellent thermal stability of the cured BDM. The DMA results illuminated that the cured blend resins had higher T_g than the cured BDM, and the T_g of the cured blend resins increased with increase in BDM content. Owing to improved processability and excellent thermal properties, the blend resins of PBPA and BDM have a potential application as matrix for advanced heat-resistant composite materials.

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