



Synthesis, preparation and properties of novel high-performance allyl–maleimide resins

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ABSTRACT

Three novel allyl–maleimide monomers (i.e., A₂B, AB and AB₂) were designed, synthesized and thermally cured to yield a series of high-performance allyl–maleimide resins. All the monomers obtained are readily soluble in common organic solvents enabling an easy solution processing. The thermal properties of the three monomers were studied by the differential scanning calorimetry (DSC). A₂B and AB showed fairly low melting temperature ($T_m < 90$ °C) and wide processing window ranging from 90 °C to 260 °C. The thermal stability of the cured allyl–maleimide resins (i.e., PA₂B, PAB and PAB₂) was studied by the thermogravimetric analysis (TGA). Dynamic mechanical analysis (DMA) was used to investigate the dynamic mechanical properties of the composites based on the cured allyl–maleimide resins. PA₂B and PAB₂ showed good glass transition temperatures ($T_g > 270$ °C) and their corresponding composites showed high bending modulus ($E' > 1900$ MPa). Allyl-compound-modified BMI resins based on AB monomer were prepared. Rheometer revealed that the processability of the prepolymer (BR–AB-pre) was improved by the addition of AB monomer. The cured BMI resins (BR and BR–AB) showed good thermal stability ($T_d > 400$ °C, both in nitrogen and in the air), high glass transition temperature ($T_g > 320$ °C), and good mechanical properties and low water uptake (<2.6%, 120 h).

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1. Introduction

Bismaleimide (BMI) resins are an important type of thermoset polymeric materials that have found wide applications ranging from microelectronics to aerospace due to their good processability, high glass transition temperature and high modulus [1–3]. However, BMI monomers are of rigid molecular structures, which leads to high melting temperature and poor solubility in common organic solvents while the cured BMI resins have high crosslinking density and rigid molecular networks, which result in an inherent brittleness.

To overcome such a problem, scientists used diamines to react with BMI monomers, which could reduce the crosslinking density and efficiently improve the toughness of the cured BMI resins [4,5]. However, the thermal properties were decreased dramatically. High-performance thermoplastics, such as polyimides and poly(aryletherketone), were blended with BMI resins to form an

interpenetrating polymer network (IPN), which showed improved toughness, but they hampered processability [6,7].

Allyl-compound-modified BMI resin is one of the most successful BMI resins [8–11]. Typically, BMI resin contains 4,4'-bismaleimidodiphenylmethane (BMDM) and 2,2'-diallylbisphenol A (DBA) [12], as shown in Chart 1. The prepolymers show good processability and the cured BMI resins possess high thermal stability, high glass transition temperature, and good toughness. It is one of the leading matrix resins for carbon fiber composite for advanced aerospace application. The curing process of such BMI resins has been widely studied, as shown in Scheme 1. It is believed that allyl groups reacted with maleimide groups at around 130 °C via the Ene reaction to yield an intermediate, and subsequently reacted with maleimide groups at around 200 °C via the Diels–Alder reaction to form crosslinking networks [13,14]. Homopolymerization of maleimide groups and copolymerization of maleimide groups and allyl groups were also existed during the curing process [15,16].

However, all of these BMI resins contained at least two components, which brought new problems: the prepolymerization is needed and different batches might be of different properties. If we design a monomer containing maleimide groups and allyl

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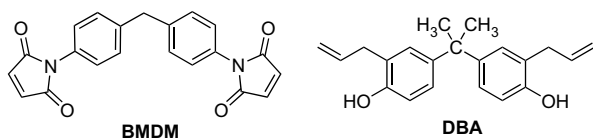


Chart 1. The molecular structures of BMDM and DBA.

groups, such monomer is a type of single component resins, which might show similar properties to allyl-compound-modified BMI resins.

In this paper, we report the synthesis and characterization of novel allyl–maleimide monomers (i.e., A₂B, AB and AB₂) containing both maleimide and allyl groups. The preparation of BMI resins based on AB monomer was also described. A₂B and AB showed good processability and thermal property. BMI resin (BR–AB) based on AB monomer showed good processability, thermal and mechanical properties.

2. Experimental

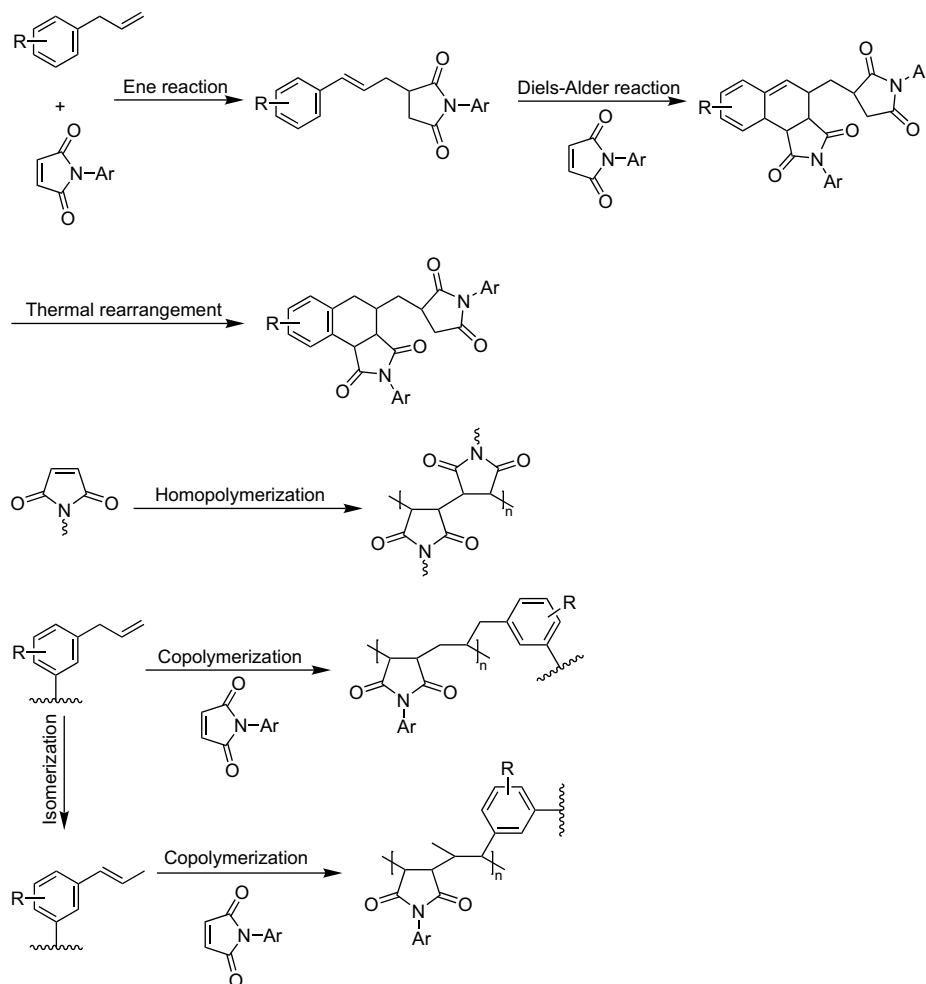
2.1. Materials

4-Maleimidobenzoic acid chloride and *N*-(4-hydroxyphenyl)maleimide were prepared according to the previous literature [17,18]. Tetrahydrofuran was dried over sodium and distilled. Triethylamine was dried over potassium hydroxide and

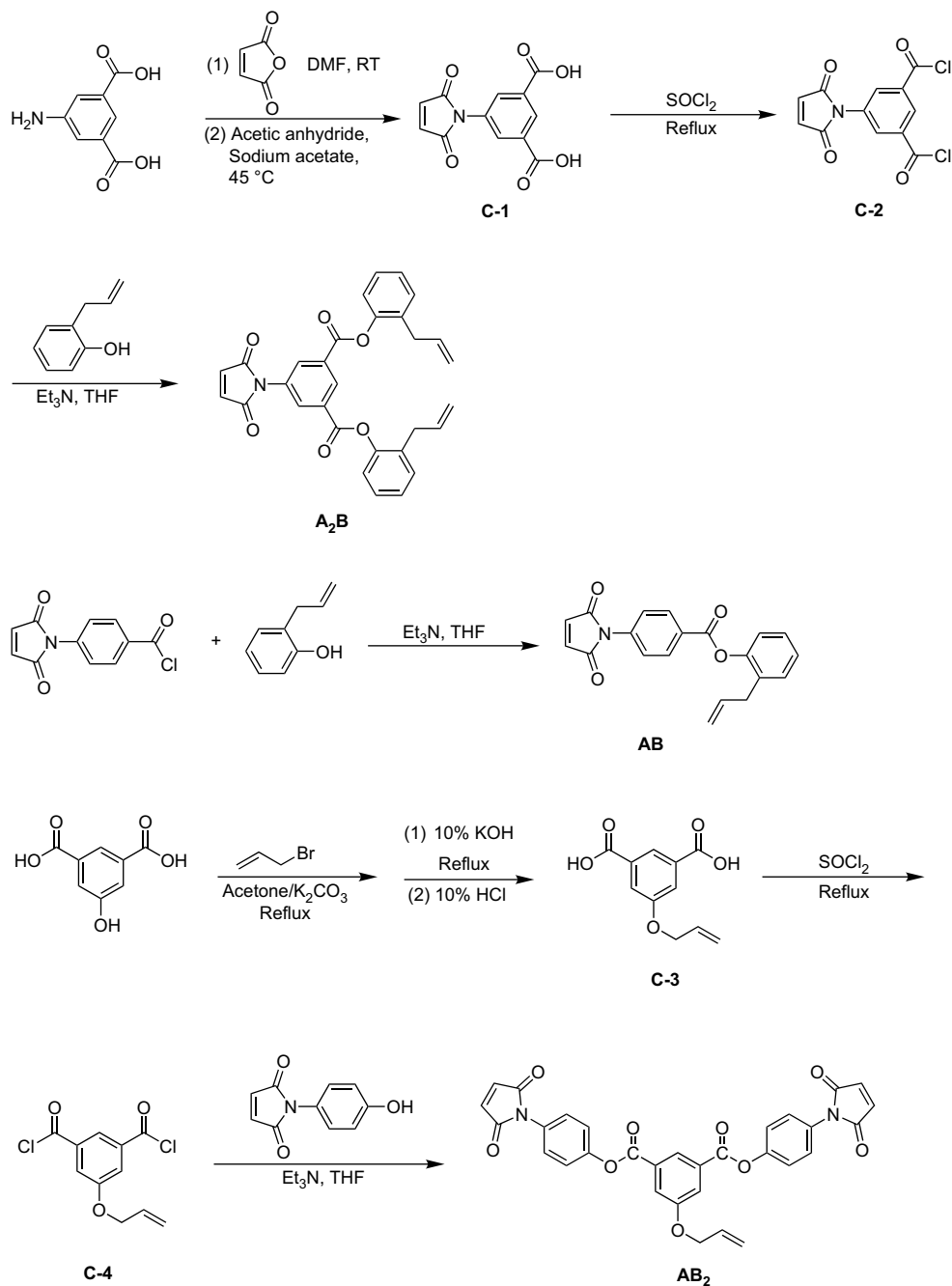
distilled. 4,4'-Bismaleimidodiphenylmethane (BMDM) was purchased from Hengxing Chemical Industrial Technology Company (Yantai, China) and purified by recrystallization from toluene. 2,2'-Diallylbisphenol A (DBA), 2-allylphenol and 5-aminoisophthalic acid were purchased from Aldrich and used as-received. 5-Hydroxyisophthalic acid was purchased from Acros and used as-received. All other chemicals were purchased from Beijing Chemical Company and used as-received.

2.2. Characterization

¹H NMR and ¹³C NMR spectra were recorded on a Bruker ARX400 spectrometer using deuterated chloroform or dimethylsulfoxide-*d*₆ (DMSO-*d*₆) as the solvent with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm scale. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna 750 Fourier transform infrared spectrometer. Elemental analysis was recorded using an Elementar Vario EL instrument. Differential scanning calorimetry (DSC) was recorded with a Thermal Analysis (TA) DSC-2010 in nitrogen at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed on a TA TGA-DSC Q600 thermogravimetric analyzer at a heating rate of 10 °C/min in nitrogen or in the air. Dynamic mechanical analysis (DMA) was performed on a NETZSCH DMA 242 C (NETZSCH, Selb, Germany) with a driving frequency of 1.0 Hz, single cantilever mode and a scanning rate of 3 °C/min in nitrogen. The size of the composites and the neat cured resins for DMA measurement was



Scheme 1. Possible reactions between allyl groups and maleimide groups.



Scheme 2. Synthetic route for the allyl-maleimide monomers A₂B, AB and AB₂.

8 mm × 5 mm × 0.5 mm and 8 mm × 5 mm × 2 mm, respectively. Viscosity was tested by rheometer (TA instrument AR2000) at a heating rate of 2 °C/min. The diameter of the specimen for viscosity test was 25 mm. Mechanical properties (tensile, flexural and impact) were measured by Chinese standards (GB/T 2567–2571-1995). Water uptake was recorded by weighing the sample after predetermined exposure times. The percentage gain after a measurement was calculated by the following equation:

$$\text{Water uptake} = (W - W_0) / W_0 \times 100\%$$

where W_0 and W denote weights of dry and immersed samples, respectively. The size of the specimen for water uptake study was 35 mm × 15 mm × 4 mm.

2.3. Synthesis

2.3.1. Synthesis of 5-maleimido-isophthalic acid (C-1)

This compound was synthesized according to the previous literature [19]. ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.25 (s, 2H, -CH=CH-), 8.20 (s, 2H, ArH), 8.47 (s, 1H, ArH), 13.52 (s, 2H, -OH).

2.3.2. Synthesis of 5-maleimido-isophthalic acid chloride (C-2)

5-Maleimido-isophthalic acid (26.1 g, 0.10 mol) was mixed with thionyl chloride (300 mL) in a 500 mL round-bottomed flask. The reaction mixture was heated slowly to a temperature of 80 °C and stirred at that temperature for 4 h. After cooling down to room temperature, the excess thionyl chloride was removed by rotavapouration to obtain C-2 (29.7 g, 100% yield).

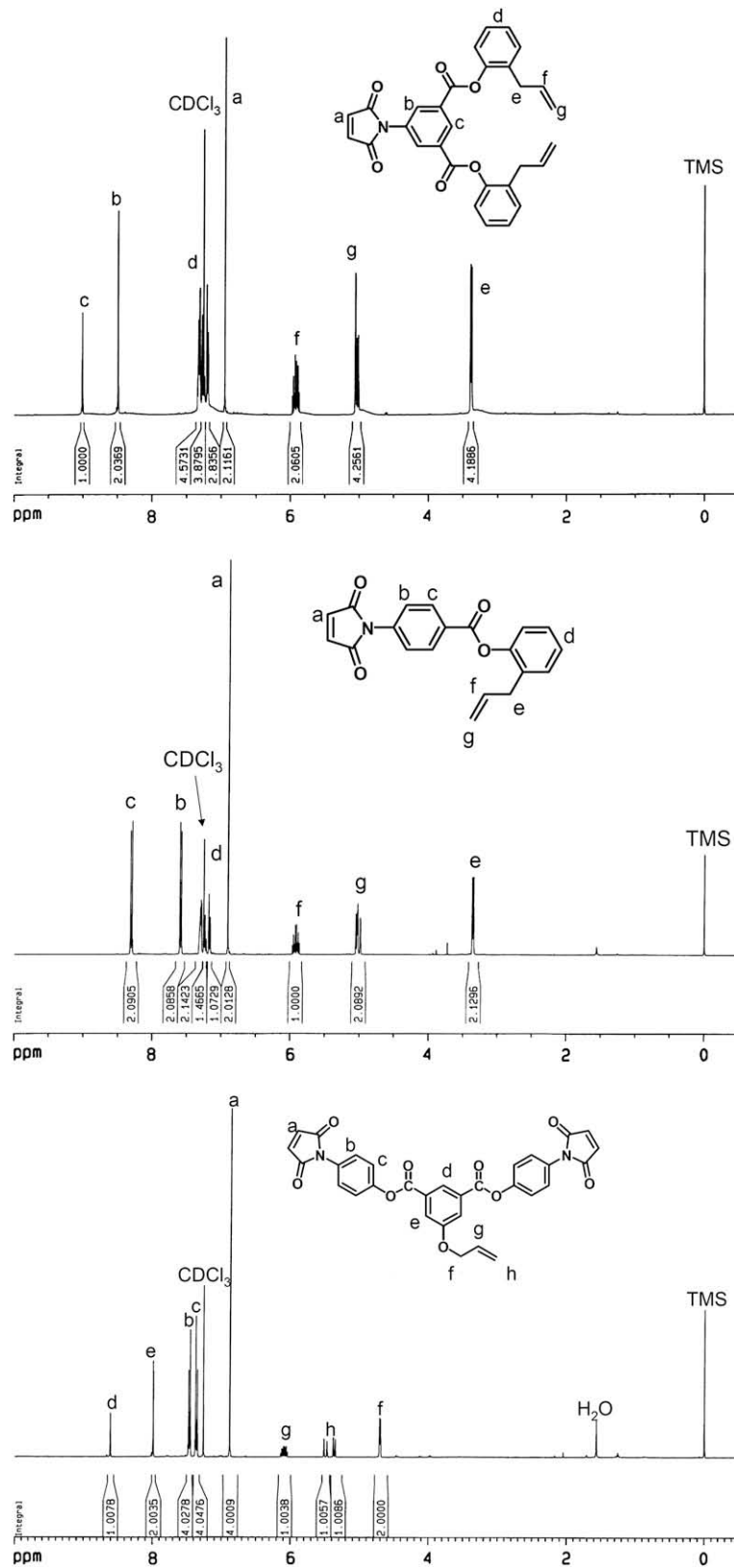


Fig. 1. ¹H NMR spectra of the allyl-maleimide monomers in CDCl₃.

Table 1
The solubility of the allyl-maleimide monomers in different solvents.^a

	Toluene	Acetone	DCM	Chloroform	THF	DMF	DMSO	NMP
A ₂ B	++	++	++	++	++	++	++	++
AB	++	++	++	++	++	++	++	++
AB ₂	--	+	++	++	+	+	++	++

^a ‘++’ = soluble (≥ 10 mg/mL), ‘+’ = soluble under heating, ‘--’ = insoluble. DCM = dichloromethane; THF = tetrahydrofuran; DMF = *N,N*-dimethylformamide; DMSO = dimethylsulfoxide; NMP = *N*-methyl-2-pyrrolidinone.

2.3.3. Synthesis of 5-maleimido-isophthalic acid bis(2-allylphenyl) ester (A₂B)

To an ice-cold solution of 5-maleimido-isophthalic acid chloride (29.7 g, 0.10 mol) in tetrahydrofuran (400 mL) in a 1000 mL round-bottomed flask was added dropwise a solution of 2-allylphenol (26.8 g, 0.20 mol) and triethylamine (29 mL, 0.20 mol) in tetrahydrofuran (200 mL). After the addition, the reaction solution was naturally warmed to room temperature and stirred for 8 h. The solution was poured into dichloromethane (200 mL) and washed in a separatory funnel with distilled water (3 × 100 mL), dried over anhydrous magnesium sulfate and rota-evaporated to give the product which was subjected to silica gel column chromatography (petroleum ether/dichloromethane, 1/3, V/V) to give pure A₂B (26.6 g, 70% yield). IR (KBr, cm⁻¹): 1743 ($\nu_{C=O}$ of ester), 1717 ($\nu_{C=O}$ of maleimide), 1579 (aromatic rings). ¹H NMR (400 MHz, CDCl₃): δ 3.39 (d, *J* = 6.5 Hz, 4H, -CH₂CH=CH₂), 5.01–5.06 (m, 4H, -CH₂CH=CH₂), 5.92 (m, 2H, -CH₂CH=CH₂), 6.95 (s, 2H, -CH=CH-), 7.19–7.34 (m, 8H, ArH), 8.49 (s, 2H, ArH), 9.01 (s, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 168.65, 163.10, 148.82, 135.54, 134.48, 132.41, 131.96, 131.92, 130.63, 130.57, 127.58, 126.55, 122.24, 116.50 and 34.72. Anal. Calcd. for C₃₀H₂₃NO₆: C, 73.01; H, 4.70; N, 2.84. Found: C, 72.95; H, 4.75; N, 2.74. MS (EI): 493 (found).

2.3.4. Synthesis of 5-maleimidobenzoic acid 2-allylphenyl ester (AB)

To an ice-cold solution of 5-maleimidobenzoic acid chloride (35.5 g, 0.10 mol) in tetrahydrofuran (200 mL) in a 500 mL round-bottomed flask was added dropwise a solution of 2-allylphenol (13.4 g, 0.10 mol) and triethylamine (14.5 mL, 0.10 mol) in tetrahydrofuran (200 mL). After the addition, the reaction solution was warmed to room temperature and stirred for 8 h. The solution was poured into dichloromethane (200 mL) and washed in a separatory

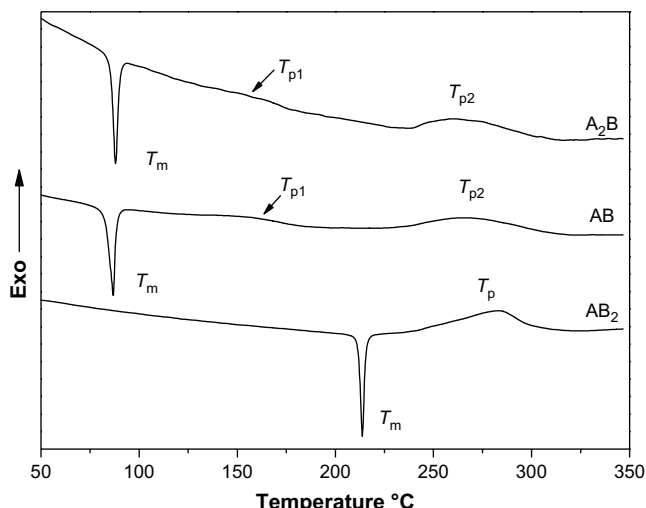


Fig. 2. DSC curves of the allyl-maleimide monomers at a heating rate of 10 °C/min.

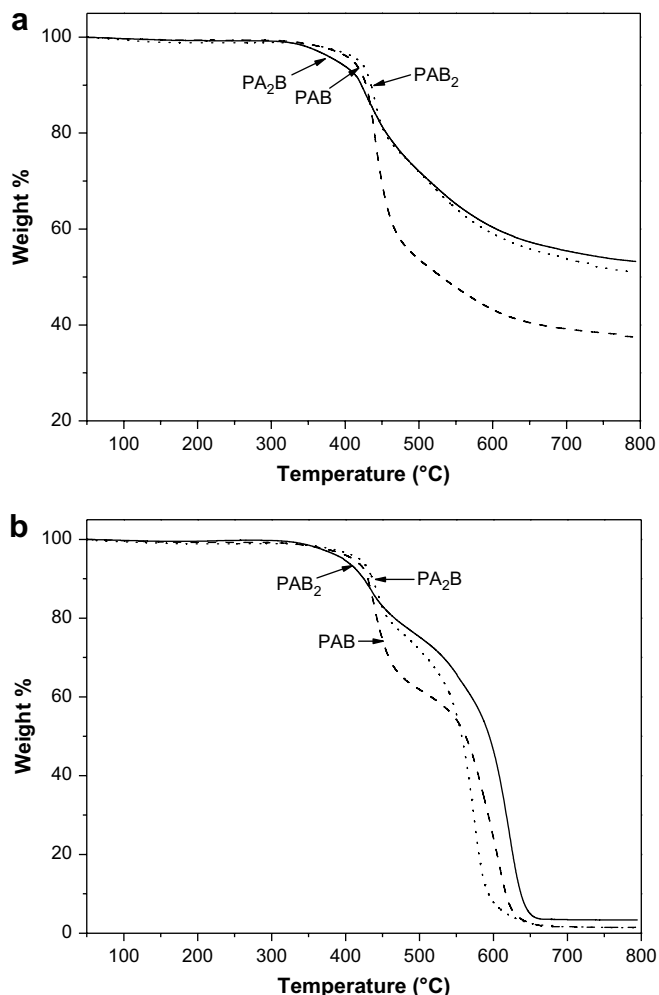


Fig. 3. TGA curves of the cured allyl-maleimide resins at a heating rate of 10 °C/min in nitrogen (a) and in the air (b).

funnel with distilled water (3 × 100 mL), dried over anhydrous magnesium sulfate and rota-evaporated to give the product which was subjected to silica gel column chromatography (petroleum ether/dichloromethane, 1/3, V/V) to give pure AB (28.0 g, 84% yield). IR (KBr, cm⁻¹): 1728 ($\nu_{C=O}$ of ester), 1712 ($\nu_{C=O}$ of maleimide), 1574 (aromatic rings). ¹H NMR (400 MHz, CDCl₃): δ 3.35 (d, *J* = 6.5 Hz, 2H, -CH₂CH=CH₂), 4.98–5.05 (m, 2H, -CH₂CH=CH₂), 5.92 (m, 1H, -CH₂CH=CH₂), 6.91 (s, 2H, -CH=CH-), 7.16–7.32 (m, 4H, ArH), 7.95 (d, *J* = 8.6 Hz, 2H, ArH), 8.31 (d, *J* = 8.6 Hz, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 168.85, 164.10, 148.98, 135.97, 135.67, 134.42, 132.01, 131.02, 130.45, 128.37, 127.48, 126.30, 125.33, 122.37, 116.34 and 34.64. Anal. Calcd. for C₂₀H₁₅NO₄: C, 72.06; H, 4.54; N, 4.20. Found: C, 72.16; H, 4.58; N, 4.11. MS (EI): 333 (found).

Table 2
Thermal properties of the cured allyl-maleimide resins.

Cured resins	<i>T_g</i> ^a (°C)	<i>T_d</i> ^b (°C)		<i>Y_c</i> ^c (%)	
		In N ₂	In air	In N ₂	In air
PA ₂ B	275	389	397	55	3
PAB	233	411	410	39	2
PAB ₂	>350	420	419	54	2

^a The glass transition temperature determined from DMA.

^b 5% weight loss temperature determined from TGA at a heating rate of 10 °C/min.

^c Char yield at 700 °C determined from the TGA analysis.

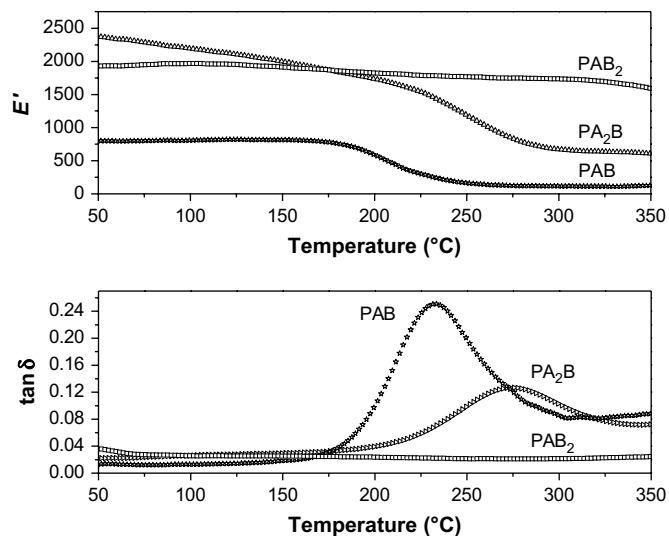


Fig. 4. DMA curves of the composites composed of cured allyl-maleimide resins and glass cloth at a heating rate of 3 °C/min in nitrogen with a single cantilever mode.

2.3.5. Synthesis of 5-allyloxy-isophthalic acid (C-3)

5-Hydroxy-isophthalic acid (18.2 g, 0.10 mol), 3-bromopropene (36.6 g, 0.30 mol), K_2CO_3 (165.6 g, 1.20 mol) and acetone (500 mL) were added to a 1000 mL round-bottomed flask. The reaction mixture was heated to 56 °C and refluxed overnight. The solution was collected by suction filtration, and then the solvent was removed by rota-evaporation to obtain a liquid residue, which was added to 10% NaOH solution. The reaction solution was refluxed for 4 h and cooled down to room temperature, followed by acidifying to a pH value of 2 to yield a white solid product. Then, it was filtrated and washed with distilled water until neutral pH value to give C-3 (20.0 g, 90% yield).

2.3.6. Synthesis of 5-allyloxy-isophthalic acid chloride (C-4)

5-Allyloxy-isophthalic acid (22.2 g, 0.10 mol) was mixed with thionyl chloride (300 mL) in a 500 mL round-bottomed flask. The reaction mixture was heated slowly to a temperature of 80 °C and stirred at that temperature for 4 h. After cooling down to room temperature, the excess thionyl chloride was removed by rota-evaporation to obtain C-4 (25.9 g, 100% yield).

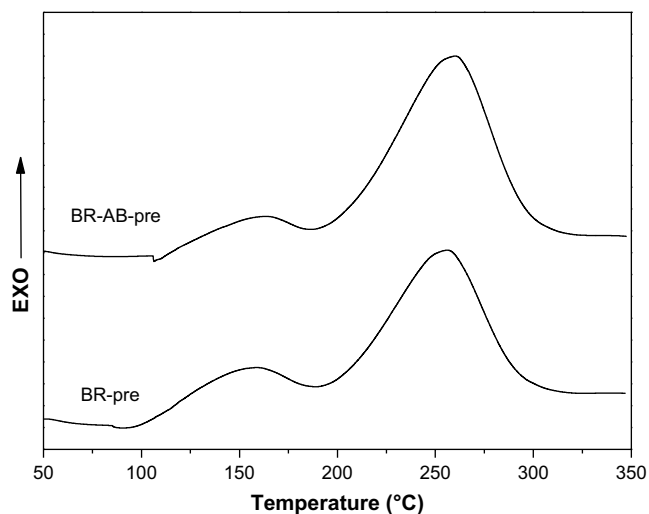


Fig. 5. DSC curves of the prepolymers (BR-pre and BR-AB-pre) at a heating rate of 10 °C/min.

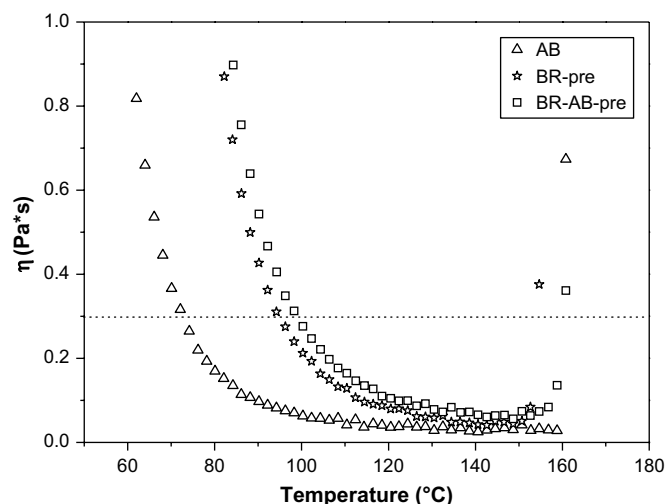


Fig. 6. Viscosity-temperature plots for the prepolymers (BR-pre and BR-AB-pre) and AB monomer at a heating rate of 2 °C/min.

2.3.7. Synthesis of 5-allyloxy-isophthalic acid bis (4-maleimidophenyl) ester (AB₂)

To an ice-cold solution of 5-allyloxy-isophthalic acid chloride (25.9 g, 0.10 mol) in tetrahydrofuran (300 mL) in a 1000 mL round-bottomed flask was added dropwise a solution of *N*-(4-hydroxyphenyl)maleimide (37.8 g, 0.20 mol) and triethylamine (29 mL, 0.20 mol) in tetrahydrofuran (400 mL). After the addition, the reaction solution was naturally warmed to room temperature and stirred for 8 h, followed by pouring into distilled water (2000 mL) to yield a yellow precipitate which was collected by suction filtration, and then washed with distilled water and dried in an oven at 80 °C. Recrystallization from THF gave the pure AB₂ (42.3 g, 75% yield). IR (KBr, cm^{-1}): 1749 ($\nu_{C=O}$ of ester), 1716 ($\nu_{C=O}$ of maleimide), 1574 (aromatic rings). ¹H NMR (400 MHz, $CDCl_3$): δ 4.71 (d, $J = 6.5$ Hz, 2H, $-CH_2CH=CH_2$), 5.35–5.52 (m, 2H, $-CH_2CH=CH_2$), 6.09 (m, 1H, $-CH_2CH=CH_2$), 6.88 (s, 4H, $-CH=CH-$), 7.36 (d, $J = 8.9$ Hz, 4H, ArH), 7.46 (d, $J = 8.9$ Hz, 4H, ArH), 8.01 (s, 2H, ArH), 8.61 (s, 1H, ArH). ¹³C NMR (100 MHz, $CDCl_3$): δ 169.24, 163.71, 158.93, 149.78, 134.22, 132.12, 131.18, 129.02, 126.97, 124.09, 122.30, 118.51 and 69.40. Anal. Calcd. for $C_{31}H_{20}N_2O_9$: C, 65.96; H, 3.57; N, 4.96. Found: C, 65.95; H, 4.08; N, 4.59. MS (EI): 564 (found).

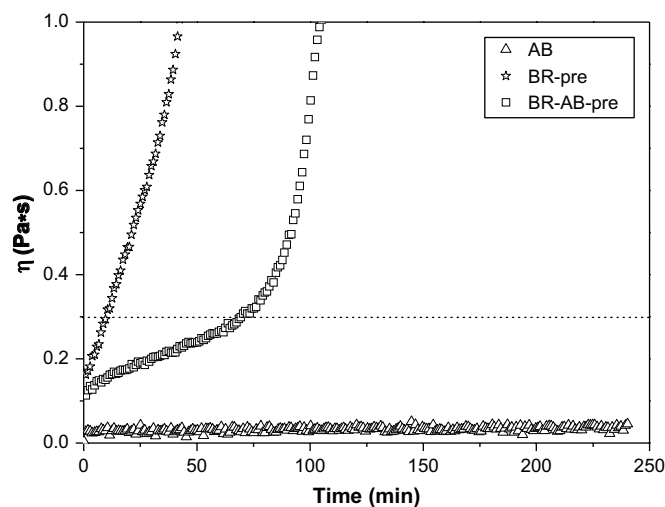


Fig. 7. Viscosity-time plots for the prepolymers (BR-pre and BR-AB-pre) and AB monomer at 110 °C.

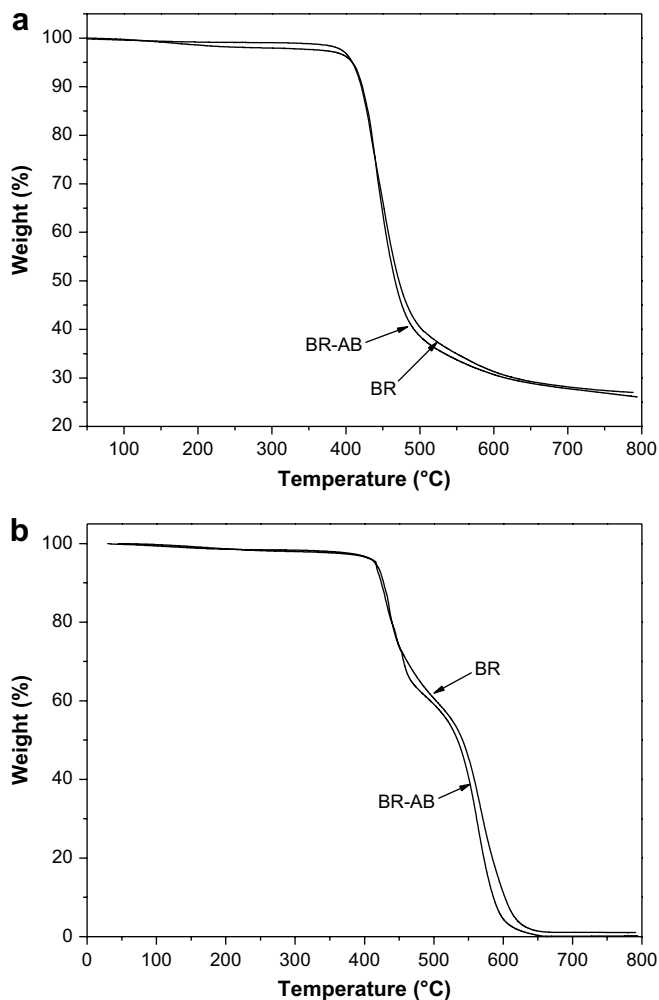


Fig. 8. TGA curves of the cured BMI resins at a heating rate of 10 °C/min in nitrogen (a) and in the air (b).

2.3.8. Preparation of the cured allyl-maleimide resins and the composites composed of the cured allyl-maleimide resins and glass cloth

The cured allyl-maleimide resins were obtained by curing the allyl-maleimide monomers by the following heating profile: 200 °C for 4 h, 250 °C for 2 h and 280 °C for 0.5 h in an oven open to the air.

A general preparation procedure of composites is described as follows: An allyl-maleimide monomer was dissolved in DMF at a concentration of 0.2 g/mL. A glass cloth of 8 mm × 5 mm × 0.5 mm was dipped into the solution and then vertically hung. The solvent was allowed to evaporate at 40 °C in a dry box in the presence of concentrated sulfuric acid. The samples were cured in a closed steel mould at a high pressure by the

Table 3
Thermal properties of the cured BMI resins.

Cured resins	T_g^a (°C)	T_d^b (°C)		Y_c^c (%)	
		In N ₂	In air	In N ₂	In air
BR	336	414	411	28	1
BR-AB	326	409	415	28	0

^a The glass transition temperature determined from DMA.

^b 5% weight loss temperature determined from TGA at a heating rate of 10 °C/min.

^c Char yield at 700 °C determined from the TGA analysis.

Table 4
Physical properties of the cured BMI resins and PAB.

Physical properties	BR	BR-AB	PAB
Tensile strength (MPa)	52	44	–
Tensile modulus (MPa)	3893	3830	3980
Elongation (%)	4.6	4.2	–
Flexural strength (MPa)	119	123	27
Flexural modulus (MPa)	4140	4520	3240
Impact strength (kJ/m ²)	9.5	7.5	0.5
Density (g/cm ³)	1.23	1.24	1.28
Poisson's ratio	0.37	0.36	0.38

following heating profile: 200 °C for 4 h, 250 °C for 2 h and 280 °C for 0.5 h in an oven open to the air. The weight percentage of the resin in the final composite was determined to be around 50% by calculating the difference in the weights of the bare glass cloth and the composites.

2.3.9. Preparation of the cured allyl-compound-modified BMI resins

A general preparation procedure is described as follows: Equimolar amounts of 4,4'-bismaleimidodiphenylmethane (BMDM) and 2,2'-diallylbisphenol A (DBA) were added to a beaker and allowed to react at 130 °C for 30 min to yield a homogeneous liquid prepolymer. The prepolymer was subsequently poured into a pre-heated (110 °C) metal mould (260 mm × 170 mm) and degassed under vacuum at 110 °C for 1 h. Then the prepolymer was cured by the following heating profile: 150 °C for 1 h, 180 °C for 1 h, 200 °C for 2 h and 250 °C for 6 h in an oven open to the air. BR is the cured BMDM/DBA resin and BR-AB is the cured BMI resin based on BR and AB monomer (BR/AB, 9/1, wt./wt.).

3. Results and discussion

3.1. Synthesis and characterization of allyl-maleimide monomers

The synthetic route for the allyl-maleimide monomers A₂B, AB and AB₂ is illustrated in Scheme 2. The molecular structures of all the allyl-maleimide monomers were confirmed by a combination of analytical techniques, such as IR, ¹H NMR, MS and elemental analysis. As shown in Fig. 1, the characteristic peaks for the maleimide groups at around 6.9 ppm for all the allyl-maleimide monomers were observed.

The solubility of all the allyl-maleimide monomers was tested in different solvents. As shown in Table 1, A₂B and AB are readily

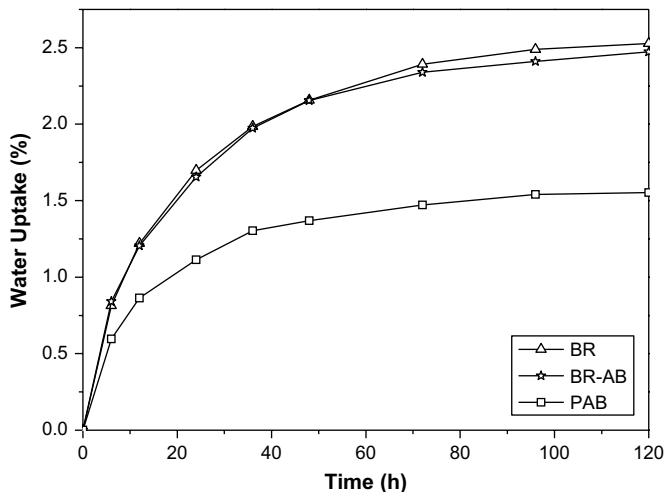


Fig. 9. Water uptake profiles of the cured BMI resins and PAB.

soluble in nearly all the common organic solvents, such as acetone, chloroform and DMF, indicating very good solution processability. AB₂ showed worse solubility than A₂B and AB, which might be because AB₂ contains two strong polar maleimide groups.

Thermal properties of all the allyl–maleimide monomers were investigated by DSC (Fig. 2). AB shows the lowest melting temperature ($T_m = 87^\circ\text{C}$) of the three monomers, which might be due to the lowest molecular weight and asymmetrical molecular structure. A₂B shows the lower melting temperature ($T_m = 88^\circ\text{C}$), which might result from two flexible allyl groups. AB₂ has high melting temperature ($T_m = 214^\circ\text{C}$), which might be due to rigid and strong polar molecular structure of AB₂. As shown in Fig. 2, A₂B and AB showed two exothermic peaks. The first exothermic peak at around 150°C corresponds to the Ene reaction and the second exothermic peak at around 260°C corresponds to the curing process, including the Diels–Alder reaction and homopolymerization of maleimide groups [13–16]. Since the Ene reaction cannot lead A₂B and AB to crosslinking networks, these two monomers possess wide processing window ranging from 90°C to 260°C . AB₂ showed sole exothermic transition ($T_p = 283^\circ\text{C}$) corresponding to the curing process.

3.2. Thermal properties of the cured allyl–maleimide resins

All the allyl–maleimide monomers, i.e., A₂B, AB and AB₂ can be thermally cured to yield cured allyl–maleimide resins, i.e., PA₂B, PAB and PAB₂. TGA was used to investigate thermal and thermo-oxidative stability of all the cured allyl–maleimide resins. Temperature at 5% weight loss was taken as the onset decomposition temperature (T_d). As shown in Fig. 3 and Table 2, all the cured allyl–maleimide resins showed high T_d both in nitrogen ($T_d > 380^\circ\text{C}$) and in the air ($T_d > 390^\circ\text{C}$), indicating good thermal and thermo-oxidative stabilities. T_d increased as the content of maleimide groups increased. An important phenomenon was observed that PA₂B showed better thermal stability in the air than in nitrogen. Torrecillas et al. [20] had reported similar results and attributed this phenomenon to the formation of oxidized protective layers at the surface of these cured resins. Char yield (Y_c) of the cured allyl–maleimide resins at 700°C was in the range of 30–60% in nitrogen and nearly zero in the air.

3.3. Dynamic mechanical properties of the composites based on the cured allyl–maleimide resins

DMA was used to study the dynamic mechanical properties of all the composites derived from the cured allyl–maleimide resins and glass cloth. The composites were prepared by dipping a glass cloth of $8\text{ mm} \times 5\text{ mm} \times 0.5\text{ mm}$ into a DMF solution of the allyl–maleimide monomers at a concentration of 0.2 g/mL , followed by drying the composites in a dry box at 40°C in the presence of sulfuric acid. The samples were cured in a closed steel mould at a high pressure according to the following heating profile: 200°C for 4 h, 250°C for 2 h, 280°C for 0.5 h. As shown in Fig. 4, composites based on PA₂B and PAB₂ exhibited high bending modulus at 50°C ($E' > 1900\text{ MPa}$) while composite based on PAB showed low bending modulus ($E' = 797\text{ MPa}$), indicating low crosslinking density of PAB.

The glass transition temperatures (T_g s) of the resulting composites were defined by the $\tan \delta$ peak temperatures. As shown in Table 2, PA₂B and PAB₂ showed high T_g above 270°C while PAB had low T_g (233°C), which might be because AB monomer tended to form linear molecular structure with low crosslinking density during the curing process.

3.4. Thermal and processing properties of the prepolymers

As mentioned above, AB monomer has good processability, e.g., low melting temperature and wide processing window. However, PAB shows lower glass transition temperature ($T_g = 233^\circ\text{C}$) than other cured allyl–maleimide resins, which is not desirable for practical applications. So we took AB monomer as an additive to the BMDM/DBA resin system in the hope of obtaining novel BMI resins with improved processability, good thermal and mechanical properties. The compositions and preparation of the prepolymers (BR-pre and BR–AB-pre) were mentioned in the Experimental section.

Thermal properties of the prepolymers, i.e., BR-pre and BR–AB-pre were studied by DSC. As shown in Fig. 5, both of the prepolymers showed two exothermic peaks at around 150°C and 260°C , corresponding to the Ene reaction and Diels–Alder reaction, respectively [13–16].

Rheometer was used to investigate processability of the prepolymers and AB monomer. As shown in Fig. 6, the viscosities decreased as the temperature increased in the range of 80 – 150°C . When heated above 150°C , the viscosities of the prepolymers increased rapidly due to the formation of crosslinking network. A resin could be processed by resin transfer molding (RTM) when its viscosity is below 0.3 Pa s and the processing time is long enough to finish the process. The viscosities of the prepolymers and AB monomer were below 0.3 Pa s at 110°C . Then, the relationship between viscosity and time at 110°C was investigated by rheometer as shown in Fig. 7. BR-pre showed very short processing time (less than 20 min) while BR–AB-pre and AB monomer showed long processing time (more than 75 min), indicating good processability of BR–AB-pre and AB monomer. It is worth to note that AB monomer possesses good processability and could be used as an additive to improve the processability of BMI resins.

3.5. Properties of the cured BMI resins

The prepolymers, i.e., BR-pre and BR–AB-pre were thermally cured to yield the cured BMI resins (i.e., BR, BR–AB). TGA was firstly used to study thermal properties of the cured BMI resins. As shown in Fig. 8 and Table 3, all the cured BMI resins showed high T_d ($>400^\circ\text{C}$) both in nitrogen and in the air, indicating good thermal and thermo-oxidative stabilities. Char yield (Y_c) of the cured resins at 700°C was around 30% in nitrogen and nearly zero in the air.

The glass transition temperatures (T_g s) of the cured BMI resins were investigated by DMA as shown in Table 3, BR and BR–AB showed high T_g above 320°C . Physical properties of the cured resins are shown in Table 4. Tensile modulus and flexural modulus of BR and BR–AB were above 3800 MPa and 4100 MPa . Compared to BR, the impact strength of BR–AB decreased slightly with the addition of AB to the BMDM/DBA resin system. PAB showed poor mechanical properties, especially low impact strength (0.5 kJ/m^2).

The water absorption behavior of the cured BMI resins was investigated by measuring the weight of samples in boiling water. As shown in Fig. 9, weight gain approached equilibrium after 120 h, and an equilibrium water uptake ranging from 1.6 to 2.6 wt% was observed.

4. Conclusions

Three new allyl–maleimide monomers (i.e., A₂B, AB and AB₂) having good solubility were designed and synthesized. DSC investigations revealed that A₂B and AB had low melting temperature ($T_m < 90^\circ\text{C}$) and wide processing window ranging from 90°C to 260°C . All the monomers could be thermally cured to yield series of

cured allyl–maleimide resins. TGA investigations revealed that all the cured allyl–maleimide resins had high decomposition temperature ($T_d > 380\text{ }^\circ\text{C}$) both in nitrogen and in the air. PA₂B and PAB₂ had high glass transition temperature ($T_g > 270\text{ }^\circ\text{C}$), which was studied by DMA. Allyl–compound–modified BMI resins based on AB monomer were prepared. Rheometer investigations revealed that AB monomer possessed good processability and could be used as an additive to improve the processability of BMI resins. The cured BMI resins (BR and BR–AB) showed good thermal stability ($T_d > 400\text{ }^\circ\text{C}$, both in nitrogen and in the air), high glass transition temperature ($T_g > 320\text{ }^\circ\text{C}$), good mechanical properties and low water uptake (<2.6%, 120 h).

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