

Fluorinated bismaleimide resin with good processability, high toughness, and outstanding dielectric properties

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ABSTRACT: In this study, novel fluorinated bismaleimide (BMI) resins were prepared by the copolymerization of 2,2'-bis[4-(4-maleimidephenoxy)phenyl]hexafluoropropane (6FBMP) and diallyl hexafluorobisphenol A (6FDABPA) to enhance their dielectric properties. The dielectric properties of the resins were investigated in the frequency range 7–18 GHz through a cavity method. Through the incorporation of a hexafluoroisopropyl group with the polymer chain, the dielectric constant (ϵ) was effectively decreased because of the small dipole and the low polarizability of the carbon-fluorine (C—F) bonds. The 6FBMP/6FDABPA resin possessed excellent dielectric properties, with ϵ being 2.88 and the dielectric loss being 0.009 at 10 GHz and 25°C. In comparison with the 4,4'-bismaleimidodiphenylmethane (BDM)/2,2'-diallyl bisphenol A (DABPA) resin, the glass-transition temperature (T_g) of 6FBMP/6FDABPA decreased. The flexible ether group in the long chain of 6FBMP was considered to disrupt chain packing and cause a decreased cross-linking density and a lower T_g . 6FBMP/6FDABPA showed a similar thermal decomposition temperature and good thermal properties like the BDM/DABPA resin, whereas the impact strength of the 6FBMP/6FDABPA resin was almost 1.6 times higher than that of the BDM/DABPA resin. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42791.

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INTRODUCTION

Bismaleimides (BMIs), which are supposed to possess an outstanding thermal stability, good mechanical properties, excellent dielectric properties, and low water absorption, are widely used in high-performance resin matrixes, microelectronics packaging, multilayer printed-circuit boards, and so on.^{1,2} Currently, the demand for denser and faster microelectronic circuits requires that printed-circuit boards should be operated at high frequencies (>1 GHz).³ The relatively high dielectric constants ($\epsilon = 3.0$ – 3.5) and dielectric losses (0.01–0.02) of current BMIs have been unable to meet the requirements for high-frequency-wave-transmitting materials and electronic insulation.⁴ In recent years, much effort has been devoted to improving the dielectric properties of BMIs. There are several approaches for decreasing ϵ and dielectric loss of a polymer. One approach is the blending of BMIs with other resins or thermoplastics that inherently have excellent dielectric properties; these include cyanate ester,^{5–7} poly(ether imide),⁸ and poly(phenylene oxide).⁹ However, the thermal resistance or processing performance of BMIs is usually sacrificed with this method.^{6,8} The introduction of pores into a matrix material can effectively decrease ϵ , but it remains diffi-

cult to control the size, distribution, and content of the close pores.^{10–12} If too large amount of pores is introduced, the mechanical properties of the material may be remarkably decreased.¹³

It has been reported that the introduction of fluorinated groups can effectively improve the dielectric properties because of the low polarizability and large free volume of C—F bonds in the polymer chains.^{12–16} Fortunately, the strong energy of C—F bonds may help maintain the thermal stability in the modified polymers.¹⁵ Polyimides with fluorinated substituents have been studied extensively.^{14–17} Maier¹⁸ studied many fluorinated polyimide structures and obtained low ϵ (2.4–2.77). This author also concluded that the incorporation of a large, branched perfluoroalkyl side chain, such as a hexafluoroisopropyl group, was an effective way to decrease ϵ . However, indiscriminate fluorinated substitution may yield an undesired effect. Hougham *et al.*¹⁹ reported that the nonsymmetric substitution of fluorine for hydrogen increased the magnitude of ϵ values. Simpson and St. Clair²⁰ synthesized a series of asymmetric and symmetric polyimides. Nonsymmetric fluorinated substitution was not beneficial for lowering ϵ , but the ϵ values

decreased almost linearly with increasing symmetric fluorine substitution content.

According to the previous reports, polarizability and fluorine content variations can both effectively change ϵ of the material, with the former more primary and the latter a little secondary. In fact, the test frequency also affects ϵ . Basically, ϵ is dependent on the polarizability of the polymer chain and unit groups. The polarizable units can be electronic, atomic, and dipolar. At optical frequencies (10^{14} Hz), where only electronic polarization occurs, ϵ is close to the square of the refractive index of the polymer, as is the limiting low value of ϵ under these conditions. As most polymers have refractive indices within the range 1.35–1.70, values of ϵ of 1.8–2.9 are usually obtained at optical frequencies.²¹ At lower frequencies (10^{12} Hz), atomic polarization also contributes to ϵ . At microwave (10^9 Hz = 1 GHz) or lower frequencies, in addition to electronic and atomic polarization, dipole polarization also contributes to ϵ .²¹ Dipole polarization is the redistribution of charge when a group of atoms with a permanent dipole align in response to the electric field. It requires considerably more time than electronic or atomic polarization. Wave-transmitting materials are generally used at high frequencies, above the gigahertz range. However, abundant dielectric properties were reported under 1 MHz, limited dielectric data for frequencies above gigahertz are available for fluorinated BMI resins.

To obtain ideal dielectric properties in BMIs, Wang *et al.*²² and Shu and Ho²³ synthesized a series of fluorine-containing BMI monomers by introducing perfluoroalkyl or hexafluoroisopropyl groups. They obtained remarkably low ϵ , 2.20–2.49 (500 MHz, 25°C), which was close to that of polyolefin. However, the decomposition temperature of the fluorine-containing BMI decreased severely to about 230–330°C, whereas common BMI has a decomposition temperature typically above 400°C.⁸ Determining a method for decreasing ϵ and the dielectric loss for BMIs at high frequencies without sacrificing thermal stability is still a big challenge. In this study, we introduced trifluoromethyl ($-\text{CF}_3$) on the side group rather than in the main chain of a BMI monomer so that the dielectric properties were significantly improved and the thermal resistance was not sacrificed. A fluorinated modifier for BMIs, a fluorinated allyl compound [diallyl hexafluorobisphenol A (6FDABPA)], was also prepared for further dielectricity modification. The influence of the fluorinated groups on the processing capability, thermal stability, and mechanical properties were investigated in detail. In addition, the dielectric properties of the cured resins in microwave frequency (7–18 GHz) were also investigated. The fluorine-containing BMI resins displayed excellent dielectric properties compared with nonfluorine BMI resins.

EXPERIMENTAL

Materials

Maleic anhydride was purchased from XiLong Chemical Reagent Co., Ltd. Bisphenol AF and 2,2'-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane were supplied by Changzhou Yangguang Chemical Reagent Co., Ltd. *p*-Toluene sulfonic acid, dimethylformamide, toluene, and ethyl acetate were obtained from Sino-pharm Chemical Reagent Co., Ltd. Propylene chloride and

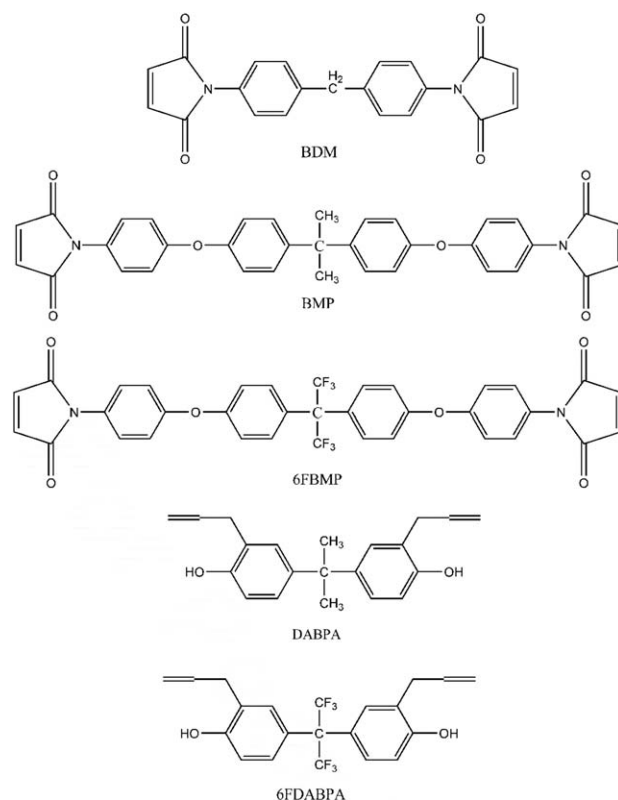


Figure 1. Chemical structures of BDM, BMP, 6FBMP, DABPA, and 6FDABPA.

ethanol were purchased from Beijing Chemical Reagent Co., Ltd. 2,2'-Diallyl bisphenol A (DABPA) was purchased from Laiyu Chemical Co., Ltd. 4,4'-Bismaleimidodiphenylmethane (BDM) was purchased from Honghu Shuangma New Material Tech Co., Ltd. 2,2'-bis[4-(4-maleimidephenoxy)phenyl]hexafluoropropane (6FBMP), 2,2'-bis[4-(4-maleimidephenoxy)phenyl]propane (BMP), and 6FDABPA were prepared in our laboratory. All chemicals were used without further purification. The chemical structures of BDM, BMP, 6FBMP, DABPA, and 6FDABPA are presented in Figure 1.

Measurements

¹H-NMR spectra were obtained on a Bruker AVANCE 400 at a proton frequency of 400 MHz. All samples were dissolved in dimethyl sulfoxide-*d*₆, and tetramethylsilane was used as an internal standard. Elemental analysis was carried out on a Flash EA 1112. A viscosity–temperature relationship study was carried out with a TA Instruments AR-2000 rheometer over the range 25–220°C at a heating rate of 4°C/min. Differential scanning calorimetry was measured with a Mettler Toledo DSC 822^e at a heating rate of 10°C/min under nitrogen flow (50 mL/min). The gel time was measured with a temperature-controlled hot plate by a standard knife method. Thermogravimetric analysis was carried out on Netzsch STA409PC thermogravimetric analysis instrument at a heating rate of 10°C/min under a nitrogen flow (50 mL/min). Dynamic mechanical analysis was performed with Netzsch STA409PC at a heating rate of 5°C/min from 25 to 380°C at 1 Hz. The glass-transition temperature (T_g) was obtained at the peak of the $\tan \delta$ curve. The dielectric

Table I. Formulations of the BMI Resins

Resin	Molar ratio					F content (%)
	BDM	BMP	6FBMP	DABPA	6FDABPA	
BDM/DABPA	1	—	—	1	—	0
BDM/6FDABPA	1	—	—	—	1	14.7
BMP/DABPA	—	1	—	1	—	0
BMP/6FDABPA	—	1	—	—	1	11.5
6FBMP/DABPA	—	—	1	1	—	11.6
6FBMP/6FDABPA	—	—	1	—	1	20.9

properties of high frequency from 7 to 18 GHz were measured according to GB/T5597-1999 with the resonant cavity method. The impact properties and flexural strength were tested according to GB/T 2567-2008 with an Instron model 3365 universal tester.

Synthesis of the BMI Monomers BMP and 6FBMP

BMP and 6FBMP were synthesized from diamine and maleic anhydride with *p*-toluene sulfonic acid as a dehydrating agent.²⁴

BMP. ¹H-NMR (400 MHz, DMSO, δ , ppm): 7.26–7.33 (m, $J = 8.8$ Hz, 8H, Ar H), 7.24–7.25 (d, $J = 8.4$ Hz, 4H, Ar H), 7.17 (s, 4H, $-\text{HC}=\text{CH}-$), 6.97–7.00 (d, $J = 8.4$ Hz, 4H, Ar H), 1.65 (s, 6H, $-\text{CH}_3$). ANAL. Calcd for BMP ($\text{C}_{35}\text{H}_{26}\text{N}_2\text{O}_6$): C, 73.67%; H, 4.59%; N, 4.91%; O, 16.82%. Found: C, 74.01%; H, 4.67%; N, 5.01%.

6FBMP. ¹H-NMR (400 MHz, DMSO, δ , ppm): 7.38–7.40 (d, $J = 8.8$ Hz, 8H, Ar H), 7.24–7.25 (t, $J = 8.8$ Hz, 4H, Ar H), 7.21 (s, 4H, $-\text{HC}=\text{CH}-$), 7.14–7.19 (q, $J = 8.8$ Hz, 4H, Ar H). ANAL. Calcd for 6FBMP ($\text{C}_{35}\text{H}_{26}\text{N}_2\text{O}_6\text{F}_6$): C, 61.95%; H, 2.97%; N, 4.13%; F, 30.97%. Found: C, 62.11%; H, 3.34%; N, 4.12%.

Synthesis of 6FDABPA

A fluorine-containing allyl compound was synthesized according to a method in the literature.²⁵ Amounts of 30.4 g of bisphenol AF and 100 mL of ethanol were first put into a flask equipped with a magnetic stirrer and thermometer at room temperature. The mixture was stirred to form a solution, and 11.2 g of KOH was slowly added. After the color of the mixture changed to pink, 16.8 g of allyl chloride was added dropwise, and the reaction system was refluxed at 80°C for 4 h. The precipitated product was filtered off, and the solvent was removed with a rotary evaporator. The product was dissolved in ethyl acetate and washed with hot water until it was neutral. After the ethyl acetate was removed, etherification fluorine containing diallyl bisphenol A was obtained and designated as 6FDABPE.

A rearrangement reaction of 6FDABPE was carried out at 180–200°C for 4 h. The product was designated as 6FDABPA.

ANAL. Calcd for 6FDABPA ($\text{C}_{35}\text{H}_{26}\text{N}_2\text{O}_6$): C, 60.58%; H, 4.36%; F, 27.38%; O, 7.69%. Found: C, 60.27%; H, 4.38%; N, 5.01%.

Preparation of the BMI Prepolymers and Cured Resins

According to Table I, equal molar amounts of the BMI monomer and allyl compound were mixed at 130°C. After a transpar-

ent liquid was obtained, the mixture was further stirred for 30 min to get the BMI prepolymers.

Each BMI prepolymer was put into a preheated mold, and this was followed by degassing at 140°C for 5 min in a vacuum oven. Then the mold was moved into an oven for curing at 180°C for 2 h, 200°C for 2 h, 220°C for 2 h, and 250°C for 5 h.

RESULTS AND DISCUSSION

Processing Behavior

The processing behaviors of a resin are usually studied with differential scanning calorimetry, viscosity–temperature correlation, and gel characterization. As the differential scanning calorimetry results show in Figure 2, BDM/DABPA exhibited two exothermic peaks around 145 and 247°C, which were assigned to the Alder-ene and Diels–Alder reactions, respectively.^{26,27} As shown in Figure 3, the ENE reaction was activated at 100–200°C, whereas the Diels–Alder reaction could only take place at temperatures higher than 220°C. The two reactions generally took place in the system of allyl-compound-modified BMIs. However, a main exothermic peak around 268°C and a very small shoulder peak around 126°C were found for 6FBMP/DABPA. Only one exothermic peak was obtained around 266°C for BMP/DABPA. This indicated that the ENE reaction was hampered or the two reactions may have proceeded simultaneously.

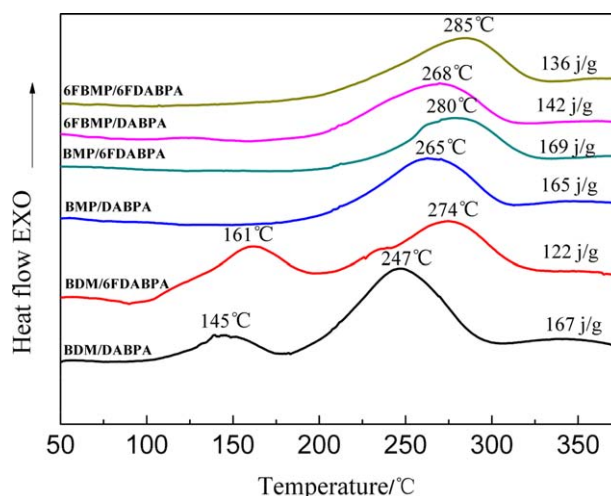


Figure 2. Differential scanning calorimetry curves of the BMI resins DABPA and 6FDABPA modifying BDM, BMP, and 6FBMP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

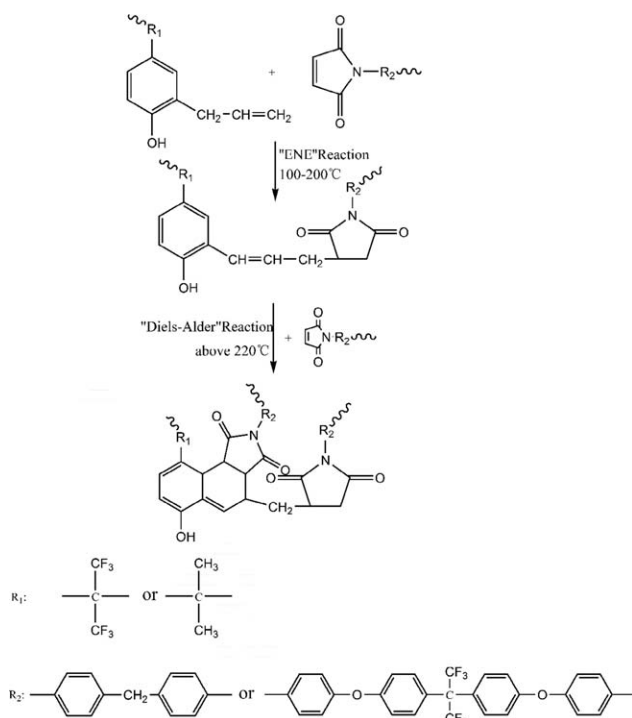


Figure 3. Reaction mechanism between the BMI monomer and the allyl compound.

The results show a reactivity order of $\text{BDM} > 6\text{FBMP} > \text{BMP}$ for the BMI monomers in this study. When 6FDABPA was used as the BMI modifier instead of DABPA, the onset and peak temperatures of the ENE and Diels–Alder reactions shifted to higher temperatures. This indicated that the reactivity of the double bond in the allyl probably decreased because of the electron-withdrawing effect of the $-\text{CF}_3$ group.^{28,29} The decreased electron density of the C–F bond versus the C–H bond in the allyl was not conducive to a nucleophilic substitution reaction with the unsaturated double bond in the maleimide ring. A higher reactivity may have reached a relatively higher crosslinking density because the main groups and chain length for BMP versus 6FBMP and DABPA versus 6FDABPA were the same for the chemical reactions. BDM had the same functional groups as BMP and 6FBMP, but the main chain was shorter. Thus, the crosslinking density of the BDM-based resins

should have been the highest compared with the other two. This played a key role in resin performance, and this is discussed later.

Figure 4 shows the temperature dependence of the viscosity for the BMI resin prepolymers. The viscosity of all of the resins decreased dramatically with increasing temperature from room temperature to 100°C. The lowest viscosity was maintained at about 200 mPa s for a temperature range for all of the resins. For BDM/DABPA, when the temperature was higher than 170°C, the viscosity dramatically increased. For BDM/6FDABPA, a similar phenomenon was observed from 195°C on. These transition temperatures for BMP/DABPA, BMP/6FDABPA, 6FBMP/DABPA, and 6FBMP/6FDABPA were higher at 210, 225, 200, and 225°C, respectively. The phenomena showed good correspondence with the differential scanning calorimetry characterization: (1) the reactivity order of BMI monomer was $\text{BDM} > 6\text{FBMP} > \text{BMP}$, and (2) compared with DABPA, the reactivity of 6FDABPA decreased a little bit.

When the samples were isothermally cured at 160°C and measured with a temperature-controlled hot plate by the standard knife method, the gel times for BDM/DABPA, BDM/6FDABPA, BMP/DABPA, BMP/6FDABPA, 6FBMP/DABPA, and 6FBMP/6FDABPA were about 1, 3, 35, 67, 15, and 50 min, respectively. This showed that the resins based on 6FBMP and BMP gelled much more slowly, with gel times that were almost 15 times longer than those of the resins based on BDM (Figure 5).

Thermal Properties

The effect of fluorine-containing substituent groups on the thermal stability was investigated by thermogravimetric analysis under nitrogen. The thermograms are shown in Figure 6, and typical parameters are summarized in Table II. The BDM systems showed the highest 5% weight loss temperature ($T_{5\%}$) at about 422°C; this was similar for BDM/DABPA and BDM/6FDABPA. For the DABPA-modified BMIs, a similar $T_{5\%}$ of about 400°C was obtained for the BMP and 6FBMP systems. However, $T_{5\%}$ increased in the 6FDABPA-modified BMP and 6FBMP systems. For the thermal stability analysis, the crosslinking density and chemical structure were the key factors.^{22,23} First, BDM had a much shorter and harder main chain compared with BMP and 6FBMP. On the contrary, the main chains of BMP and 6FBMP were longer and more flexible than that of BDM. This may have resulted in the highest $T_{5\%}$ observation

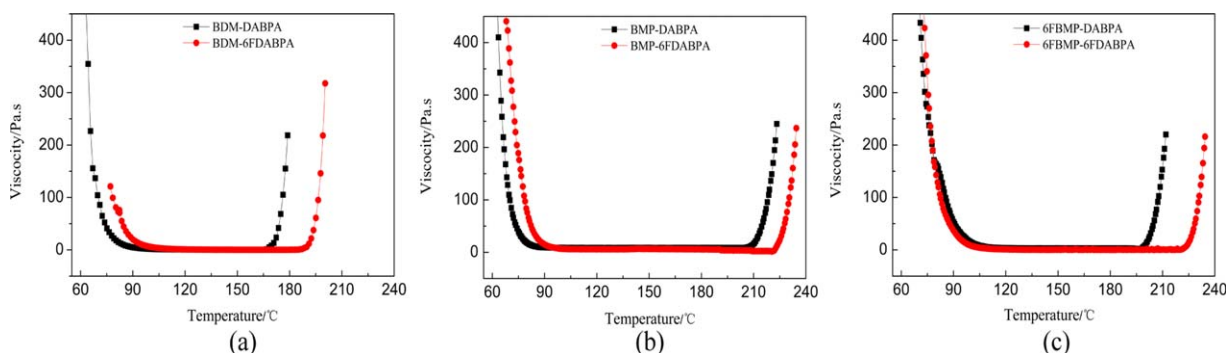


Figure 4. Viscosity change with temperature for the BMIs: (a) BDM/DABPA and BDM/6FDABPA, (b) BMP/DABPA and BMP/6FDABPA, and (c) 6FBMP/DABPA and 6FBMP/6FDABPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

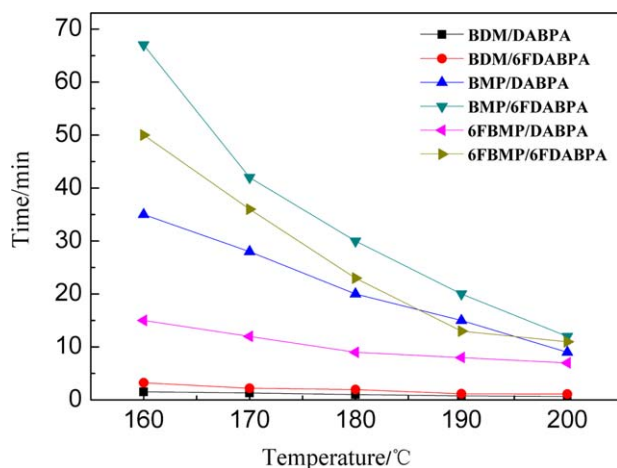


Figure 5. Influence of the temperature on the gel time of the resin systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for the BDM-based resins. The bond energy of C—F (452 kJ/mol) was larger than that of C—H (414 kJ/mol), as may not have been notable for the flexible and long BMP main chain, but was not significant for the shorter and harder DABPA chains. This probably indicated that the higher $T_{5\%}$ was obtained when 6FDABPA was used instead of DABPA. This effect was also found in the results of the char yield at 800°C. As shown in Table II, the char yields at 800°C of BDM/6FDABPA, BMP/6FDABPA, and 6FBMP/6FDABPA were 43, 43, and 41%, respectively, whereas those of the resins with DABPA were significantly lower at about 29, 25, and 34%, respectively.

The heat resistance of BMIs is usually sacrificed with the introduction of fluorinated groups.^{22,23,30} Such a problem was not found in our modified systems. According to the weight loss at various temperatures, shown in Figure 7, the weight loss slowly increased at temperatures lower than 350°C. After the samples were treated at 350°C for 30 min, BDM/DABPA showed the highest weight loss of 3.54%, whereas 6FBMP/6FDABPA showed

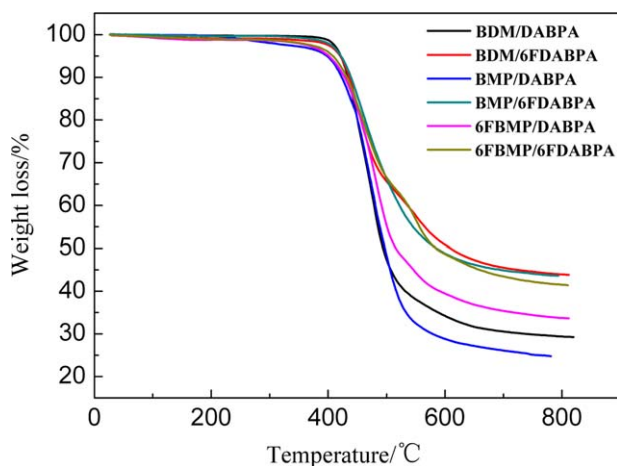


Figure 6. Thermogravimetric analysis thermograms of the cured BMI resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Typical Parameters of the Thermogravimetric Analysis of the Cured BMI Resins

Cured resin	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield at 800°C (%)
BDM/DABPA	422	432	29
BDM/6FDABPA	423	436	43
BMP/DABPA	398	423	25
BMP/6FDABPA	422	439	43
6FBMP/DABPA	400	429	34
6FBMP/6FDABPA	409	431	41

$T_{10\%}$, 10% weight loss temperature.

the lowest weight loss of 0.54%. The weight loss of the 6FDABPA-modified resins was lower than that of the DABPA-modified resins. These phenomena were attributed to the large energy of the C—F bond, as was consistent with the thermal stability, and also showed that the introduction of halogen (F in this study) enhanced the flame retardance and hampered the carbonization under the oxidation environment at high temperatures.²²

Dynamic mechanical analysis was used for the qualitative assessment of the viscoelastic properties of the crosslinked polymers. T_g was obtained from the peaks of the $\tan \delta$ curves. As shown in Figure 8, only one peak and relaxation process were found for each cured BMI resin. The T_g values of the BDM/DABPA, BMP/DABPA, and 6FBMP/DABPA cured resins were 307, 267, and 276°C, respectively. The sequence of T_g was consistent with the reactivity of the BMI monomer: BDM > 6FBMP > BMP. This phenomenon was attributed to the shorter backbone structure and higher crosslinking density of BDM/DABPA. Moreover, the presence of more flexible ether linkages in BMP and 6FBMP raised the mobility of the chain and caused loose chain packing, which resulted in a lower T_g in the resins. With BMP/DABPA

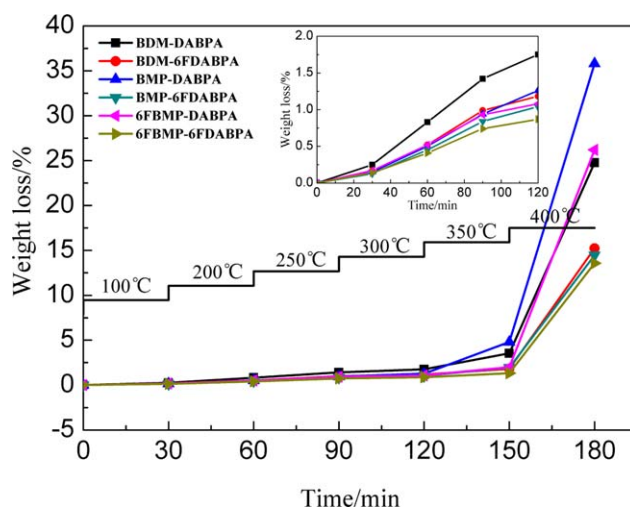


Figure 7. Weight losses of the cured BMI resins when the samples were thermally treated at various temperatures for 30 min in a muffle furnace. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

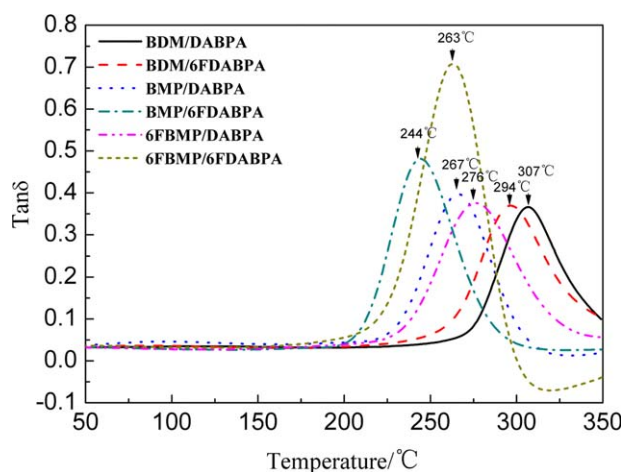


Figure 8. Dynamic mechanical analysis thermograms of the cured BMI resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and 6FBMP/DABPA as examples, the T_g of the former was lower than that of the latter. This result was contrary to the increased flexibility, free volume, and decreased chain packing caused by the $-\text{CF}_3$ group. However, this result was consistent with the higher chemical reactivity of 6FBMP versus that of BMP. Because the monomer concentration, functional groups, and main-chain length of 6FBMP and BMP were the same, the higher reactivity of 6FBMP may have caused a higher crosslinking density; this was determined before the diffusion-controlled late stage of the reaction. The increased reactivity may have offset the steric effect of 6FBMP to some extent. Thus, a slightly higher T_g was observed in 6FBMP/DABPA than in BMP/DABPA.

Mechanical Properties

Figure 9 shows the impact strengths of the cured BMI resins. Compared with the resins based on BDM, the impact strengths of the resins based on 6FBMP and BMP increased about 1.6 times. For example, in BDM/DABPA, BMP/DABPA, and 6FBMP/DABPA, the impact strengths were 22, 35, and 36 kJ/m^2 , respectively. 6FDABPA-modified BMIs systems exhibited a similar sequence at lower values. These comparisons were con-

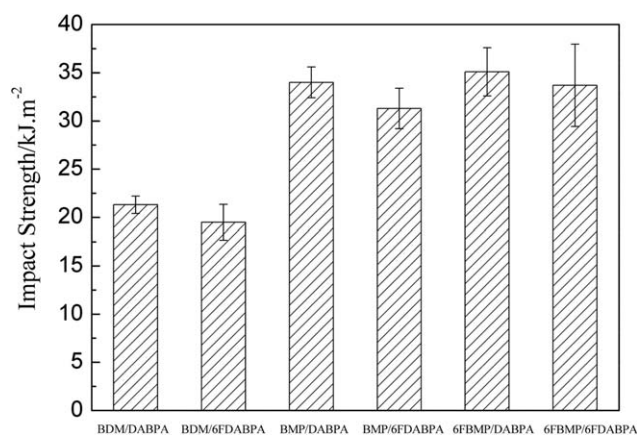


Figure 9. Impact strength of the cured BMI resins.

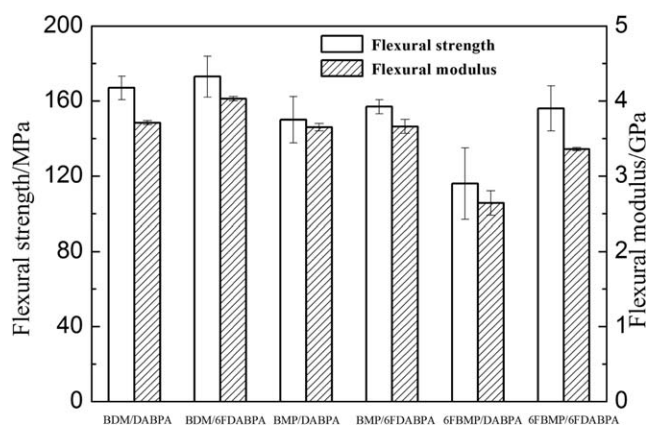


Figure 10. Flexural properties of the BMI resins.

sistent with the reactivity difference, as shown in Figures 2 and 3. For the impact strength, the extended flexible main chains of BMP and 6FBMP significantly increased this property. However, the decreased reactivity, chain packing, and crosslinking density caused by the $-\text{CF}_3$ group resulted in a worse impact performance when 6FDABPA was used to modify the resins instead of DABPA.

Flexural tests were needed to further evaluate the effect of fluorine on the mechanical properties. Figure 10 shows the flexural strengths and moduli of the cured BMI resins. Compared with the resins based on BDM, the resins based on BMP and 6FBMP had lower flexural strengths and moduli. For example, the flexural strength of the BDM/DABPA resin was about 1.4 times that of the 6FBMP/DABPA resin. This phenomenon was mainly attributed to denser chain packing and higher crosslinking density in the BDM/DABPA resin. However, the resin based on 6FDABPA had a higher flexural strength than the resin based on DABPA. We expected that the increased flexural strength of the materials primarily arose from the combination of the improvement in stiffness and toughness.³¹ So, the improvement in the moduli of the resin based on 6FDABPA was beneficial for improving the flexural strength.

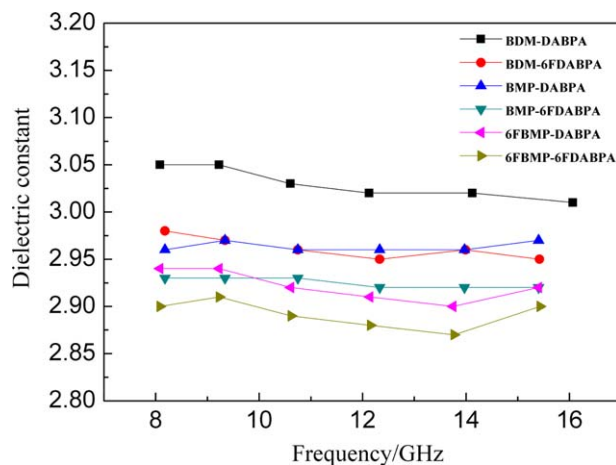


Figure 11. E curves for the cured BMI resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

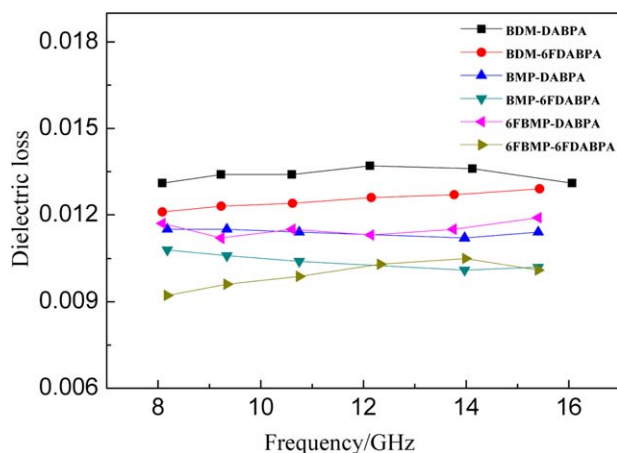


Figure 12. Dielectric loss curves for the cured BMI resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dielectric Properties

The results of the dielectric properties of the cured BMI resins were presented in Figures 11 and 12. For each sample, ϵ of the cured resins did not change obviously in the wide frequency range. The ϵ values of BDM/DABPA, BMP/DABPA, and 6FBMP/DABPA were 3.03, 2.98, and 2.93, respectively, although the ϵ values of the resins showed correspondingly lower values when 6FDABPA was used as the modifier instead of DABPA. At frequencies over the gigahertz range, dipole polarization is the main polarization.¹⁸ The small dipole and low polarizability of the C—F bond in 6FDABPA contributed to the lower ϵ values in the 6FDABPA-modified resins compared with those modified by DABPA.¹⁹ Another effect of fluorinated substituents was the increased hydrophobicity, which accordingly reduced moisture absorption and thus decreased ϵ .^{14,15} Free volume was another factor controlling the dielectric properties, as was confirmed in the comparison between BMP/DABPA and BDM/DABPA. The flexible and long chain resulted in loose segments packing, caused additive free volume, and decreased ϵ of the former resin. In our study, the ϵ variations were in correspondence with the fluorine content. Through the introduction of the symmetric substitution of hexafluoroisopropyl groups, ϵ was successfully reduced with increasing fluorine content. As shown in Table I, the lowest ϵ , about 2.88, was obtained in 6FBMP/6FDABPA with the highest fluorine content. Such a chemical structure design was expected to simultaneously obtain reduced dielectric loss values. This was confirmed in the dielectric loss results, as shown in Figure 12. With the introduction of flexible ether groups in 6FBMP, the chain segment mobility increased, and polar groups became free to orient and relax by overcoming internal friction. The small dipole and low polarizability of the C—F bond also contributed to the decrease in the dielectric loss.³² The lowest dielectric loss, about 0.009, was achieved in the 6FBMP/6FDABPA system.

CONCLUSIONS

A fluorinated BMI monomer (6FBMP) and fluorinated BMI modifier (6FDABPA) were successfully synthesized in this study. Novel fluorinated BMI resins based on 6FBMP and 6FDABPA

were prepared. Compared with the BDM/DABPA resin, 6FBMP/6FDABPA showed a wider processing window, stronger impact strength, enhanced dielectric properties, and similar thermal stability. A strong C—F bond energy and symmetric hexafluoroisopropyl groups were considered a benefit for these improvements. The 6FBMP/6FDABPA resin would be a promising candidate for high-performance resin matrixes and high-frequency-wave-transmitting materials.

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