High-Performance Hyperbranched Poly(phenylene oxide) Modified Bismaleimide Resin with High Thermal Stability, Low Dielectric Constant and Loss

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ABSTRACT: High-performance hyperbranched poly(phenylene oxide)-modified bismaleimide resin with high thermal stability, low dielectric constant, and loss was developed, which is made up of hyperbranched poly(phenylene oxide) (HBPPO), 4,4'-bismaleimidodiphenylmethane (BDM), and o,o'-diallylbisphenol A (DBA). The curing reactivity, morphology, and performance of BDM/DBA/HBPPO resin were systemically investigated, and similar investigations for BDM/DBA resin were also carried out for comparison. Results show that BDM/DBA/HBPPO and BDM/DBA resins have similar curing mechanism, but the former can be cured at lower temperature than the later; in addition, cured BDM/DBA/HBPPO resin with suitable HBPPO content has better thermal stability and dielectric properties (lower dielectric constant and loss) than BDM/DBA resin. The difference in macroproperties between BDM/DBA/HBPPO and BDM/DBA resins results from the different chemical structures and morphologies of their crosslinking networks. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 451–457, 2011

Key words: hyperbranched poly(phenylene oxide); bismaleimide; dielectric property; thermal stability

INTRODUCTION

At present, high-performance polymer-based dielectrics with outstanding thermal stability, low dielectric constant, and loss have been gained increasing demands by many cutting edges such as electric, aerospace, and military.[1,2]

Bismaleimide (BMI) resin is one of the most important thermosetting polymers due to its superior thermal resistance, outstanding dielectric property, good fatigue resistance at high humidity, and acceptable performance-to-cost ratio,[3,4] showing great potentialities to be used as high-performance dielectrics. However, being a thermosetting resin, original BMIs resin suffer from brittleness and poor processing features, such as high melting point and narrow work life, so toughening and improving processing characteristics have been the main targets on the

investigation of BMI resins. 4,4'-Bismaleimidodiphenylmethane (BDM) is the most widely used building block of BMI family, because its precursor diamine is readily available at low cost. Almost all researches and applications on BMI resins focus on BDM. Up-to-date, many methods, such as blending with engineering thermoplastics[5,6] or thermosetting resins and[7,8] reinforcing by fillers[9] or fibers,[10] have been developed to modify BDM. Among them, the modification of BDM by o,o'-diallylbisphenol A (DBA) has been proved to be an effective route, which not only effectively improves the toughness but also improves the processing characteristics of BDM.[11] However, the dielectric properties and thermal stability of BDM/DBA system still needs to be improved for high-performance dielectrics.

Poly(phenyl oxide) (PPO) is one of the most promising materials for high-performance dielectrics, which has major advantages in mechanical properties, high dimensional stability, good flame resistance, low moisture uptake, and outstanding electrical properties (low dielectric constant and loss)[12,13]; however, PPO has a high melt viscosity and poor film-forming ability.[14] A lot of researches have been done to solve these problems, for example, synthesizing PPO with lower molecular weight,[15] or preparing thermosetting PPO by introducing allyl groups.[16] However, these syntheses methods are complex.

To overcome the poor processing feature of PPO, a technique of hyperbranched polymerization is

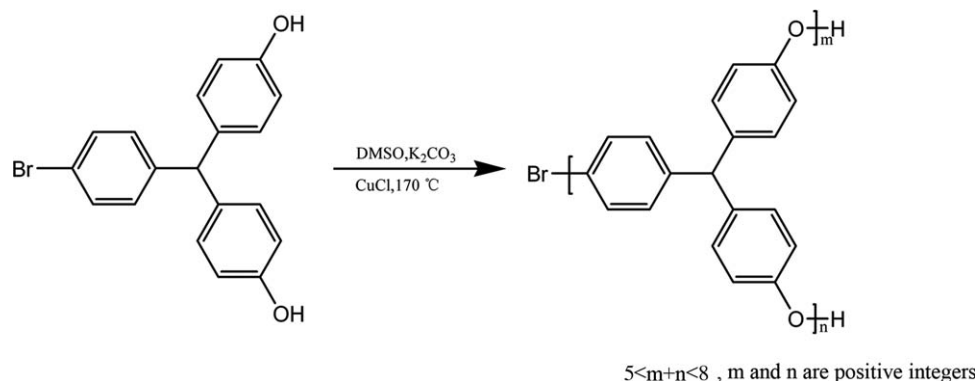$5 \leq m+n \leq 8$, m and n are positive integers

Figure 1 Synthesis of HBPPO.

used in this article because the synthesis of hyperbranched polymers is easy to be carried out. In addition, compared with their linear analogues, it is known that hyperbranched polymers possess considerably lower viscosities due to the unique structure,[17] and moreover, the existence of many terminal functional groups provides great possibilities to chemical modifications.[18,19] Based on these merits of hyperbranched polymers, a hyperbranched poly (phenylene oxide) (HBPPO) with terminal phenolic groups, which is expected to combine the advantages of PPO and hyperbranched polymers, is synthesized in this study and then used to develop a new kind of high-performance polymeric dielectrics; in addition, the relationship between the structure and properties of the developed system is intensively investigated.

EXPERIMENTAL

Materials

4, 4'-Bismaleimidodiphenylmethane (BDM) was supplied by HuBei Fengguang Chemicals (China), and o, o'-diallyl bisphenol A (DBA) was purchased from Laiyu Chemical Factory (China).

Synthesis of HBPPO

HBPPO was synthesized according to the procedure described in the literature,[20] as shown in Figure 1.

The weight-molecular weight (M_w) is 2200.

IR(KBr): 3420 cm^{-1} (ν OH), 1263 cm^{-1} (ν Ph—O—Ph), 823 cm^{-1} (ν Ph—H).

^{1}H-NMR (DMSO-d_6): δ 5.29–5.34 (t,-(Ph)$_3$CH), δ 6.43–7.63 (Br, Ph—H), δ 9.84 (s, —Ph—OH)

Preparation of cured resins

The weight ratio of BDM and DBA was 1 : 0.86.

Preweighted BDM and DBA were placed in a flask equipped with a mechanical stirrer and ther-

mometer. The mixture was heated to 130–135°C and maintained for 35 min with stirring till a clear brown homogeneous liquid was obtained, denoted as BDM/DBA.

Preweighted BDM and DBA were heated to 130–135°C and maintained for 15 min, and then appropriate amount of HBPPO was added into the flask with stirring. The mixture was maintained for 20 min to obtain a brown–red transparent liquid. The resultant liquid was put into a preheated mold followed by degassing at 135°C for 30 min in a vacuum oven. After that, the mold was put into an oven for curing and postcuring per the procedures of 150°C/ 2 h + 180°C/2 h + 200°C/2 h, and 220°C/2 h, respectively. Finally, the mold was cooled to room temperature naturally, followed by cutting specimens with suitable dimensions for tests. The resultant resin was coded as BDM/DBA/nHBPPO, where n means the weight loading of HBPPO per 100 g BDM/DBA.

Measurements

Fourier transform infrared (FTIR) spectra were measured using a Nicolet (USA) FTIR spectrometer. The specimen was prepared by coating the sample on a potassium bromide (KBr) disk and subsequently heated in an oven.

Nuclear magnetic resonance (NMR) spectra were recorded on an Unity Inova 400 NMR spectrometer system (USA), DMSO-d_6 was used as the solvent.

Differential scanning calorimeter (DSC) was carried out using a TA calorimetry (2910 MDSC, TA) from room temperature to 300°C. The measurement was conducted at a heating rate of 10°C/min under a nitrogen atmosphere.

Dynamic mechanical analyses (DMA) scans were measured using TA DMA Q800 apparatus from TA Instruments (USA) under a single cantilever clamping geometry from room temperature to 325°C with a heating rate of 3°C/min at 1 Hz. The sample dimension was 35 × 11 × 1.6 mm^3.
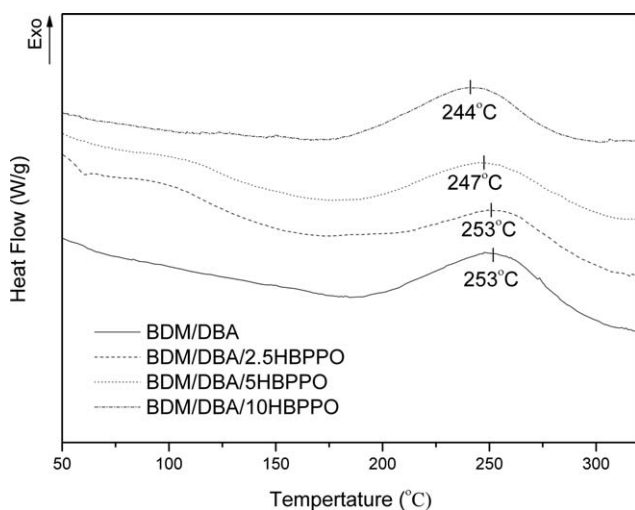
Figure 2 DSC curves of BDM/DBA and BDM/DBA/HBPPO systems.

Thermogravimetric (TG) analyses were performed on a TA Instruments PerkinElmer Pyris 1 (USA) from 25 to 700°C under a nitrogen atmosphere with a flow rate of 100 mL/min and a heating rate of 10°C/min.

The dielectric constant and loss were measured by a Broad Band Dielectric Spectrometer (Novocontrol Concept 80, Germany) at the frequency between 1 and 10^9 Hz. The sample with a dimension of 2.5 mm (thickness) × 20 mm (diameter) for testing in a low-frequency range ($1–10^6$ Hz) and that with a dimension of $6 \times 6 \times 1$ mm^3 for testing in a high-frequency range ($10^6–10^9$ Hz).

RESULTS AND DISCUSSION

Effect of HBPPO on the reactivity of BDM/DBA

The curing behavior of BDM/DBA and BDM/DBA/HBPPO blends as investigated by DSC is shown in Figure 2. All blends show one exclusive exothermic peak; however, the onset and peak temperatures of the exothermic peak shift to lower temperatures with the increase of the content of HBPPO, indicating that HBPPO has a catalytic effect on the curing of BDM/DBA.

To find further evidences about the effect of the addition of HBPPO on the curing behavior of BDM/DBA, FTIR analyses have been done, and corresponding spectra are shown in Figure 3; the FTIR spectrum of HBPPO was also supplied for comparison. With careful observations, it can be seen that the FTIR spectra of BDM/DBA/HBPPO is the simple combination of those spectra of BDM/DBA and HBPPO; in addition, the variety of FTIR spectrum of BDM/DBA/HBPPO at different curing stages is as the same as that of BDM/DBA. Hence, it can be

stated that the presence of HBPPO does not change the polymerization mechanism of the BDM/DBA system.

Figure 3 shows the FTIR spectra for both BDM/DBA and BDM/DBA/HBPPO systems, the vibration absorption attributing to the C=C groups at 829 cm^{-1} can be used to monitor the curing processes, which can be chosen to calculate the conversion (α) of C=C bonds. The peak at 1508 cm^{-1} attributing to the phenyl ring bands is selected as the reference because it is assumed that does not change during the whole curing process. The α value of C=C group can be calculated by using eq. (1):

$$\alpha = 1 - \left(\frac{(A_{C=C}/A_{\text{phenyl ring}})_{T,t}}{(A_{C=C}/A_{\text{phenyl ring}})_{T,t=0}} \right) \quad (1)$$

where $A_{C=C}$ and $A_{\text{phenyl ring}}$ are the area of the vibration bands of C=C group and phenyl ring, respectively. T is the temperature for isothermal curing, and t is a curing time.

The conversion of the maleimide group as a function of the HBPPO content after cured at various stages was calculated and plotted in Figure 4. BDM/DBA/HBPPO has bigger conversion than BDM/DBA after cured with the same procedure; however, the conversion of the former is also affected by the content of HBPPO. The small addition of HBPPO into BDM/DBA initially increases the conversion; however, further increasing the content of HBPPO, the conversion decreases and then almost levels off.

HBPPO has two opposite effects on the curing behavior of BDM/DBA. First, as stated above, HBPPO catalyzes the curing reaction of BDM/DBA, so the addition of HBPPO tends to increase the
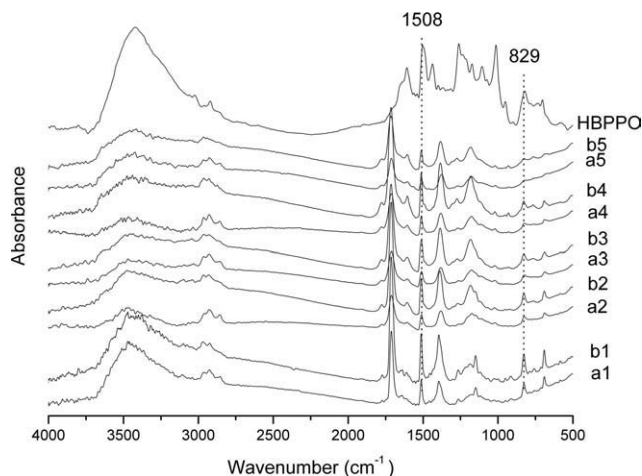

Figure 3 FTIR spectra of HBPPO at 25°C, BDM/DBA (a) and BDM/DBA/10HBPPO (b) after cured for various procedures: (1) 25°C, (2) 150°C/2 h, (3) 150°C/2 h + 180°C/2 h, (4) 150°C/2 h + 180°C/2 h + 200°C/2 h; (5) 150°C/2 h + 180°C/2 h + 200°C/2 h + 220°C/2 h.
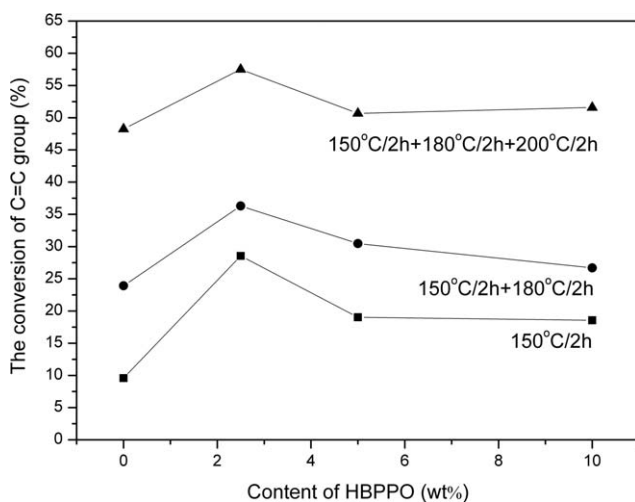
Figure 4 Conversion of C=C group in BDM/DBA and BDM/DBA/HBPPO systems after cured by different curing stages.

conversion of C=C bonds. However, second, the addition of HBPPO does not change the curing mechanism of BDM/DBA, meaning that the presence of HBPPO reduces the concentration of reactants, and thus retarding the curing reaction. When a small content of HBPPO is added into BDM/DBA, the first influence is bigger than the second one, resulting in a faster conversion. With the increase of the content of HBPPO, the second influence cannot be neglected and offsets the first influence; consequently, the conversion of C=C bond does not increase with the increase of the content of HBPPO.

Dynamic mechanical properties

DMA measures the stiffness and mechanical damping of a cyclically deformed material as a function of temperature, moreover, which is also an effective method for measuring the T_g value of a thermosetting network. In this article, T_g is defined as the peak (maximum) temperature in the tan δ-temperature plot from DMA tests.

Figure 5 shows the dependence of tan δ on temperature for cured BDM/DBA and BDM/DBA/HBPPO resins. The shape of tan δ peak may be used as a convenient indicator of the morphology state of a polymer. It can be seen that BDM/DBA, BDM/DBA/2.5HBPPO, or BDM/DBA/5HBPPO resin has a single and sharp tan δ peak, suggesting that these cured resins have homogeneous and single phase structure; otherwise, even if there exists phase domains, their sizes are so small that the whole morphologies of these resins "look like" molecularly homogeneous at least up to the scale of DMA test.[21] However, the magnitude of T_g value of the three resins follows the order of BDM/DBA/2.5HBPPO (at

276°C) > BDM/DBA (at 269°C) > BDM/DBA/5HBPPO (at 250°C), suggesting that the content of HBPPO has significantly influence on the T_g value. The improvement of T_g value by the small addition of HBPPO is mainly contributed to the catalysis role of HBPPO on the curing of BDM/DBA, whereas the decreased T_g value by the addition of 5 wt % HBPPO may predominately results from the retarded curing reaction.

On the other hand, BDM/DBA/10HBPPO shows an additional small shoulder besides the sharp and big peak, indicating that the resin has multiphase structure. By Gaussian fitting,[22] each curve can be divided into two peaks, one big peak appears at 245°C, and another small peak appears at 290°C. From the curing behavior as discussed above, the multiphase structure consists of BDM/DBA phase and HBPPO phase, so the big peak at about 245°C mainly reflects the transition temperature of HBPPO, whereas the small peak at about 290°C is predominately attributed to the transition temperature of BDM/DBA network.

Figure 6 shows overlay storage modulus (E') as a function of temperature for cured BDM/DBA and BDM/DBA/HBPPO resins. Compared with BDM/DBA resin, BDM/DBA/HBPPO resins with small HBPPO loading have bigger E' value at room temperature, and bigger HBPPO loading seems beneficial to increase the storage modulus. However, when the content of HBPPO is 10 wt %, the resin shows lower E' value than BDM/DBA resin. As analyzed above that there is a multiphase structure of BDM/DBA/10HBPPO resin, the relatively low crosslinking density from the retarded curing reaction by the presence of HBPPO with big content and the flexibility with the rotational freedom -O-linkage of HBPPO-rich phase are responsible for the lower
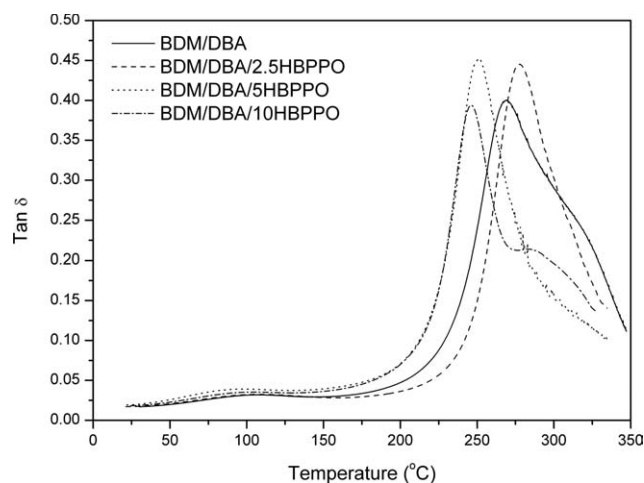

Figure 5 Overlay curves of tan δ as a function of temperature from DMA tests for cured BDM/DBA and BDM/DBA/HBPPO resins.
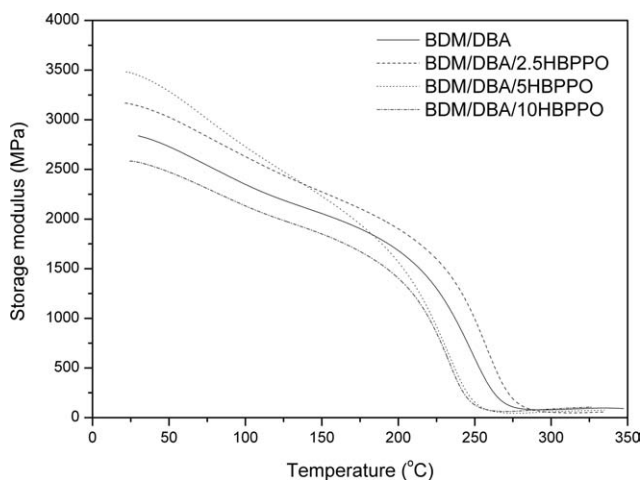
Figure 6 Overlay curves of storage modulus versus temperature for cured BDM/DBA and BDM/DBA/HBPPO resins.

storage modulus of BDM/DBA/10HBPPO resin at room temperature.

Thermal stability of cured resins

The TG and DTG curves of all cured resins are shown in Figure 7, and the corresponding typical data such as the initial degradation temperature (T_{di}), the temperature of the maximum degradation rate (T_{max}), and the char yield (Y_c) at 700°C are summarized in Table I. T_{di}, which is usually used to evaluate the thermal stability of materials, is defined as the temperature at which the weight loss is 5 wt %.

As shown in Table I, three BDM/DBA/HBPPO resins have significantly higher T_{di} values than BDM/DBA resin. Specifically, the addition of 2.5 wt % HBPPO into BDM/DBA resin can increase the T_{di} value with a gap of 43°C; further increasing the HBPPO loading to 5 wt %, the increment of the T_{di}
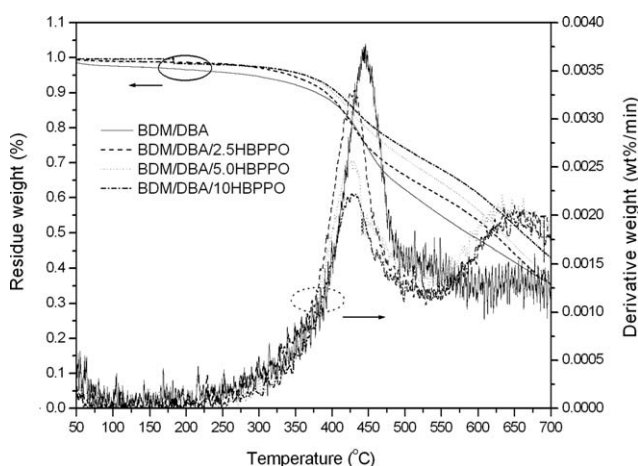
value is as big as 61°C; however, when the HBPPO loading is 10 wt %, the T_{di} value almost does not increase any more.

On the other hand, it is interesting to find that BDM/DBA/HBPPO resins have different DTG shapes with BDM/DBA resin. BDM/DBA resin only has one peak of the maximum degradation rate at about 446°C, which shifts to a lower temperature (about 430°C) with the addition of HBPPO because the main thermal degradation of HBPPO takes place when the temperature is higher than 350°C, attributing to the cleavage of ether bridge (Ph—O—Ph) in the chain of HBPPO. Interestingly, BDM/DBA/HBPPO resins have an additional small peak of the maximum degradation rate at about 645°C; however, the char yields at 700°C of BDM/DBA/HBPPO resins are equal (for BDM/DBA/2.5HBPPO) or greatly higher (for BDM/DBA/10HBPPO) than that of BDM/DBA resin, indicating that the addition of HBPPO is beneficial to improve the char yield of resins. The investigation carried out by Hwang et al.[23] proves that PPO can improve charring due to its aromatic structure, which may serve as a heat and mass-transfer barrier to retard the fire propagation. The thermodegradation data of BDM/DBA/HBPPO resins reflect that HBPPO also inherits the feature of PPO. On the other hand, there are —OH groups in the networks of BDM/DBA/HBPPO resins, so hydrogen bonds will form among HBPPO molecules, and between HBPPO and BDA. These hydrogen bonds strengthen the interactions of molecules and, thus, leading to improved thermal stability.

Dielectric properties

For signal propagating, a material with low dielectric constant and loss is good for enhancing the speed and reducing the loss, so low dielectric constant and loss are necessary and characterized feature of the resins for producing high-performance dielectrics.

Figure 8 depicts the dielectric constant of various BDM/DBA/HBPPO resins over a wide frequency from 1 to 10^9 Hz. It can be observed that all BDM/DBA/HBPPO resins have similar variations of dielectric constant on frequency as BDM/DBA resin,

Figure 7 TG curves and DTG curves of cured BDM/DBA and BDM/DBA/HBPPO resins.

TABLE I
Typical Thermodegradation Data of Cured BDM/DBA and BDM/DBA/HBPPO Resins

Resin	T_{di} (°C)	T_{max} (°C)	Char yield at 700°C (%)
BDM/DBA	300	446	35.4
BDM/DBA/2.5HBPPO	343	432	35.4
BDM/DBA/5HBPPO	361	428	36.8
BDM/DBA/10HBPPO	363	430	43.0

suggesting that the former remains outstanding stability of dielectric constant on frequency as the later. In addition, the dielectric constant of any BDM/DBA/HBPPO resin is significantly lower than that of BDM/DBA resin because the structure of HBPPO has low polarity and good symmetry, so the addition of HBPPO is beneficial to decrease the dielectric constant, and bigger HBPPO content tends to obtain lower dielectric constant. However, this expectation is not true for BDM/DBA/10HBPPO. In detail, the dielectric constant of BDM/DBA/HBPPO follows the order: BDM/DBA/2.5HBPPO < BDM/DBA/10HBPPO < BDM/DBA/5HBPPO. The unexpected result shown by BDM/DBA/10HBPPO is believed to be attributed to its multiphase morphology. In the case of a multiphase material, its dielectric constant is mainly dictated by the polarity of each phase and those interfaces in subsurface (the area immediately next to the sample surfaces) of the material. The appearance of the second phase increases the quantity of the accumulated charge due to an additional contribution from the polarization of phase interfaces and, thus, increases the dielectric constant. It is suggested that dielectric constant and loss are not only content dependent but also morphology dependent.

The dielectric loss of all systems over the frequency range from 1 to 10^9 Hz is shown in Figure 9. In the frequency range of $1–10^6$ Hz, the dielectric loss of BDM/DBA/2.5HBPPO resin is the same as that of BDM/DBA resin, which is slightly bigger than those values of BDM/DBA/5HBPPO and BDM/DBA/10HBPPO resins, indicating that the addition of HBPPO is good for reducing dielectric loss. Even in the high frequency range from 10^6 to 10^9 Hz, the dielectric loss of BDM/DBA/HBPPO has better stability on frequency than that of BDM/DBA
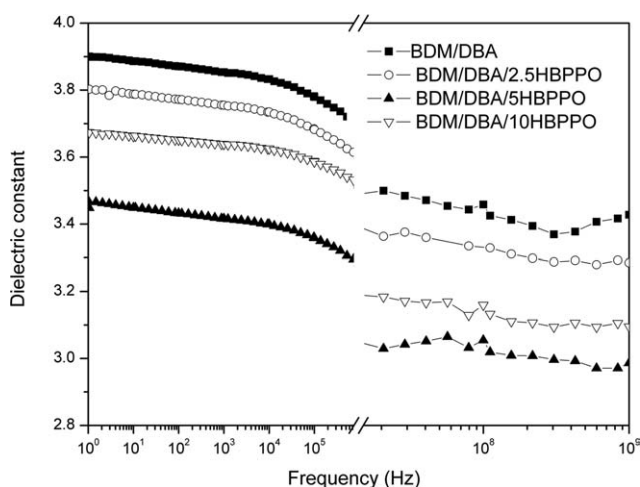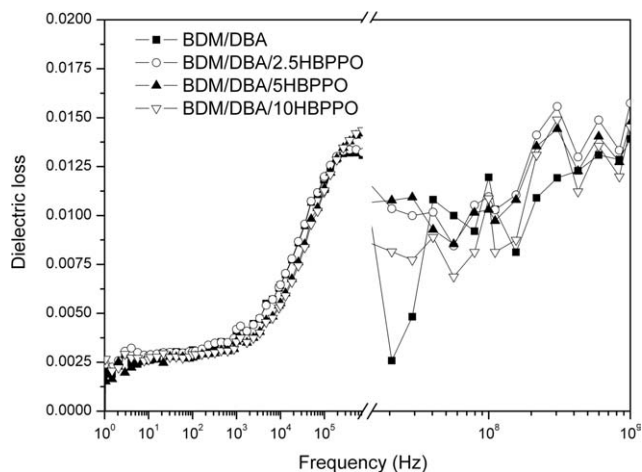

Figure 9 Dependence of dielectric loss on frequency of cured BDM/DBA and BDM/DBA/HBPPO resins.

resin, and the value reduces with the increasing of HBPPO content.

From above data, it can be concluded that BDM/DBA/HBPPO resins possess better dielectric properties in the range from 1 to 10^9 Hz than BDM/DBA resin.

CONCLUSIONS

BDM/DBA/HBPPO system has significantly different properties from BDM/DBA. The addition of HBPPO does not change the curing mechanism but catalyze the curing of BDM/DBA system. The thermal stability, dynamic mechanical, and dielectric properties of BDM/DBA/HBPPO system are closely related with the content of HBPPO. BDM/DBA/2.5HBPPO and BDM/DBA/5HBPPO resins have homogenous single morphologies, whereas BDM/DBA/10HBPPO shows a multiphase morphology. Three BDM/DBA/HBPPO resins developed in this article possess better dielectric properties in the frequency range from 1 to 10^9 Hz than BDM/DBA resin. The addition of HBPPO into BDM/DBA resin can obviously improve the thermal stability and dielectric properties of the resin. The integrated properties of BDM/DBA/HBPPO resin with suitable content of HBPPO show great potentiality to be used for producing high-performance dielectrics.

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Figure 8 Dependence of dielectric constant on frequency of cured BDM/DBA and BDM/DBA/HBPPO resins.

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