Polyimide Foams with Ultralow Dielectric Constants

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ABSTRACT: To explore ultralow dielectric constant polyimide, the crosslinked polyimide foams (PIFs) were prepared from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 4,4′-oxydianiline (ODA), and 2,4,6-triaminopyrimidine (TAP) via a poly(ester–amine salt) (PEAS) process. FTIR measurements indicated that TAP did not yield a negative effect on imidization of PEAS precursors. SEM measurement revealed the homogeneous cell structure. Through using TAP as a crosslinking monomer, the mechanical properties of PIFs could be improved in comparison with uncrosslinked BTDA/ODA based PIF. The crosslinked PIFs still exhibited excellent thermal stability with 5% weight loss temperatures higher than 520°C. In the field with frequency higher than 100 Hz, the dielectric constants of the obtained PIFs ranged from 1.77 to 2.4, and the dielectric losses were smaller than 3×10^{-2} at 25–150°C. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1734–1740, 2006

Key words: polyimide; foam; dielectric property; poly(ester–amine salt)

INTRODUCTION

Low dielectric constant is one of the most important characteristics for insulators in electronic devices.[1–3] In general, materials with dielectric constant greater than that of silicon nitride ($\varepsilon > 7$) are classified as high dielectric constant materials.[4] Low dielectric materials possess dielectric constant lower than 7. With the development of microelectric industry, the future generation insulators require ultralow dielectric constants below 2.2.[3] In the past attempts, a wide variety of organic polymeric materials have been evaluated to explore low dielectric materials. Combining the outstanding thermal stability, chemical stability, and mechanical property, polyimides have been the favored candidates for high performance dielectric materials.[5–8] To achieve lower dielectric polyimides, many researchers have focused on polyimide foams (PIFs) obtained by introducing air cell into the polyimide matrix. The ever-reported methods of preparing PIFs included (1) thermal decomposition of labile oligomer blocked or grafted copolyimides[9–14]; (2) thermolysis of polyimide composites containing thermally labile particles[15–17]; (3) introducing voids into polyimide matrix by the evaporation of dissolved supercritical CO_2[18,19]; (4) foaming and imidizing from poly(ester–amine salt) (PEAS) process, in which the porosity resulted from the foaming effects of small molecules (e.g., alcohol,

methanol, or water) eliminated during polycondensation herein.[20–22] Considering the preparation efficiency, PEAS precursor process should be a most effective route to PIFs. Also, PIFs derived from PEAS precursor could have higher porosities, while PIFs from the other three methods usually possess porosities lower than 60%. Theoretically, the higher porosity would result in PIFs with much lower dielectric constant. However, the dielectric properties of high porosity PIFs prepared from PEAS have been rarely mentioned so far. In this work, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4′-oxydianiline (ODA) based PIFs were prepared via a PEAS process, and their dielectric properties were investigated. Unlike the ever-reported PIFs that consisted only of linear polyimide, the PIF matrices were fabricated into crosslinked structure by using 2,4,6-triaminopyrimidine (TAP) as crosslinking monomer. It was expected that such crosslinked BTDA/ODA/TAP polyimide foams should have lower dielectric constant and improved mechanical properties as well.

EXPERIMENTAL

Materials

Monomers of BTDA, ODA, and TAP were purchased from Aldrich Chemical and purified by vacuum sublimation prior to use. Anhydrous methanol was distilled over magnesium ribbon and iodine.

Synthesis of BTDA/ODA/TAP PEAS precursors

Synthesis of BTDA/ODA/TAP based PEAS precursor were realized following a typical operation route: by

refluxing the suspension of BTDA (32.223 g, 100 mmol) in 100 mL anhydrous methanol for 2 h, a solution of 3,3′,4,4′-benzophenenone diacid dimethyl ester derivative in methanol was yielded. A calculated amount of ODA (18.021 g, 90 mmol) and TAP (0.833 g, 6.7 mmol) were added to the above solution, and the mixture was stirred for 3 h at room temperature to yield a homogeneous poly(ester–amine salt) solution. After removing the excess methanol on a rotary evaporator, the fine powders of BTDA/methanol/ODA/TAP based PEAS precursors were obtained. In this PEAS sample, the monomer molar ratio of TAP/(ODA+TAP) was 0.069 and this precursor was simplified as PEAS3. By changing the molar ratio of TAP/(ODA+TAP) and controlling the molar amounts of anhydride group equal to the total molar amounts of amine group in ODA and TAP, various PEAS precursors shown in Table I were obtained following a similar operation.

Preparation of BTDA/ODA/TAP PIFs

Polyimide foam was prepared through foaming and curing of the corresponding solid PEAS precursor in closed molds with fixed cavity shape and volume. In a typical preparation process, 1.430 g PEAS3 was placed into a stainless steel mold having a diameter of 5.95 cm and depth of 0.31 cm (inside dimensions), and then the mold was sealed and placed into an oven. The oven temperature was increased to 160°C at a heating rate of 20°C/min and kept at 160°C for 1.5 h for PEAS3 to foam. Then, the oven temperature was raised to 300°C and kept for 1.5 h to cure the foam. After cooling the mold to room temperature, the mold was opened and the foam of PIF3, filling the entire mold cavity, was obtained. The final weight of this sample (PIF3 sample) was 1.180 g. In comparison with the weight of the added PEAS3, 17.42% mass loss was found for this PIF3. Such mass loss was coincident with the theoretical value caused by the elimination of methanol and water during imidization of PEAS3. Based on the weight and volume of PIF3, the porosity of this sample was calculated as 88%. Other PIFs with different compositions and comparable porosities (Table I) were prepared via the same process. The chemical structures of crosslinked PIF samples were presented in Figure 1. Besides, by adding 3.97, 3.10, and 2.48 g PEAS3 precursors into the sealed mold, and by foaming and curing under the aforementioned conditions, PIF3s with porosity of 68, 75, and 80% was obtained, respectively.

Characterizations

The chemical structures of PEAS and PIF were characterized on a Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer, using finely ground

sample buried in KBr pellets. The adopted resolution was 2 cm^{-1}. The morphologies of PIFs were imaged on a scanning electron microscope (SEM; Cambridge S260). The cell size of PIF was examined on a Quantachrome PokeMaster 60 mercury porosimeter. The reported datum of each sample was the average of two testing specimens. Thermal gravimetric analysis (TGA) was performed on a Perkin–Elmer TGA-7 instrument in a nitrogen atmosphere with a heating rate of 10°C/min. Porosities (P) of PIFs were determined by density measurement according to eq. (1).[23]

$$P = \left(1 - \frac{\rho_{PIF}}{\rho_{PI}} \right) \times 100\% \qquad (1)$$

where ρ_{PIF} and ρ_{PI} is the density of a PIF and a corresponding dense polyimide film with the same composition, respectively. Density was calculated from the ratio of mass to volume. The precisions of the measures were 0.001 g and 0.01mm, respectively. At least two specimens were used for each density measurement and each PIF specimen was measured for three times. Mechanical property of each sample was evaluated from the average value from tests of five specimens on a tensile tester (Model 5500R, Instron) at room temperature. The size of the tested sample was $50 \times 20 \times 3.1$ mm^3. The dielectric properties of PIFs were measured following a capacitance method and were calculated from eq. (2).[24]

$$\varepsilon = \frac{C}{\varepsilon_0} \frac{L}{A} \qquad (2)$$

where ε is the dielectric constant, C is the capacitance, ε_0 is the permittivity of free space (8.854×10^{-12} F/m), L is the sample thickness and A is the electrode area. In measurement, the silver gel ($\phi = 40$ mm) was coated on the two surfaces of the foam plates as electrodes. The capacitance and dielectric loss of PIFs were measured on a HP 4276A LCR electrometer at different frequencies and temperatures.

RESULTS AND DISCUSSION

Structures and mechanical properties of BTDA/ODA/TAP PIFs

The dense polyimides containing TAP monomer have been prepared successfully via corresponding poly(amic acid) precursors.[25,26] It was approved that adoption of TAP did not influence the imidization of poly(amic acid) precursor, and the mechanical strength of the dense polyimide materials could be improved effectively. However, no report was found on the crosslinked PIFs prepared via PEAS process. In this study, the influences of TAP on imidization of PEAS precursors were investigated by FTIR measurements.
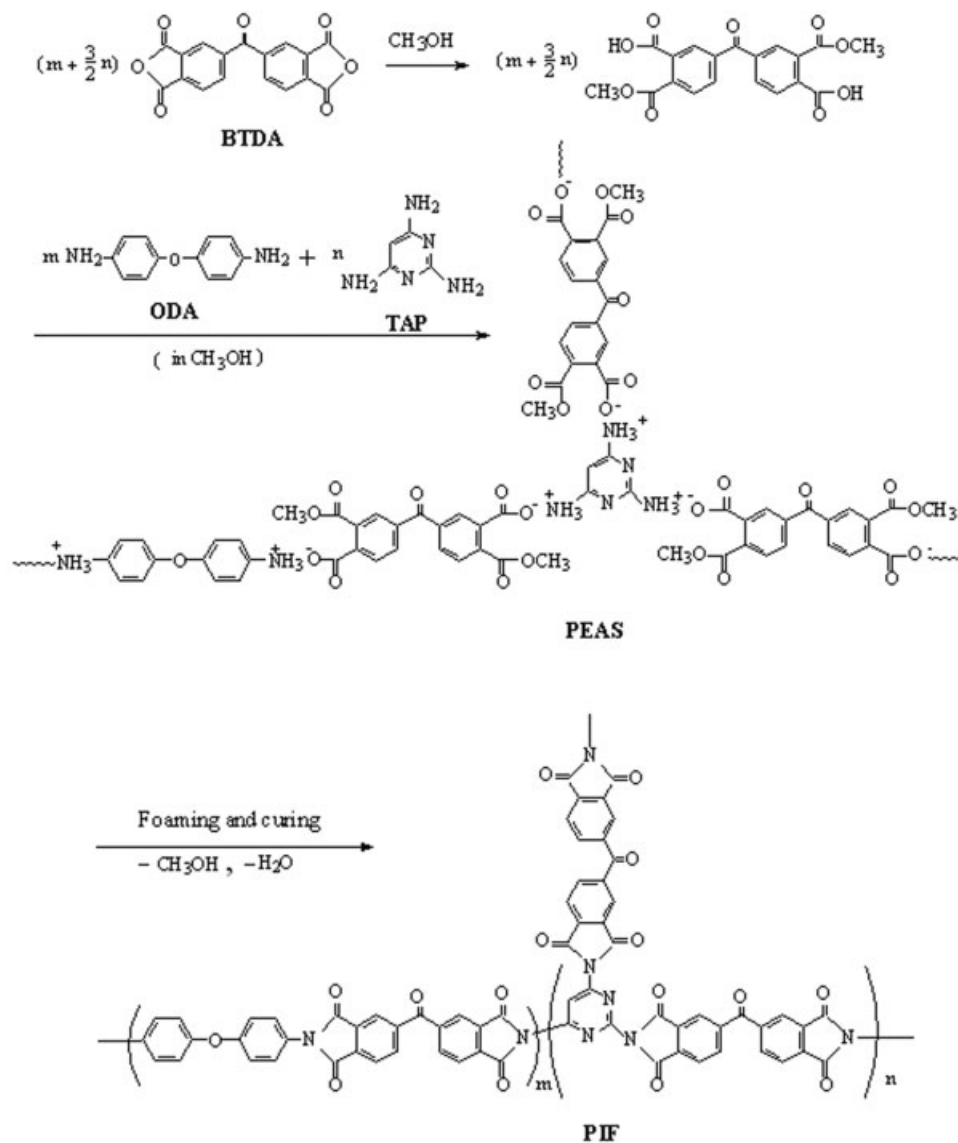
Figure 1   Schematic preparation of BTDA/ODA/TAP based PEAS and PIF.

The FTIR spectra of the sample of PEAS4 and PIF4, with the highest content of TAP, are presented in Figure 2. Upon foaming at 160 °C for 1.5 h and imidizing at 300 °C for 1.5 h, the absorbance of aromatic amine salt at 2600 cm^{-1} and the absorbance of O—H and N—H units at 3300–3400 cm^{-1} disappeared thoroughly. The shift of C=O bond absorbance from 1724 cm^{-1}(in ester unit) to 1720 cm^{-1} (in imide unit) implied the imidization of PEAS. Most obviously, the combination of characteristic absorbancies at 1776 (asymmetrical stretching vibration of C=O bond in imide ring), 1720 (symmetrical stretching vibration of C=O bond in imide ring), 1380 (stretching vibration of C—N bond) and 720 cm^{-1} (imide ring deformation) indicated the successful formation of polyimides.[27] Similar to the results of imidization of TAP containing poly(amic acid) precursor, these results revealed that TAP did not have a negative effect on the imidization of PEAS precursors either.

Figure 3 illustrates the morphologies of PIFs with different contents of TAP and comparable porosities. It was clear that all the PEASs were converted into PIFs with uniform porous structure. Observed from the transect appearances and SEM images of these PIFs, the inner of samples showed foam structure mainly in open cells, while the surface of samples was dense. The void cell size in these PIFs ranged from 40 to 200 μm. The average cell size found from mercury porosimetry measurements for these four PIFs was 141, 149, 153, and 162 μm, respectively (Table I). From the results of tensile and compressive tests shown in Table I, it was found that the crosslinking of TAP could effectively improve the mechanical properties of PIFs. PIF4 with the largest content of TAP had the tensile and compressive modulus as high as 13.41 and 17.62 MPa, respectively.

TABLE I
Compositions and Properties of BTDA/ODA/TAP Based Polyimide Foams

Molar ratio of TAP/(ODA + TAP)	0.0	0.034	0.069	0.105
PEAS number	PEAS1	PEAS2	PEAS3	PEAS4
PIF number	PIF1	PIF2	PIF3	PIF4
Density (g/cm³)	0.156 ± 0.007	0.146 ± 0.009	0.137 ± 0.006	0.122 ± 0.01
Porosity (%)	87 ± 1	88 ± 1	88 ± 1	90 ± 1
Average cell size (μm)	141 ± 5	149 ± 5	153 ± 5	161 ± 5
Tensile strength (MPa)	1.03 ± 0.06	1.29 ± 0.05	1.36 ± 0.05	1.39 ± 0.07
Tensile modulus (MPa)	5.49 ± 0.45	9.23 ± 0.57	12.12 ± 0.73	13.41 ± 0.68
Compressive strength (MPa) (at 10% deflection)	0.91 ± 0.07	1.12 ± 0.08	1.28 ± 0.06	1.44 ± 0.09
Compressive modulus (MPa)	10.76 ± 0.76	13.24 ± 0.63	15.07 ± 0.65	17.62 ± 0.57

Thermal properties of PIFs

The thermogravimetric curves of BTDA/ODA/TAP based PIFs were presented in Figure 4. The degradation temperatures (T_d) at 5% weight loss for pure BTDA/ODA based PIF1 was 557°C, while the value for TAP-crosslinked foams of PIF2, PIF3, and PIF4 was 551, 549, and 527°C, respectively. Compared with uncrosslinked PIF1, TAP-crosslinked PIFs showed slightly lower thermal stability. This property might be resulted from the poor thermal stability of residue pyrimidine rings of TAP. The C—N bond joining two nitrogen atoms in pyrimidine ring has more activity and less stability than the bonds in benzyl ether units. Besides, the nitrogen atom in imide ring provided by TAP had higher energy than the nitrogen atom provided by ODA. This was similar to the TAP containing polyimides prepared from poly (amic acid) precursors.[28] The increased content of TAP residue segments could promote the initial degradation of TAP-crosslinked PIFs. Although the thermal stability of the PIFs decreased slightly with the incorporation of TAP, the crosslinked PIFs still have relatively high thermal stability with a degradation temperature of 5 wt % loss above 520 °C and no thermal degradation occurred below 350°C. Such stability is sufficient to meet the requirements of high-performance polymeric foam candidates for most potential applications.

Dielectric properties of PIFs

Figure 5 exhibits the dielectric constants and the dielectric loss of PIFs in 100, 1000 and 10,000 Hz fields, respectively. The dielectric constant of the PIF decreased with the increasing frequency of the applied field. In the higher frequency field, the polarizable units had shorter time to polarize, and thus the material exhibited a smaller dielectric constant. These phenomena are the intrinsic behaviors of dielectric materials. Comparing with the dielectric constant of dense BTDA-ODA polyimide film (3.4), the lower dielectric constants of PIFs mainly originated from their higher porosity. The dielectric constant of PIF4 containing 10.5 mol% TAP was as low as 1.77 at 10,000 Hz. Concerning the comparable porosities of these samples, it could be further inferred that the crosslinking also yielded an influence on dielectric constant of PIFs to a certain degree. With the introduction of TAP, the formation of crosslinking structures and the increasing linkages in polyimide backbones reduced the chain packing density of PIF matrix. In this work, the measured density of the dense polyimide film prepared from poly(amic acid) precursor with monomer composition similar to PIF1, PIF2, PIF3, and PIF4 was 1.25, 1.21, 1.19, and 1.17 g/cm³, respectively. Such result was coincident with the ever-reported explanation that the lower chain packing density was beneficial to reducing the dielectric constant.[29] The dielectric losses of all PIFs were smaller than 3×10^{-2} in the field with frequency higher than 100 Hz. However, the influence of TAP content on the dielectric loss was different from that on dielectric constant. The dielec-
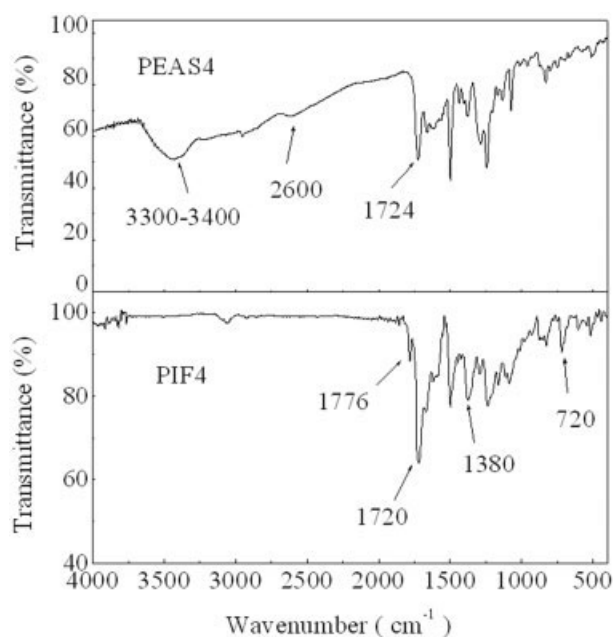
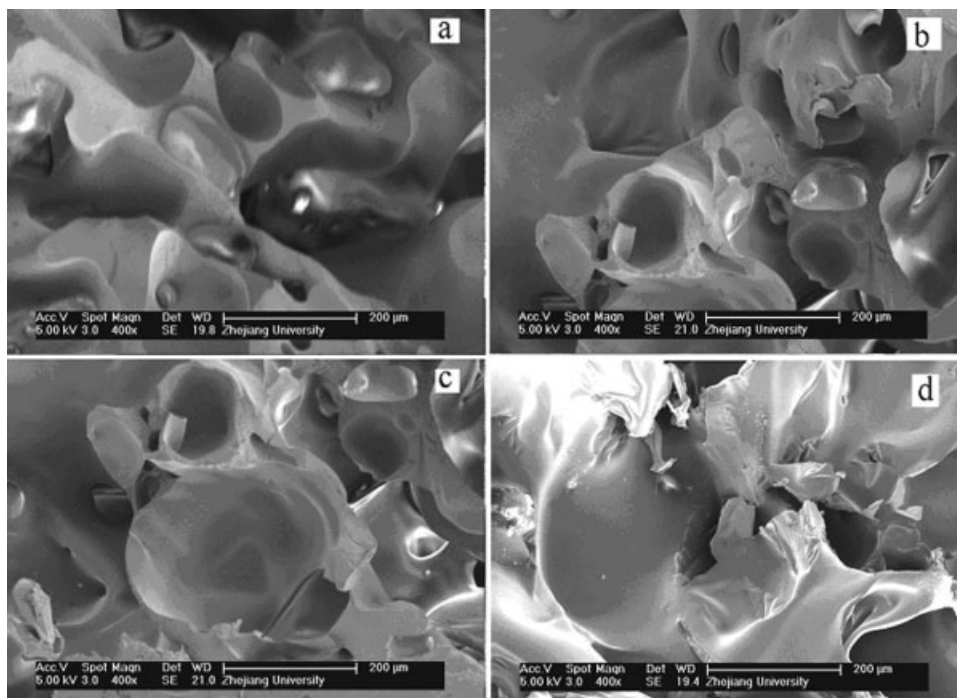**Figure 2** FTIR spectra of BTDA/ODA/TAP based PEAS4 and corresponding PIF4.

Figure 3 SEM images of BTDA/ODA/TAP based polyimide foams; (a) PIF1, (b) PIF2, (c) PIF3, and (d) PIF4.

tric loss increased gradually with the TAP content in PIF. This might be caused by the polarity of residue units of TAP, which is higher than that of ODA.

Figure 6 shows the variation of dielectric constant and dielectric loss of the crosslinked PIFs at different temperatures. The increases of both dielectric constant and dielectric loss with increasing temperature was generated from the enforcement of polarization and the intensification of the chaotic thermal oscillations of molecules at higher temperature.[30] When the temperature was elevated from 25 to 150°C, the dielectric constants of all PIFs were still smaller than 2.4, and the

increase of absolute dielectric constant was smaller than 0.26 in 10,000 Hz field. In the same condition, the dielectric losses only increased less than 20%. These results revealed that BTDA/ODA/TAP PIFs could exhibit relatively stable dielectric properties in a certain range of temperature. Such properties are very necessary in many applications.

To investigate the dependence of the dielectric property on porosity, several PIF3 samples were prepared in this work with porosity of 68, 75, 80, and 88%, respectively. The comparison of dielectric constants among these PIFs is given in Figure 7. For PIF3 with
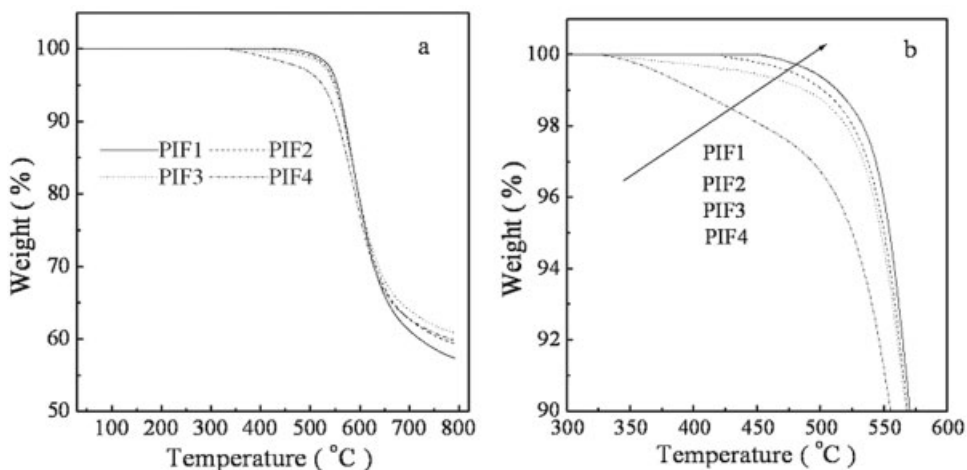

Figure 4 TGA curves of BTDA/ODA/TAP based PIFs; (a) full temperature range; (b) zoomed section around the beginning of degradation.
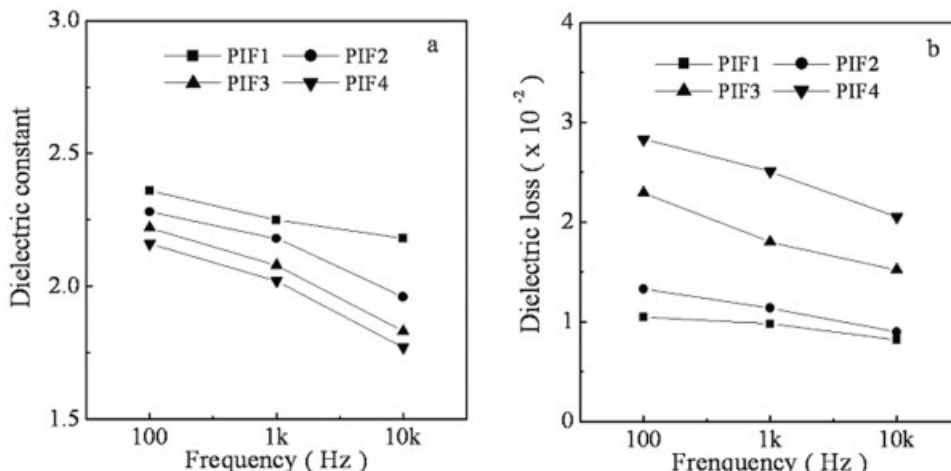
Figure 5 Dependence of (a) dielectric constant and (b) dielectric loss on frequencies (25°C).

porosity of 68 and 88%, the dielectric constant was 2.30 and 2.04, respectively. When porosity increased by 29%, the reduction in dielectric constant was only 11%. It is clear that the dielectric constant decreased at a slow rate for these PIF3s. In principle, both porosity and the crosslinking of TAP contribute to the decrease of dielectric constant. However, the experimental dielectric constants of these PIFs were larger than the values calculated from the universal Maxwell-Garnett theory shown as eq. (3).[31]

$$\varepsilon = \varepsilon_2 \left(\frac{\varepsilon_1 + 2\varepsilon_2 + 2P(\varepsilon_1 - \varepsilon_2)}{\varepsilon_1 + 2\varepsilon_2 - P(\varepsilon_1 - \varepsilon_2)} \right) \quad (3)$$

where P is the porosity, ε_1, ε_2, and ε is the dielectric constant of void ($\varepsilon_1 \approx 1.0$), polymer matrix (2.94, adopted as the measured value of dense polyimide film with the same chemical composition as PIF3) and foam, respectively. The deviation between obtained

and calculated data might be due to the high porosities of the PIFs in this work. The particularly quantitative contribution of porosity and crosslinking to dielectric constant will be further examined based on more experimental data and rectifying related models.

CONCLUSIONS

The novel BTDA/ODA/TAP based polyimide foams containing crosslinked structures were prepared via a poly(ester–amine salt) process. These foams had higher porosities with average cell diameters of 140–165 μm. The crosslinking of TAP could improve the mechanical modulus of PIFs. For all PIFs, the dielectric constants were smaller than 2.4, and the dielectric losses were smaller than 3×10^{-2} in the frequency field higher than 100 Hz at room temperature. For the PIF containing 10.5 mol % TAP with a porosity of 90%, the dielectric constant reached as low as 1.77 in 10,000
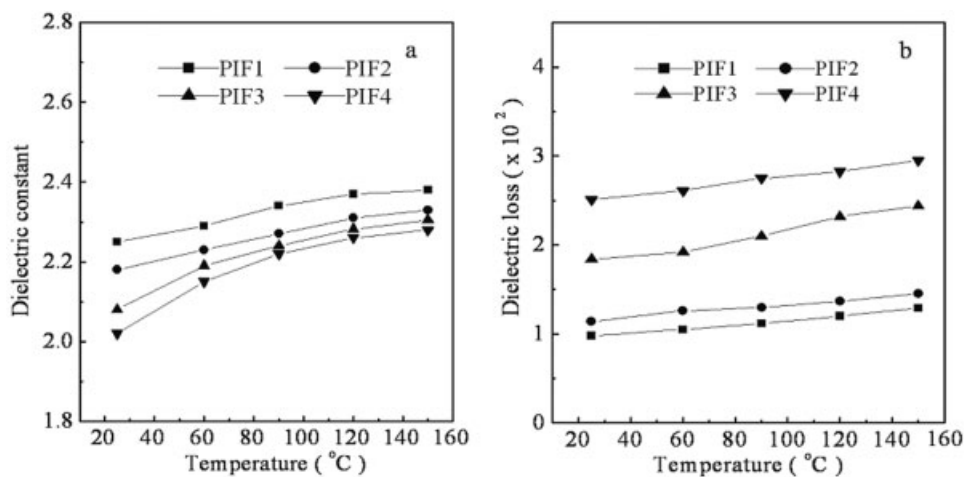

Figure 6 Influences of temperature on (a) dielectric constant and (b) dielectric loss of PIFs (1000 Hz).
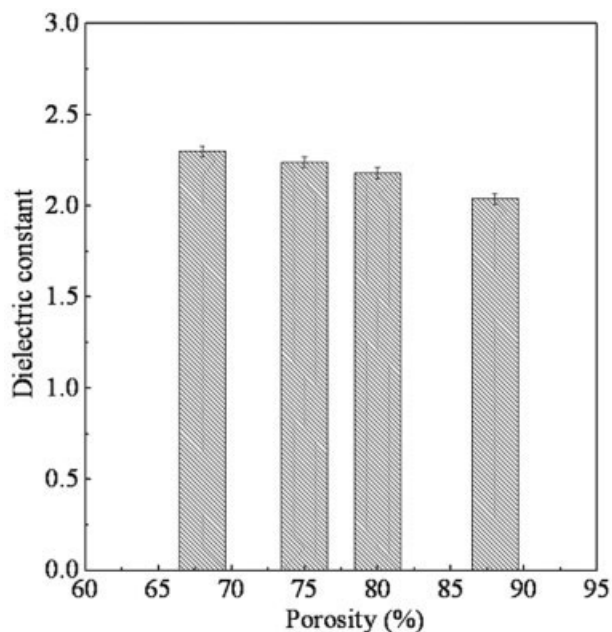
Figure 7 Dielectric constant of PIF3 with different porosities (25°C, 1000 Hz).

Hz field. Also, the dielectric properties were relatively stable at 25–150°C. Together with their excellent thermal resistance and proper mechanical properties, BTDA/ODA/TAP based PIFs will be high-performance dielectric candidates for insulator in electric devices.

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