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Thermal and dielectric properties of electrospun fiber membranes from polyimides with different structural units

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ABSTRACT: In this work, electrospinning technique was used to prepare low dielectric constant membranes. First, three kinds of polyimide (PI) fiber membranes were fabricated by electrospinning of poly(amic acid) (PAA) solutions which are from polycondensation of 4,4′-oxidianiline (ODA) and three dianhydrides, pyromellitic dianhydride (PMDA), 2,2′-bis(3,4-dicarboxyphenyl) hexafluropropane dianhydride (6FDA) and 1,2,4,5-cyclohexanetetracarboxylic dianhydride(HPMDA), followed by imidization at higher temperature. The relationship of the fiber morphology, thermostability and dielectric properties of the membranes with the polymer structure were discussed. Under the same conditions, PAAs with more flexible structure are easier to form low viscosity solution and fabricate high pore fraction membranes which are low dielectric constant materials. Under the coupling effect of fluorine-containing groups and contribution of pores, the dielectric constant of 6FDA-containing PI is lowered to 1.21 at 1 KHz with lower dielectric loss which accords with the calculated one. Also the 5% weight loss temperature of the three kinds of PIs is all higher than 400°C. The formed electrospun membranes are thermostable low dielectric constant materials. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43081.

KEYWORDS: dielectric properties; electrospinning; membranes; polyimides

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INTRODUCTION

With the improvement of integration degree in integrated circuit, super low dielectric constant materials are urgently needed. Polyimide (PI) is one kind of widely used dielectric materials due to its perfect dielectric properties, higher thermo-stability, and excellent resistance to general solvent.[1] Now-a-days, lowering the dielectric constant of PI to satisfy its application is one major topic in integrated circuit.

The methods for preparation of low dielectric constant PI materials mainly compose of producing pores in PI membranes and introducing low polar and large volume structural units to the polymer chains,[2,3] such as cyclohexane,[4] adamantine,[5] silane,[6] and fluorine containing units.[7–9] In the former methods, addition pore-containing fillers,[10–15] solvent etching fillers,[16,17] and pyrolysis heat instable polymer or block in PI matrix, such as PEO, PPO, PS, PMMA, and PCL, are commonly used.[18–21] But the decrease degree of dielectric constant only relying on one method is limited. So the low dielectric PI films based on multiple techniques are developed. For example, Ye *et al.*[22,23] introduced fluorine and pore containing silane squioxane into PI films and the dielectric constant of the final PI film decreased from 3.19 to 2.12. Wang *et al.*[24] grafted PP onto fluorine-containing poly(amic acid) (PAA) and degraded the PP block to give porous fluorine-containing PI. The dielectric constant of the target film decreased to 1.9. Our group[25] addition SiO_2 into fluorine-containing PI, after etching the SiO_2 particles by HF solution, the dielectric constant of the PI film was also decreased to 1. 9.

Electrospinning is an easy performing method for preparation of fiber membranes. Some works for PI membranes based on electrospinning are reported, but the focus is mainly on preparation of uniform PI fibers as supports to form organic-inorganic composites[26–28] and on preparation of carbon fibers.[29,30] Actually, the random intertexture of the fibers makes the as-prepared membranes containing large number of pores which are useful of decreasing the dielectric constant.[31] And the dielectric properties of electrospun membranes is rarely reported.[32,33] Li *et al.*[26] report the dielectric properties of PMMA, PS, PVDF and PVP membranes by electrospinning.[26] Chen *et al.*[27] prepared PI fiber membrane with dielectric constant as low as 1.4 by electrospinning fluorine-containing PAA. The obvious decrease of dielectric constant was due to the coeffect of low polar fluorine element and the large amount of pores in the film. So electrospinning is a useful technique lowering dielectric constant and is needed to develop. Most importantly, it is reported small structural difference in PIs will result in great changes in dielectric properties.[34] So the relationship of structural difference and pore content with dielectric properties in electrospun membranes are worthy to be study.

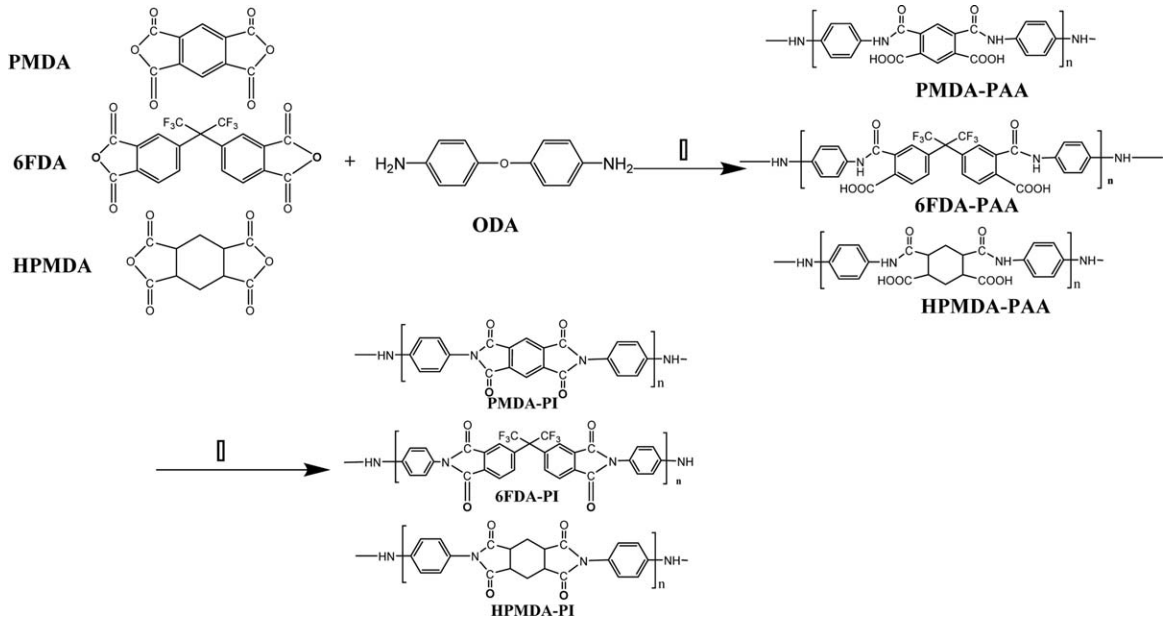

Figure 1. Synthesis of the PI polymers with different structure, (I) DMF, 0°C, 6 h, (II) 150, 250, and 300°C each for 1 h.

In the present study, 4, 4′-oxidianiline (ODA) polymerizes with three kinds of dianhydrides to form PAAs at first. Then the PAA solutions were electrospun and imidized to form full aromatic PI, aliphatic unit containing and fluorine–containing PI fiber membranes. The structural difference on thermo-stability and dielectric properties of the PIs were studied in detail. For the first time, the dielectric properties of aliphatic unit containing and fluorine–containing PI fiber membranes were discussed. The dielectric constant of PI fiber membrane containing fluorine groups was lowered to be 1.21. Also the 5% weight loss temperature of the three kinds of PIs is all higher than 400°C. The formed electrospun membranes are thermostable low dielectric constant materials.

EXPERIMENT

Materials

Pyromellitic dianhydride (PMDA), ODA, and 2,2′-bis(3,4-dicarboxyphenyl) hexafluropropane dianhydride (6FDA) were all analytical grade and purchased from Aladdin Chemical Reagent, 1,2,4,5-Cyclohexanetetracarboxylic dianhydride (HPMDA) was supplied by the group of professor Liu Jingang in the Chinese Academy of Sciences Institute of Chemistry. The monomers were purified by vacuum sublimation before use. *N,N*-Dimethylformamide (DMF, 99.9%, anhydrous) was purchased from Beijing Chemical Reagent Factory which was analytical grade and used without further purification.

Synthesis of PAA

The precursors of polyimides, PAAs, were synthesized by the polycondensation of dianhydrides and diamine as reported.[35,36] In a typical experiment, a 100 mL of three-necked flask fitted with a mechanical stirrer was charged with 2.0024 g (10 mmol) of ODA and appropriate DMF. After complete dissolution of ODA, 2.2139 g of PMDA (4.6664 g of 6FDA and 2.2642 g of HPMDA, 10.01 mmol with 1 mol % excess) was added gradually into the stirring solution. After vigorously stirring in an ice bath for 6 h, an amber transparent viscous solution with 25 wt % of PAA was finally obtained.

Fabrication of PAA Fiber Membranes

The viscous polymer solutions were loaded in a 5 mL of syringe equipped with a 0.50 mm (inner diameter) stainless steel gauge needle. The needle was connected to a high voltage power supplying system capable of providing a DC voltage up to 30 kV. The solution was constantly and continuously supplied by a syringe pump. The feed rate was set as 0.1 mm/min. The applied voltage in this work was adjusted from 13 kV to 18 kV. The electrospun fibers were collected onto the rotating aluminum collector with a diameter of 20 cm and a width of 0.4 m, which was 15 cm away from the needle. The membrane was dried overnight at 60°C in air and then in vacuum for 2 h to remove the residual solvent.

Imidization of PAA Fibers

The thermal imidization of PAA fibers was performed by the following program: heating the PAA fiber membrane up to 150, 250, and 300°C at a heating rate of 3°C/min, annealing at each temperature for 1 h and then cooling down naturally. The final membranes from PMDA, 6FDA, and HPMDA monomers were denoted as PMDA-PI, 6FDA-PI, and HPMDA-PI, and their corresponding precursors were assigned as PMDA-PAA, 6FDA-PAA, and HPMDA-PAA, respectively. The synthesis route and the structure of the three kinds of PIs were shown in Figure 1.

Characterizations

The surface morphology of the samples was observed with scanning electron microscope (SEM, HITACHI S-4300) operated at an acceleration voltage of 5 kV. The Fourier transform infrared (FTIR) spectra in the $4000-400\ cm^{-1}$ region were recorded using a Perkin Elmer Spectrum 100 FTIR spectrometer. Air was used as a background. The dielectric properties were determined by an impedance analyzer (Agilent 4294 A) at frequencies ranging from 10^2 Hz to 10^7 Hz. Silver electrodes were fabricated on each sides of the 1 cm^2 strips cut accurately from the fiber membranes

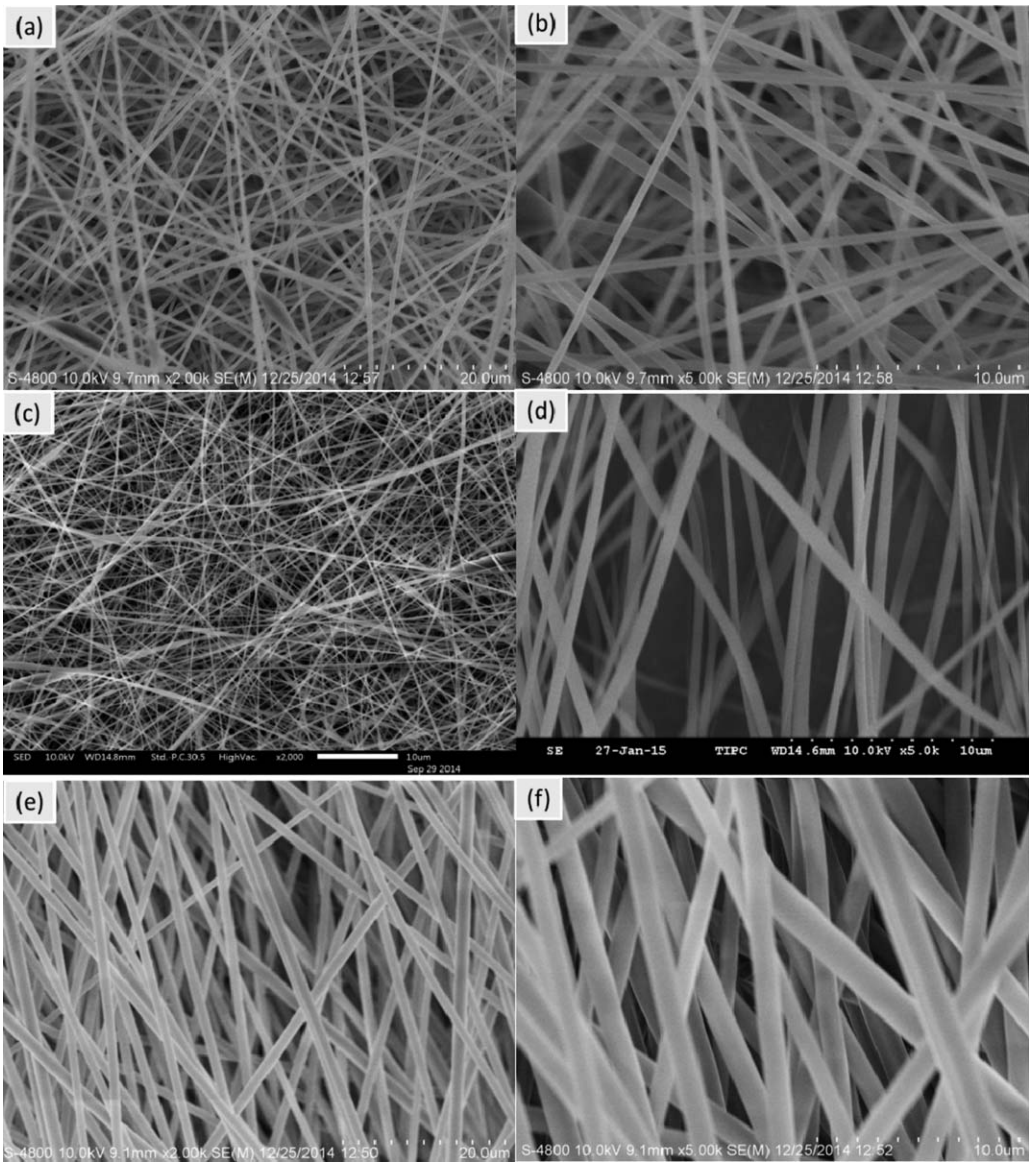

Figure 2. Morphology of PMDA-PI (a,b), 6FDA-PI (c,d), and HPMDA-PI (e,f) fibers from 25 wt % of PAA solutions.

with conductive silver paint (Agar no. 0443). To avoid measurement errors on the porous membranes by Bench Thickness Gauge, the thickness of the membrane for dielectric constant calculation is the average of nine time of measurement at different point of the strips. Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer TGA 7 with a heating rate of 20°C/min ranging from 25°C to 800°C in air. The viscosity of PAA solutions were measured by Thermo Scientific HAAKE RotoviscoI. The pore fraction (f %) was determined by measuring the volume of the fiber membranes and dense films with the same weight based on eq. (1).

$$f\% = \frac{V_a}{V_m} = \frac{V_m - V_s}{V_m} \times 100 \quad (1)$$

Where V_m, V_s, and V_a are the volume of the membrane, dense film, and pores in the membrane.

RESULTS AND DISCUSSION

Morphology of the PI Fibers

The morphology of the three kinds of PI fiber membranes from 25 wt % of PAA solutions were observed by SEM and shown in Figure 2. As the content of PAA is 25 wt %, all of the three kinds of PAAs can form fibers by electrospinning. But PMDA-PAA and HPMDA-PAA can form very uniform ones [Figure 2(a,c)], and the average fiber diameters are ~600 nm and ~1000 nm, respectively. The fibers from 6FDA-PAA [Figure 2(b)] are not homogeneous as that from PMDA and HMPDA. The average diameter of the three kinds of fibers are in the order of HPMDA-PI > PMDA-PI > 6FDA-PI. It is reported the fiber diameters will depend mainly on the jet sizes and the polymer contents in the jets or the solution viscosity. But during the traveling of a solution in electrospinning, as long as splitting is avoid, one of the most dramatic parameters influencing the fiber diameter is the solution viscosity.[37] A higher viscosity solution

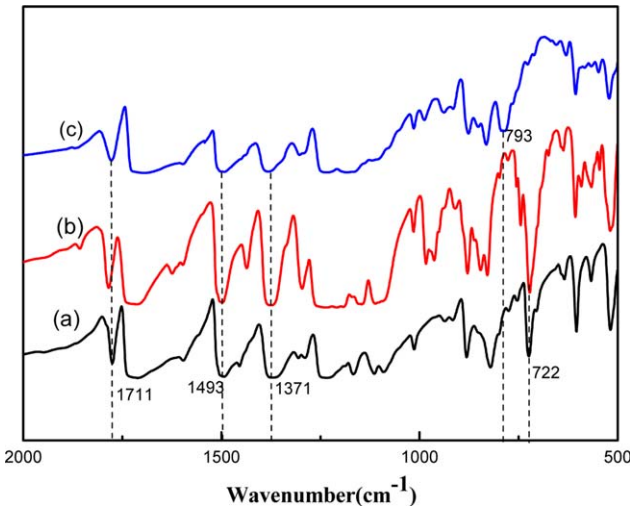

Figure 3. FTIR spectra of PMDA-PI (a), 6FDA-PI (b), and HPMDA-PI (c) fibers from 25 wt % of PAA solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

forms a larger diameter fiber.[38] Based on the diameter difference of the three kinds of PIs, it is speculated that although the synthesis conditions are the same, the viscosity of HPMDA-PAA, PMDA-PAA, and 6FDA-PAA is in the same order as their formed fiber diameters. The viscosity measurement confirms the above speculation. The viscosity of HPMDA-PAA, PMDA-PAA, and 6FDA-PAA is 11.02 Pa S, 9.14 Pa S, and 7.98 Pa S, respectively that is the reactivity order of the dianhydrides is HPMDA > PMDA > 6FDA. Just as shown in Figure 1, in PMDA and 6FDA the conjugated benzene units homogenize the electrons in the whole molecules and their reactivity with ODA is decreased. So polymers with relatively low molecular weight (low viscosity) are given and inhomogeneous fibers are fabricated correspondingly.

FTIR Spectra of the Three Kinds of PI Fibers

Although the structure of dianhydrides used for the three kinds of PIs are different, but ODA exists in all of the three kinds of polymers, so the functional groups of all the PIs are similar giving similar FT-IR (Figure 3). In the FTIR spectra of the three kinds of polymers, the bands at 1493 cm^{-1} and 1600 cm^{-1} attribute to the backbone vibration of C═C in the benzene rings. The strong band at 1371 cm^{-1} indicates the C—N stretching in the polymer backbone structure. The symmetric stretching bands of the —C═O are shown at 1668 and 1710 cm^{-1}, respectively.[39] But the bands at 722 cm^{-1} in the FTIR spectra of PMDA-PI [Figure 3(a)] and 6FDA-PI [Figure 3(b)] corresponding to bending of —C═O groups left shift to 793 cm^{-1} as the benzene groups connecting the imide rings in PMDA-PI and 6FDA-PI are substituted by aliphatic rings in HPMDA-PI [Figure 3(c)]. No absorption bands are found at 1720 cm^{-1} corresponding to —C═O stretching of carboxylic acid, indicating complete conversion of PAAs to PIs during imidization.[27]

Thermostability of the Three Kinds of Fibers

The thermo-stability of PMDA-PI, 6FDA-PI and HPMDA-PI fiber membranes were examined and shown in Figure 4. PMDA-PI [Figure 4(a)] and 6FDA-PI [Figure 4(b)] exhibit one-step degradation. The degradation temperature of PMDA-PI (5% weight loss temperature) is 561°C, and consistent with most of the reports on PMDA-PI fibers.[28,33] While the degradation temperature of 6FDA-PI decreases to 526°C.

As structural units from PMDA in PMDA-PI are replaced by that from 6FDA, the flexibility of 6FDA-PI is increased as chemical bonds capable of rotation are introduced in, meanwhile the bulky -CF_3 groups in the dianhydride moiety in 6FDA-PI limit the growth of ordered domains. So the conjugation or "π stack" in 6FDA-PI is decreased compared with PMDA-PI,[40] yielding loose compact of molecules in each 6FDA-PI fibers. Lower compact density decreases its resistance ability toward heat. As for HPMDA-PI [Figure 4(c)], two-step degradation is observed, the weight loss at 350 − 500°C is attributed to the degradation of the structural unit from HMPDA, and the degradation between 500 and 600°C is from the benzyl units in HPMDA-PI. So HPMDA-PI degrades to small blocks first and then further decomposes to even smaller molecules. It is reported that the amount of bent and nonplanar structural units was proportion to the amorphous part of PI film.[35] Therefore, the conjugation content of 6FDA-PI is the lowest and its thermal stability is lowered. But the thermal degradation of the three kinds of PIs (5% weight loss temperature) is all higher than 400°C. The process of electrospinning does not sacrifice the thermal stability of PIs.

Dielectric Properties of PMDA-PI, 6FDA-PI, and HPMDA-PI Fiber Membranes

The dielectric properties of the three kinds of fiber membranes from 25 wt % of PAAs as a function of frequency were summarized in Figure 5. The dielectric constant of PMDA-PI, 6FDA-PI, and HPMDA-PI are 1.95, 1.21, and 1.44 respectively and all lower than that of PI film from PMDA and ODA which is 3.64 [1 KHz, Figure 5(a)] due to the introduction of air, whose dielectric constant is 1, into the pores of the membranes. These results indicate that initial introduction of pores into materials plays an important role in generating a low *k* material. The conjugated structure reduction in HPMDA-PI makes its dielectric constant decrease compared to PMDA-PI. It is reported that if the fiber diameter of a membrane is large, the

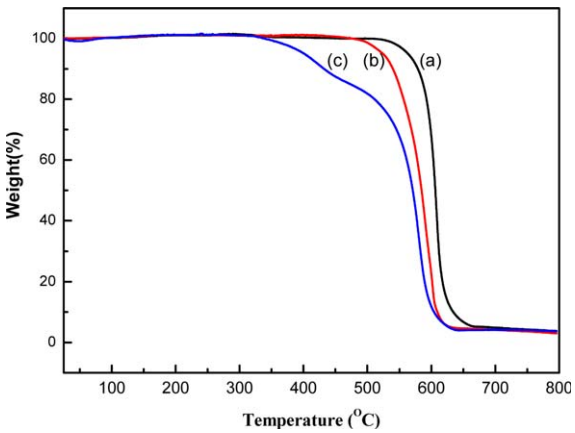

Figure 4. TGA curves of PMDA-PI (a), 6FDA-PI (b), and HPMDA-PI (c) fibers from 25 wt % of PAA solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

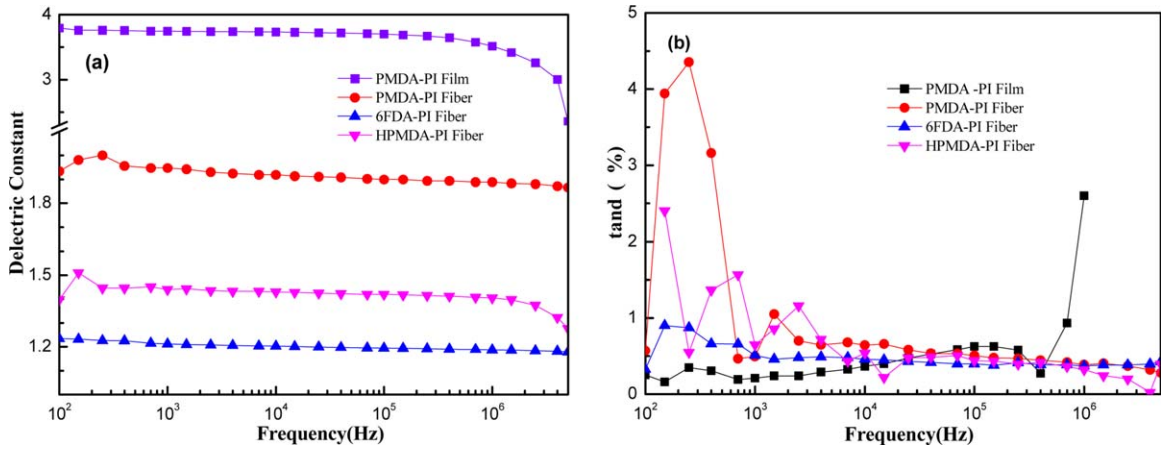

Figure 5. Dielectric constant (a) and dielectric loss (b) of PMDA-PI, 6FDA-PI, and HPMDA-PI fibers from 25 wt % PAA solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

porosity of the membrane will be low and its dielectric constant will be high correspondingly[26] compared to other membranes obtained under the same electrospinning conditions. The relationship of fiber diameter and dielectric constant of PMDA-PI and HPMDA-PI does not follow the above principle, so the structure difference is the major factor causing the dielectric constant decrease of HPMDA-PI rather than the diameter difference of fibers. As conjugated structure, which is electron rich unit, is easy to be polarized, and giving relatively higher dielectric constant. The greatly lower dielectric constant of fully aliphatic polyimide compared to that of PMDA-PI (3.64) confirms the above principle and is due to the decrease of conjugated structure.[41]

As further introduction of fluorine-containing unit into the fiber membrane by substitution of dianhydrides with 6FDA, the dielectric constant of the final membrane decreases to 1.21 due to the coupling effect of fluorine and flexible structural unit. The activity of electrons attracted by the fluorine are significantly reduced causing difficulty in polarization in 6FDA-PI by external electric field and resulting in a decreased k value.[42,43] This dielectric constant is lower than that of a electrospinning membrane reported by Chen F ($\varepsilon = 1.42$).[27] In the literature, the diamine used is 4,4-bis [3′-trifluoromethyl-4′(4′-amino benzoxy) benzyl] biphenyl(TFABB) which has relatively low reactivity due to the existence of fluorine groups in the unit compared to ODA used in the present work. So higher molecular weight PAA and PAA solution with relatively appropriate viscosity for electrospinning to give high pore containing membranes are formed. Finally, low dielectric constant membrane is given. The dielectric constant of PIs, in general, is known to decrease gradually with increasing frequency as the interface polarization and molecular polarization are difficult to follow the switching of external electric field at high frequency. The orientation of interface polarization and molecular polarization need a longer time than electronic and ionic polarizations. In electrospun fibers, every molecule tends to orient with the fiber direction due to the effect of electric field in the spinning process. So in the membrane vertical direction or the direction of external electric field, the polarization mainly consists of electronic and ionic polarizations. So the dielectric constant of the PIs is frequency independent. Also the dielectric loss of the three kinds of PIs is very low and mostly lowers than 0.02 [Figure 5(b)].

The dielectric constant of the formed membranes is calculated according to the linear dielectric mixing model shown as eq. (2) and summarized in Table I.

$$\varepsilon = \frac{\rho}{\rho_s}\varepsilon_s + \left(1 - \frac{\rho}{\rho_s}\right)\varepsilon_a \quad (2)$$

Where ρ and ρ_s are the density of the porous solid and dense solid, ε and ε_s are the relative dielectric constant of the porous

Table I. Conditions for Electrospinning and the Properties of the Target Fiber Membranes

	Conditions for electrospinning			Dielectric constant	
Samples	Acceptance speed (m/min)	Concentration of PAA (wt %)	Pores (vol %)	Experimental	Calculated
6FDA-PI	1	23.4	76.64	2.6	1.74
6FDA-PI	2.5	23.4	84.74	1.75	1.27
6FDA-PI	1	25	83.15	1.30	1.23
6FDA-PI	2.5	25	87.91	1.21	1.22
HPMDA-PI	2.5	25	84.52	1.44	-
PDMA-PI	2.5	25	90.03	1.91	1.28

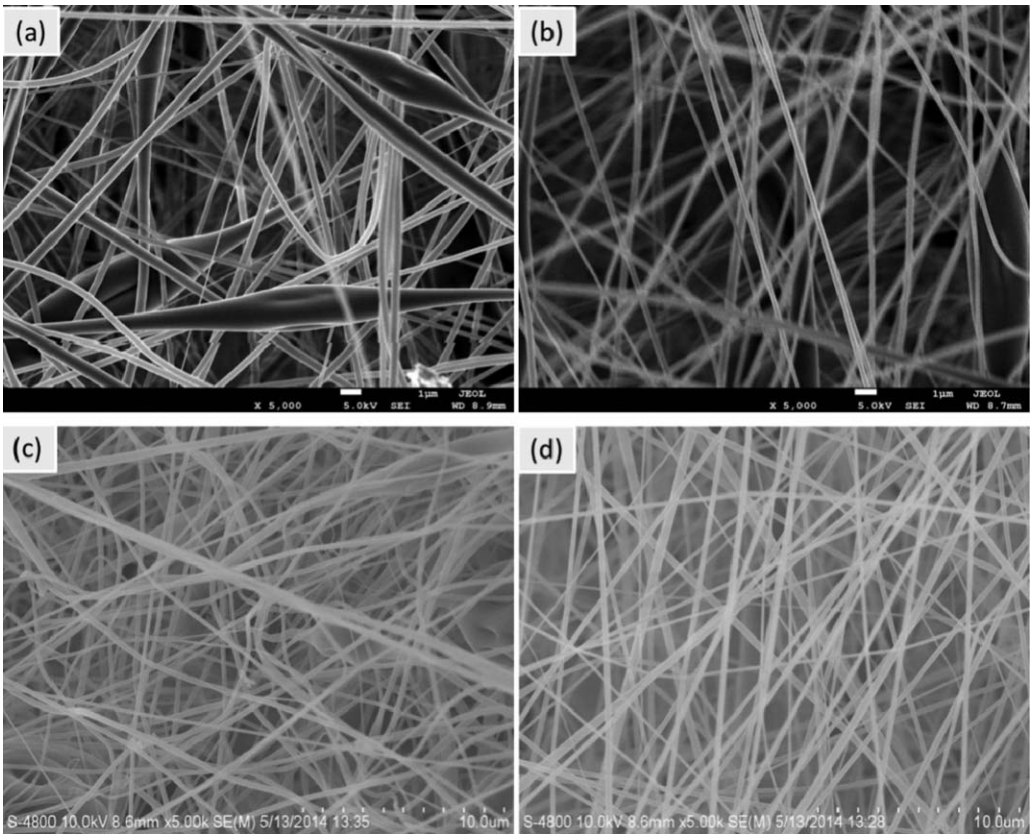

Figure 6. Morphology of 6FDA-PI from 23.4 wt % (a,b) and 25 wt % (c,d) of PAA solutions with an acceptance speed of (a,c) 1.0 m/min and (b,d) 2.5 m/min.

solid and dense solid, and ε_a is the relative dielectric constant of air which is 1.

In the present work, the density of PI film is 1.43 g/cm^3, the dielectric constant of dense PMDA-PI and 6FDA-PI are 3.64 and 2.78. As the content of 6FDA-PAA is 25 wt % and its corresponding viscosity is 7.98 Pa·S, the calculated dielectric constant of the given 6FDA-PI membranes is 1.22 and accords with the experimental one ($\varepsilon = 1.21$). Although the pore fraction of PMDA-PI is about 90 vol % higher than 6FDA-PAA, but the deviation degree of the experimental dielectric constant with calculated one is still large indicating some pores are ineffective to dielectric constant enhancement.

As the dielectric constant of 6FDA-PI is the lowest in the three kinds of PIs synthesized under the same conditions, therefore, the dielectric constant of 6FDA-PI formed at different acceptance rate in electrospinning and PAA content were further studied and shown in Figure 6. As for 6FDA-PAA, homogeneous fibers are not easily to be formed; the content for electrospinning for fibers is narrow. As the content of PAA solution increases in the measurement content, the fibers become more uniform, less dropping and less conglutination take place, and the porous density increases resulting in lower dielectric constant. When the content of PAA is slightly increased from 23.4 to 25 wt %, the viscosity is increased from 4.67 Pa S to 7.98 Pa S greatly. Correspondingly, more homogeneous fibers are formed and relatively low dielectric constant is obtained.

Also the dielectric constant increases with the acceptance speed, higher acceptance speed will result in lower dielectric constant (Table I). The dielectric constant of 6FDA-PI from 23.4 wt % and 25 wt % with acceptance speed of 2.5 m/min ($\varepsilon = 1.27$ and 1.22) is all lower than that formed at a speed of 1 m/min ($\varepsilon = 1.74$ and 1.23). This is because under higher acceptance rate the formed fibers exist in a stretching state [Figure 6(b,d)] and the fibers are more uniform, while the fibers formed with lower acceptance rate are in flexible form [Figure 6(a,c)]. The accumulation density of flexible fibers is higher and the porosity of the target membrane is low. The pore content difference of the membranes formed at different acceptance speed can be seen directly in SEM figures (Figure 6). Also the porosity measurement directly confirms pore difference in the membranes. The pore fraction of 6FDA-PI from 23.4 wt % and 25 wt % of PAA solutions with acceptance rate of 2.5 m/min is 84.74 and 87.91 respectively and higher than that of the corresponding membranes formed at a acceptance rate of 1 m/min which is 76.64 and 83.15. So porosity results in lower dielectric constant. Electrospinning is an effective way of fabrication of low dielectric constant and dielectric loss porous membranes.

CONCLUSIONS

Three kinds of PI membranes are fabricated by electrospinning of PAA solutions from polycondensation of three dianhydrides with ODA. The relationship of the morphology of the fibers,

thermostability and dielectric properties of the membranes with the polymer structure were discussed. PAAs with more flexible structure are easier to form high viscosity solution and fabricate high pore fraction membranes which are low dielectric constant materials. Under the coeffect of fluoro-containing groups and the pores, the dielectric constant and dielectric loss of 6FDA-PI is as low as 1.21 and 0.02, respectively. Also the 5% weight loss of the three kinds of PIs is all higher than 400°C. The formed electrospun membranes are thermostable low dielectric constant materials.

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