

Facile Fabrication of Macroporous Polyimide Films with Pores Distributing on One Side

Yongqiang Deng, Hongwei Zhou, Guodong Dang, Xianhua Rao, Chunhai Chen

Department of Chemistry, Alan G. Macdiarmid Institute, Jilin University, Changchun 130012, People's Republic of China

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ABSTRACT: Herein, we report on direct preparation of macroporous polyimide (PI) films with pores distributing on one side, the method of which relies on sedimentation of ceramic spheres in polyamic acid (PAA) solutions in a gravitational field and imidization of PAA/ceramic spheres mixtures to obtain PI/ceramic spheres hybrid films followed by curing in dilute hydrofluoric (HF) acid. In this strategy, the curing of the hybrid films in HF acid leads to the formation of pores. The introduction of pores

makes the room-temperature dielectric constants of the macroporous films lower than that of pure PI film. Moreover, the macroporous PI films have improved Young's moduli and higher thermal stability in nitrogen atmosphere. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 261–266, 2007

Key words: polyimides; macroporous polymers; ceramic spheres; templates; sedimentation

INTRODUCTION

As a high performance polymer material, polyimide (PI), which exhibits outstanding dielectric, mechanical properties, thermal stability, and low coefficients of thermal expansion (CTEs),^{1,2} has become an indispensable material for lots of areas. Porous PI is also of interest for many applications such as low dielectric insulators, gas separation membranes, and light-weight heat insulators.

A number of techniques have been introduced to prepare porous PI films. These include the use of blowing agents,³ the phase inversion of cast films,^{4,5} pyrolysis of thermally labile phase-separated compounds,^{6–10} microwave processing,¹¹ and self-organizing systems as templates. In the last method, these template systems include surfactants,¹² biological systems,¹³ liquid-drop-let surfaces,¹⁴ emulsions,^{15,16} and arrays of polymer or silica spheres.¹⁷ The macroporous polymer films prepared by use of the arrays of spheres as templates have many advantages comparatively. These include: porous structures are steady and do not collapse easily, the size of the pores can be adjusted by the diameter of the monodisperse spheres.¹⁷

According to this, we have prepared some PI/ceramic spheres hybrid films with hollow ceramic spheres distributing on one side by controlling the sedimentation of spheres in polyamic acid (PAA) solutions in a gravitational field. Then the ceramic spheres were dissolved away by dilute hydrofluoric (HF) acid to obtain macroporous PI films with pores distributing on one side. Visualization of the films, using scanning electron microscopy (SEM), reveals that the spheres distributing on the bottom side of the films can be dissolved away easily. The size of the pores can be adjusted by the diameter of the spheres, and porosity can be controlled by controlling the amount of filling spheres.

The aim of this work is to develop an excellent method for creating macroporous PI films appropriate to be modified further. By use of the pores distributing on one side as templates, lots of materials, such as metal oxides, metal complex, metal clusters and so on, can be filled into the pores or functional groups can be grafted onto the inner surface of the pores, which will be a good method to prepare functional membranes. Because the pores are distributing on one side, the functional membranes prepared by this method will have some novel functionalities and new applications. Recently, we have succeeded in filling mental argentine (Ag) into the pores, which will be described in our subsequent publication.

Correspondence to: C. Chen (cch@jlu.edu.cn).

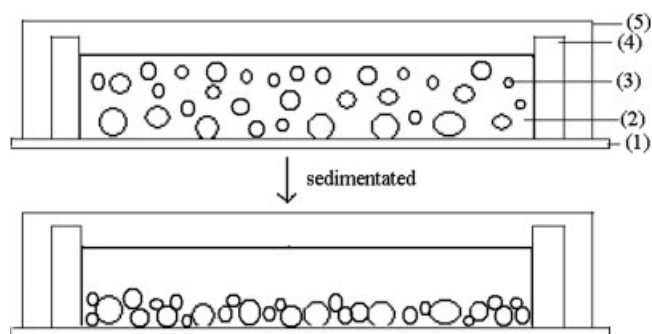
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EXPERIMENTAL

Materials

4,4'-Oxydianiline (4,4'-ODA) was purchased from Bengbu Zuguang Chemical Company in China and



Scheme 1 Schematic diagram of the apparatus for preparation of hybrid films: (1) glass substrate; (2) PAA solution; (3) ceramic sphere; (4) trough; (5) nappy.

used without further purification. 3,3',4,4'-biphenyl-tetracarboxylic acid dianhydride (*s*-BPDA) was a gift from College of Material Science and Technology of Tianjin University of China and Jida Plastic Product Company. *N,N*-dimethylacetamide (DMAc, analytical reagent grade) was purchased from Tianjin Chemical Reagents Company and desiccated by anhydrous sodium sulfate before used. Hollow ceramic spheres (density: 1.78 g/cm³, diameter: 3–6 μm, dielectric constant: 2.3–2.4, containing more than 55 wt % SiO₂, 31 wt % Al₂O₃, 1.1 wt % TiO₂, 1.0 wt % MgO, 2.0 wt % CaO, 1.0 wt % K₂O, and less than 3.0 wt % Fe₂O₃) were obtained from Shenzhen Microspace Special Materials Company in China and used as received. Hydrofluoric acid (HF, more than 40 wt %, analytical reagent grade) was purchased from Beijing Chemical Plant and diluted to 4 wt % before used.

Instruments

The morphology of the PI/ceramic spheres hybrid and macroporous PI films was observed using a SHIMADZU SSX-550 SUPERSCAN SEM. The glass transition temperatures (T_g) of the films were determined by a METTLER YOLEDO STAR^e DSC 821^e differential scanning calorimeter (DSC) at a heating rate of 20°C/min from 50 to 350°C. Thermal gravimetric analysis was performed on a Perking–Elmer Pyris 1 thermogravimetric analyzer at a heating rate of 5°C/min from 200 to 800°C in flowing nitrogen (20 mL/min). The mechanical properties of PI, PI/ceramic spheres hybrid and macroporous PI films were recorded on a SHIMADZU AG-1 universal tester at a drawing rate of 10 mm/min at room temperature. Density (D) measurements were obtained with a volume measuring tube and an electronic balance. The volume (V) of the films was measured by the volume measuring tube and the mass (M) of films by the electronic balance. $D = M/V$. Dielectric constants (at AC 10 MHz) of the films were measured by the HEWLETT-PACKARD 4194A impedance/gain-phase analyzer with voltage of 1 V at room temperature.

Preparation of PAA

4,4'-ODA (2.5432 g, 0.0127 mol) was dissolved in 60 mL of DMAc and then *s*-BPDA (3.7368 g, 0.0127 mol) was added to the solution and vigorously agitated by a mechanical stirrer for 4 h under air atmosphere at room temperature. A viscous PAA solution was prepared and preserved in a refrigerator at 0°C. The final concentration of the viscous PAA solution was 10 wt %.

Preparation of macroporous PI films and pure PI film

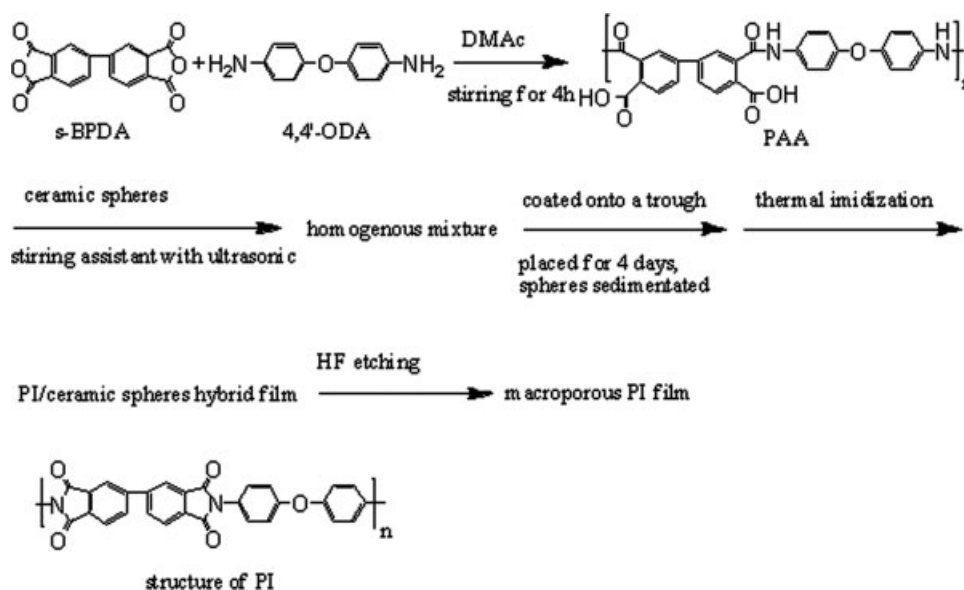
About 45.4 mL of 10 wt % PAA solution and 0.4848 g hollow ceramic spheres were added in a conical flask and vigorously agitated assistant with ultrasonic until the ceramic spheres dispersed homogeneously in the PAA solution. First, 4.5 mL of the resulting mixture was coated onto a trough (the trough is 7.5 cm long and 6 cm wide), which was fabricated on a glass substrate. Then the trough was obturated with a nappy and placed at 0°C for 4 days (S4 days). During these days, the hollow ceramic spheres were sedimentating. The sedimentating diagram of ceramic spheres is shown in Scheme 1. After that the nappy was removed, and the film was treated at 60°C for 2 h, 80°C for 2 h, and 120°C for 2 h in an oven under air atmosphere and then 180°C for 2 h, 250°C for 1 h, and 300°C for 1 h in a vacuum oven. The PI/ceramic spheres hybrid film were obtained and removed from the glass substrate. Afterward the free-standing hybrid film was soaked in a 4 wt % HF acid for 20 days (S4 days cured 20 days) to dissolve the ceramic spheres. The preparation diagram of macroporous film is shown in Scheme 2. The resulting macroporous film was air-dried at 80°C overnight.

In addition, a hybrid film with about 42 wt % ceramic spheres, which had sedimentated for 2 days (S2 days) in a dilute (5 wt %) PAA solution, was prepared and a half of the film was soaked in a 4 wt % HF acid for 8 days to obtain a macroporous PI film (S2 days cured 8 days). For comparison, a pure PI film (Pure PI) was obtained from the same 10 wt % PAA and cut into two parts, one part of the film was soaked in a 4 wt % HF acid for 20 days (PI cured 20 days). All of the films obtained were about 70 μm in thickness.

RESULTS AND DISCUSSION

Preparation of macroporous PI films

The density of ceramic spheres is 1.78 g/cm³, which is much higher than that of the 10 wt % and 5 wt % PAA solutions, so the sedimentation of ceramic spheres can be achieved easily. After the spheres have sedimentated completely in PAA solutions, the spheres distributed on the bottom side. Considering the fast volatilization of DMAc would give a force upwards to the spheres and disturb the spheres, which have sedimentated com-



Scheme 2 Schematic diagram of the procedure for making macroporous films.

pletely, especially to the small spheres, a slow temperature rise in steps from 60 to 120°C (60°C/2 h, 80°C/2 h, 120°C/2 h) was necessary. Most of the solvent volatilized tardily in low temperature for a long time, and then imidization was carried out through temperature rise in steps up to a maximum of 300°C.

Only when the ceramic spheres have sedimentated completely to bottom side in the hybrid films, high-quality macroporous PI films can be prepared. Because the matrix of PI in fully imidized form is so compact that the HF do not diffuse easily in it. That is to say, dissolving away of the ceramic spheres distributing in the middle of the hybrid films will be much harder. Moreover, to obtain high-quality macroporous polymer films by this method, the polymer matrices must have the property of resistance to dilute HF acid. The *s*-BPDA/4,4'-ODA PI is indiscerptible in dilute HF acid and can't react with it, which make it a good matrix for the preparation of macroporous films. The curing of PI in dilute HF acid has no influence on the thermal and the mechanical properties of PI matrix.

Morphology analysis of macroporous PI films

The PI/ceramic spheres hybrid film with spheres sedimentated for 4 days was prepared and its morphology was studied by SEM. Figure 1 shows the SEM photographs. Almost all of the spheres in S4 days have sedimentated to the bottom side of the film. By comparing the photographs of top surface and undersurface of S4 days, it can be observed that there are quite more spheres distributing on the bottom side than the top side. It confirms that the spheres can sedimentate to bottom side by this method. Then the PI/ceramic spheres hybrid film was soaked in a dilute HF acid solution for 20 days, and a corresponding porous film was obtained.

Figure 1(B, E) are the SEM photographs of the S4 days cured 20 days. It can be seen that the spheres distributing on bottom side are dissolved away completely by HF acid. The SEM photograph [Fig. 1(E)] clearly shows the presence of pores. The pores in the lowermost layer are open porous structures and connect with environment outside.

The concentration of PAA is a significant factor affecting the sedimentating velocity of ceramic spheres. A hybrid film with about 42 wt % ceramic spheres, which have sedimentated for 2 days (S2 days) in a 5 wt % PAA solution, was prepared. The SEM photographs of S2 days and corresponding macroporous film (S2 days cured 8 days) are showed in Figure 2. It can be seen that the spheres sedimentated in 5 wt % PAA solution only for 2 days [Fig. 2(A)] had sedimentated more completely than those sedimentated in 10 wt % PAA for 4 days [Fig. 1(A)]. The more completely the spheres had sedimentated, the easier the spheres were dissolved away. The macroporous film from 5 wt % PAA is easier and better quality.

The volume (V) and mass (M) of the samples were measured roughly by a volume measuring tube and electronic balance, respectively. Then the densities (D) of the films were calculated ($D = M/V$) and summarized in Table I. The densities of PI/ceramic spheres hybrid films are higher than that of pure PI. That's because the density of ceramic spheres is higher than that of PI matrix. The densities decrease after the hybrid films have been cured by dilute HF acid, and the decrease of the densities indicates the fabrication of pores.

Dielectric properties characterization

The dielectric constants (at AC 10 MHz) of the films were studied at room temperature. The dielectric constants of the pure PI, hybrid film (S4 days) and macro-

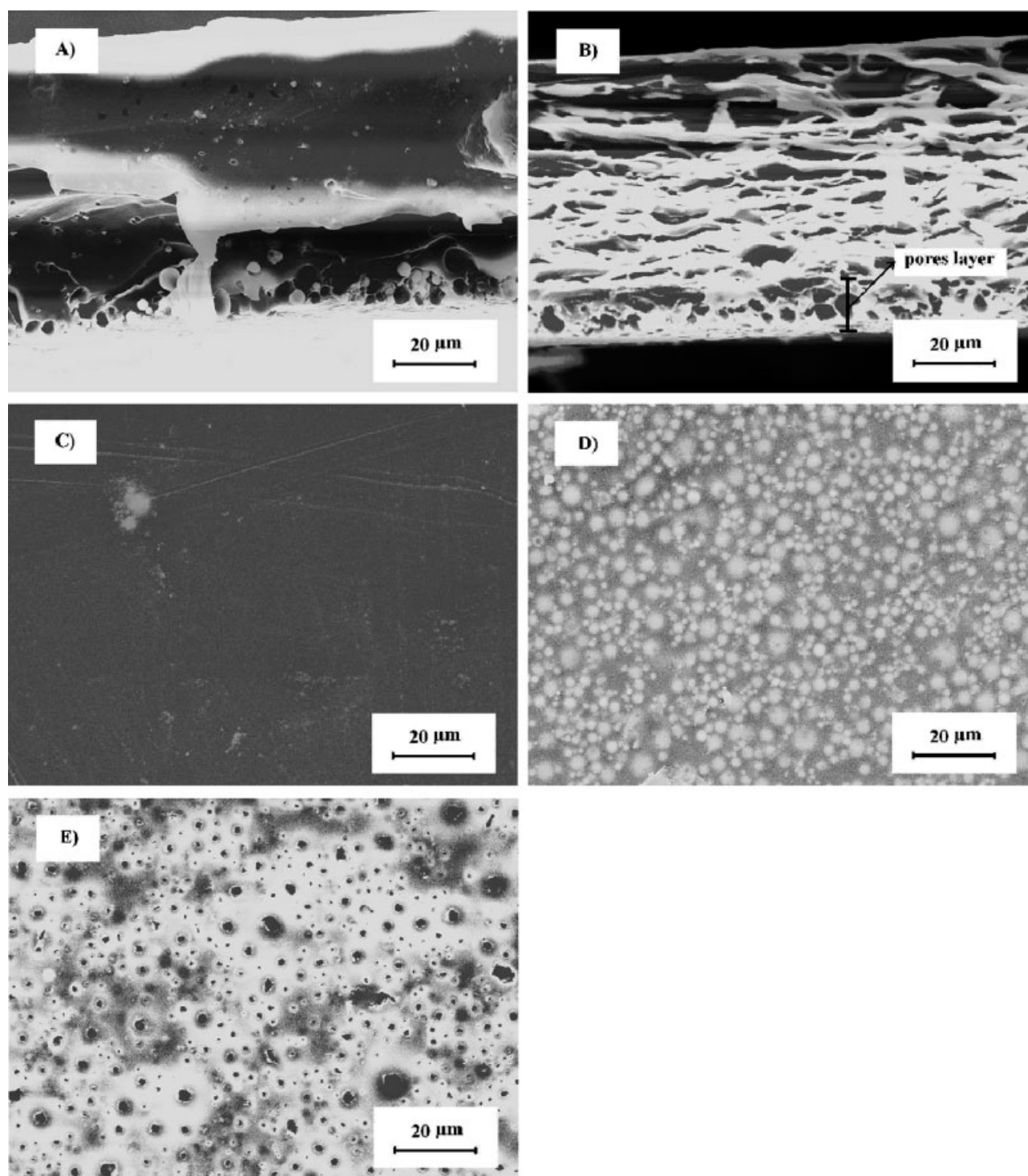


Figure 1 SEM photographs of PI/ceramic spheres hybrid film with spheres sedimentated for 4 days in a 10 wt % PAA solution and corresponding macroporous PI film. Cross sections of (A) S4 days; (B) S4 days cured 20 days; (C) top surface of S4 days; (D) undersurface of S4 days; and (E) undersurface of S4 days cured 20 days.

porous film (S4 days cured 20 days) were measured. The room-temperature dielectric constant of the PI/ceramic spheres hybrid film drops to 3.27. The contribution of inclusion of hollow ceramic spheres to the reduction of dielectric constant is only 0.02. After the hollow ceramic spheres have been dissolved away, the room-

temperature dielectric constant of the macroporous film drops to 3.20, the macroporous film shows a total reduction of the bulk dielectric constant is 0.09. The data show that the contribution of the pores to the reduction of dielectric constant is greater than that of the hollow ceramic spheres.

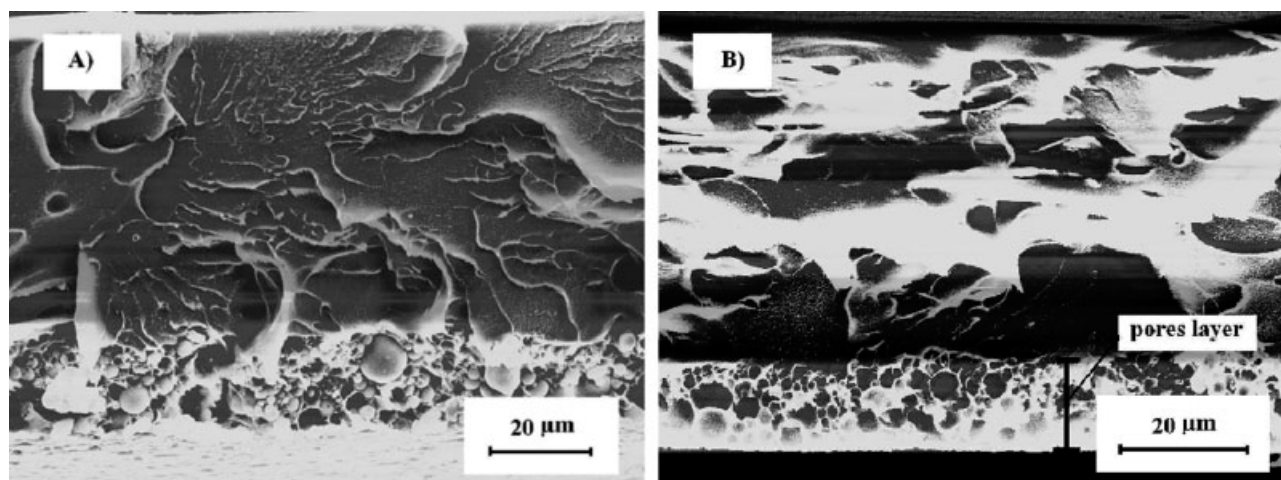


Figure 2 SEM photographs of PI/ceramic spheres hybrid film with spheres sedimentated for 2 days in a 5 wt % PAA solution and corresponding macroporous PI film. Cross sections of (A) S2 days and (B) S2 days cured 8 days.

Thermal properties of the films

Thermal data for hybrid and macroporous PI films are presented in Table II. The T_g of PI cured 20 days is equal to that of pure PI. And the T_d of PI cured 20 days is approximate to that of pure PI. So it can be concluded that the curing of PI in dilute HF acid has no apparent influence on the thermal properties of PI matrix, including T_g and T_d . The T_g s of hybrid and macroporous films are approximate to that of pure PI film. The ceramic spheres are added into the PI matrix in the form of small particles and they are phase-separated with the PI, which can be observed in the SEM photographs, there is no crosslinking of chain via interaction between spheres and PI molecules. After the spheres have been dissolved away, the residual substances are the PI matrix, so the T_g s of macroporous PI films are approximate to that of PI film.

In nitrogen atmosphere, the thermal stability of the hybrid and macroporous PI films is higher than that of pure PI. The temperatures at which there is 5% weight loss of PI/ceramic spheres hybrid and macroporous films are 22 and 11°C higher than that of the corresponding PI films, respectively. It also can be seen that

the thermal stability of macroporous films are lower than that of hybrid films.

PI/ceramic spheres hybrid film and the corresponding macroporous film, prepared from 5 wt % PAA solutions, exhibit lower thermal stability than samples prepared from 10 wt % PAA solutions. Nonetheless, the thermal stability of these samples is more than adequate for most purposes.

Mechanical properties of the films

Mechanical properties of the pure PI, PI/ceramic spheres hybrid and macroporous films are studied and showed in Table III. It can be seen that the curing of PI in dilute HF acid has no influence on the mechanical properties of PI matrix. The Young's moduli of the PI/ceramic spheres hybrid films are slightly higher than that of pure PI. After the hybrid films have been cured by HF acid, the Young's moduli of macroporous films decrease a little, but remain higher than that of pure PI. The tensile strengths of the hybrid and macroporous films decrease slightly and the elongations at break are lower by about 30% than that of pure PI. The tensile

TABLE I
Densities and Dielectric Constants of the Films

Sample	Density (g cm ⁻³)	Dielectric constant
Pure PI	1.35	3.29
S4 days	1.49	3.27
S4d cured 20 days	1.29	3.20
S2 days	1.50	- ^a
S2d cured 8 days	1.11	- ^a

^a Data not measured.

TABLE II
Thermal Data of the Pure PI, PI/Ceramic Spheres Hybrid, and Macroporous PI Films

Sample	T_g (°C)	T_d^a (°C)
Pure PI	277	591
PI cured 20 days	277	589
S4 days	277	613
S4d cured 20 days	274	600
S2 days	276	595
S2d cured 8 days	276	574

^a The temperature at which there is 5% weight loss of the samples determined by TGA under nitrogen.

TABLE III
Mechanical Properties of the Pure PI, PI/Ceramic Spheres Hybrid, and Macroporous PI Films

Sample	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Pure PI	1.8	155	78
PI cured 20d	1.7	165	84
S4d	2.2	154	60
S4d cured 20d	2.0	144	50
S2d	2.3	114	8.8
S2d cured 8d	1.8	102	8.4

strengths of hybrid film with spheres content about 42 wt % and its corresponding porous film (S2 days and S2 days cured 8 days) decrease further, and the elongations at break are only about 8%, much lower than those of pure PI. The reduction of the tensile strengths and elongations at break of hybrid and macroporous films can probably be attributed to the notch sensitivity of the PI. The ceramic spheres added into the PI in the form of small particles, which are phase-separated with the PI, and pores remained in the PI can be considered to have an effect equivalent to that of large defects.^{18,19}

CONCLUSIONS

It has been demonstrated that macroporous PI films with pores distributing on one side can be prepared by curing the PI/ceramic spheres hybrid films in HF acid, which were obtained by gravitational sedimentation method. The approach here is simple and versatile. The porous structures of the macroporous films are steady and hard to be destroyed. The dielectric constants of the macroporous film are lower than that of pure PI. The thermal stability and Young's moduli of macroporous films are approximate to pure PI matrix; even a little bit

higher because of the existence of some undissolved sphere particles in the middle of the fibers.

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