



# Preparation and properties of porous polyimide films with TiO<sub>2</sub>/polymer double shell hollow spheres

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## ABSTRACT

Without the template removal process, double shell hollow spheres were prepared by encapsulating the polymeric hollow spheres with TiO<sub>2</sub> shells. TiO<sub>2</sub> encapsulated hollow spheres were incorporated with the polyamic acid solutions and imidized to prepare the porous polyimide films. The final porous texture of the film depends on the as-doped arrangement and the properties of the hollow spheres. The TiO<sub>2</sub> shell exhibits good thermal stability and chemical resistance to prevent the collapse of hollow spheres during the polyamic acid solution/hollow particle mixing and the imidization procedures. The effects of preparation conditions on the morphology of the encapsulated hollow spheres were investigated. The dielectric constant of the porous polyimide films (pore diameter around 0.6 μm) decreased to 2.8. The influences of hollow particles on the porous textures, the dielectric and dynamic mechanical properties of the porous films were studied.

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## 1. Introduction

Polyimides have been widely used as inter-dielectric materials in microelectronics. As the circuits are scaled down, interconnect delay becomes increasingly dominant over intrinsic gate delay. It is necessary to use materials with lower dielectric constant to decrease the capacitance between the metal interconnection and reduce the RC delay time. There are several approaches to reduce the dielectric constant of the polyimide, including incorporation of fluorinated substituents into polymers [1], thermal degradation of the block or graft chains in the polyimide copolymers [2], and introduction of nanopores into polymers [3]. Zhang et al. [4] incorporated hollow silica tubes into polyimide to reduce the dielectric constant of the composites. Lin et al. [5] reported the preparation of PI composite films containing the mesoporous silica via in situ polymerization and thermal imidization. Hollow spheres were studied for applications such as drug delivery system [6], catalysis, and low dielectric-constant materials [7]. Hollow spheres are prepared by microemulsion [8] and template-based methods. Aluminosilicate [9], silica [10] and polymer [11] can be used as templates. Etching or high temperature calcination is necessary for removing the template to get the hollow structure.

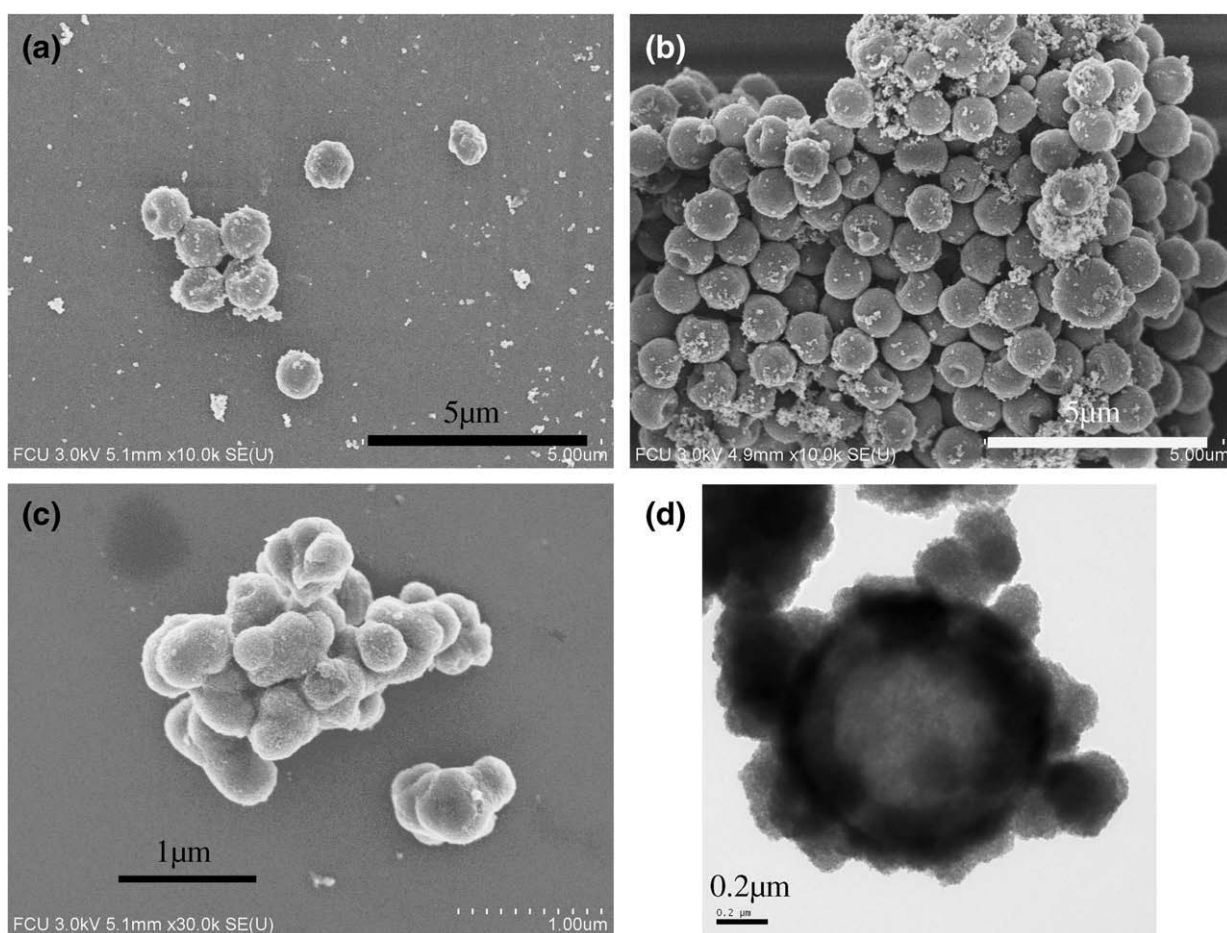
In this study, by encapsulating TiO<sub>2</sub> shells on the hollow polymeric spheres through sol–gel reaction, double-shell hollow spheres were prepared without the template removal process. Porous polyimide films were fabricated by incorporation of these hollow spheres. Polymeric hollow spheres are not suitable for the method because of

their poor chemical resistance and thermal stability. Since the polyamic acid (PAA) precursor is dissolved in the polar solvent, polymeric hollow spheres will be dissolved during the PAA solution/spheres mixing step or collapse in the imidization procedure. These TiO<sub>2</sub> encapsulated double-shell hollow spheres can be incorporated directly into the PAA solution and imidized at elevated temperature to fabricate the porous polyimide film. The thermal stability and chemical resistance of the TiO<sub>2</sub> encapsulated hollow sphere, together with the textures, dynamic mechanical properties and dielectric constants of the porous films were investigated.

## 2. Experimental

HP1 (Ropaque HP1055, Rohm and Haas, diameter: 800–900 nm) and HP2 (Ropaque ultra, Rohm and Haas, diameter: 300–400 nm) were the hollow acrylic/styrene sphere dispersed in water. For the growth of the TiO<sub>2</sub> shell, 0.5 g of the HP1 dispersion (solid content: 26.7%) was mixed with 20 ml ethanol containing 0.1 g polyvinylpyrrolidone (PVP, Mw = 10000). Then 0.05 ml of deionized water and 0.02 g HCl (aq) was added. Finally, X g of titanium tetraisopropoxide (TTIP) in 10 ml of ethanol was rapidly added under vigorous stirring. The TiO<sub>2</sub>X-HP1 hollow spheres were obtained after reacting at 25 °C for 3 h. The amounts of added TTIP for TiO<sub>2</sub>A-HPY, TiO<sub>2</sub>B-HPY and TiO<sub>2</sub>C-HPY (Y = 1 or 2) are 2 g, 3 g and 1.15 g respectively. 3,3',4,4'-benzophenonetetracarboxylic anhydride (BTDA) and 4,4'-diaminodiphenylether (ODA) are dried in the vacuum oven at 120 °C for 3 h prior to use. ODA and BTDA were dissolved in *N,N*-dimethylformamide (DMF) and stirred at room temperature for 3 h to make the PAA solution. Dried TiO<sub>2</sub>A-HP1 hollow spheres were dispersed in DMF and mixed with the PAA solution. The

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**Fig. 1.** FESEM images of  $\text{TiO}_2$  coated hollow spheres (a)  $\text{TiO}_2\text{C-HP1}$  prepared with PVP (b)  $\text{TiO}_2\text{C-HP1}$  prepared without PVP (c)  $\text{TiO}_2\text{B-HP2}$  prepared with PVP and (d) TEM image of  $\text{TiO}_2\text{A-HP1}$ .

precursor mixture is coated on the glass substrate and heated (imidized) at 50, 100, 150, 200, 250, 300 °C for 30 min each to fabricate the porous polyimide film. The dielectric constant was measured by a Jiehan 3532-50 LCR meter. The cross-sectional morphology was observed by a HITACHI S4800 cold field emission scanning electron microscope and energy dispersive spectrometer. XRD studies were carried out with a MAC SCIENCE MXP3 diffractometer. The dynamic mechanical analysis was measured with a DuPont DMA 2980 at a heating rate of 2 °C/min and at 1 Hz frequency. Experimental data presented are representative of those obtained in at least three separate experiments.

### 3. Results and discussion

Fig. 1(a) shows the FESEM image of  $\text{TiO}_2\text{C-HP1}$  hollow spheres prepared with PVP.  $\text{TiO}_2$  shells were fabricated on the polymeric hollow spheres. For the  $\text{TiO}_2$  encapsulated hollow spheres prepared without PVP (Fig. 1b), the aggregates formed by closely packed spheres.  $\text{TiO}_2$  was grown on the outer surface of each sphere. The shape of each  $\text{TiO}_2$  coated hollow sphere is still distinguishable. The dispersing properties of the spheres did not deteriorate after encapsulation.  $\text{TiO}_2$  coated spheres in Fig. 1(a) and (b) can be separated by mechanical stirring during the mixing of  $\text{TiO}_2$  encapsulated spheres and PAA solution. However,  $\text{TiO}_2\text{B-HP2}$  spheres exhibited totally different morphology (Fig. 1c). Aggregates with several spheres covered by a continuous  $\text{TiO}_2$  layer. These  $\text{TiO}_2$  layer connected  $\text{TiO}_2\text{B-HP2}$  spheres are difficult to be redispersed into separate spheres. Zhang et al. [12] demonstrated a route to prepare polystyrene (PS)/Ag/ $\text{TiO}_2$  multilayered colloids with controllable shell thickness by using acetone and polyvinylpyrrolidone (PVP).

Because the PVP shell increased the affinity of the Ag shell to  $\text{TiO}_2$ , the hydrolyzed titania particles could deposit directly onto the core to form the outer  $\text{TiO}_2$  shell. In this study, total surface area of smaller hollow spheres (HP2) is larger than that of larger hollow spheres (HP1). More PVP should be added to make redispersible  $\text{TiO}_2\text{B-HP2}$  spheres. Since same amount of PVP were added to prepare  $\text{TiO}_2\text{B-HP2}$  and  $\text{TiO}_2\text{C-HP1}$  spheres, it may be the reason why  $\text{TiO}_2$  layer of  $\text{TiO}_2\text{B-HP2}$  sphere prepared with more TTIP and smaller hollow sphere (HP2) shows different morphology compared with  $\text{TiO}_2\text{C-HP1}$  spheres. The hollow spheres should be uniformly distributed in the polyimide film to get a porous PI film with well-distributed pores. Adding PVP and controlling the TTIP/HP1 ratio are important to fabricate the porous PI film with well distributed pores. TEM image (Fig. 1d) shows that the produced spherical particles are composed of hollow inner cavity, thin polymeric shell and outer  $\text{TiO}_2$  shell. The formation of double-shell hollow sphere is confirmed. The morphology of the  $\text{TiO}_2$  shell is strongly dependent on the precursor/HP sphere ratio and the addition of PVP.

Fig. 2 shows the XRD pattern of the calcined  $\text{TiO}_2\text{A-HP1}$  hollow spheres. The formation of crystalline  $\text{TiO}_2$  was confirmed. The XRD pattern can be indexed to (101), (004), (200), (105), (211), (002) and (116) planes of tetragonal phase anatase  $\text{TiO}_2$  (JCPDS card no. 89-4921). It confirms the formation of crystalline  $\text{TiO}_2$  shell.

The HP1 sphere deformed when the baking temperature reached 120 °C (Fig. 3a). After being coated with the  $\text{TiO}_2$  shell, the shape of the  $\text{TiO}_2\text{A-HP1}$  hollow spheres did not change after being baked at 140 °C (Fig. 3b). Encapsulation of  $\text{TiO}_2$  shell enhanced the thermal stability of the polymeric hollow spheres. It helps to maintain the hollow structure within the composite PI film during the imidization process.

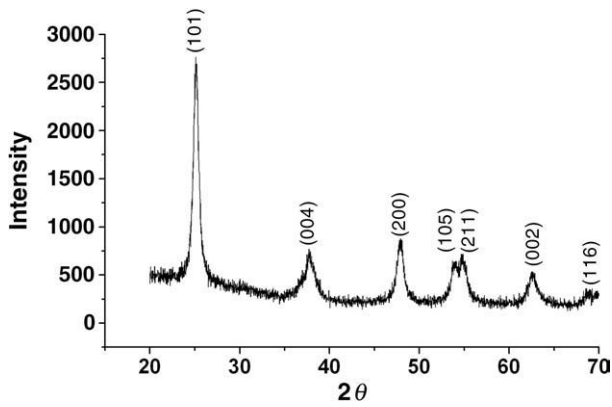


Fig. 2. XRD pattern of the calcined  $\text{TiO}_2\text{A-HP1}$  hollow spheres.

No pores are found in the cross-sectional FESEM images of the HP1-PI film (Fig. 4a). The HP1 hollow spheres may be dissolved by the DMF solvent or collapsed during the imidization process. The HP1 hollow spheres were replaced by  $\text{TiO}_2\text{A-HP1}$  spheres to fabricate the  $\text{TiO}_2\text{A-HP1-PI}$  composite film. Round pores of cross-cut  $\text{TiO}_2\text{A-HP1}$  are uniformly distributed in the cross-sectional FESEM images of the  $\text{TiO}_2\text{A-HP1-PI}$  film (Fig. 4b). The diameter of the round pore is close to the core size of the polymeric HP1 hollow sphere. The core size and the shell thickness of the polymeric hollow spheres were measured by TEM (Fig. 1d). The HP1 hollow particle had an inner pore diameter of 0.6  $\mu\text{m}$ . The  $\text{TiO}_2$  coated hollow sphere exhibits good thermal stability

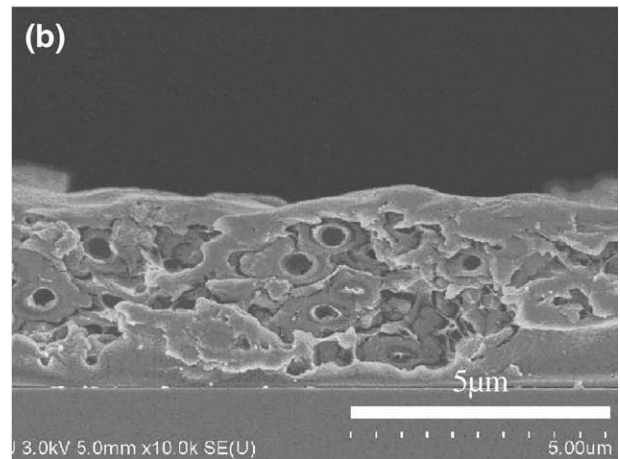
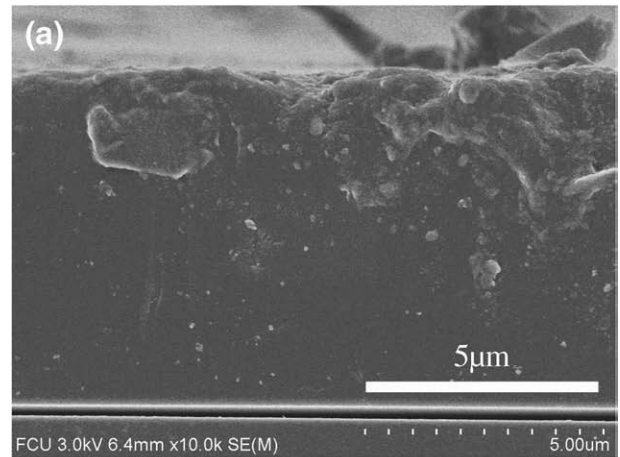


Fig. 4. Cross-sectional FESEM images of (a) HP1-PI composite film (b)  $\text{TiO}_2\text{A-HP1-PI}$  film.

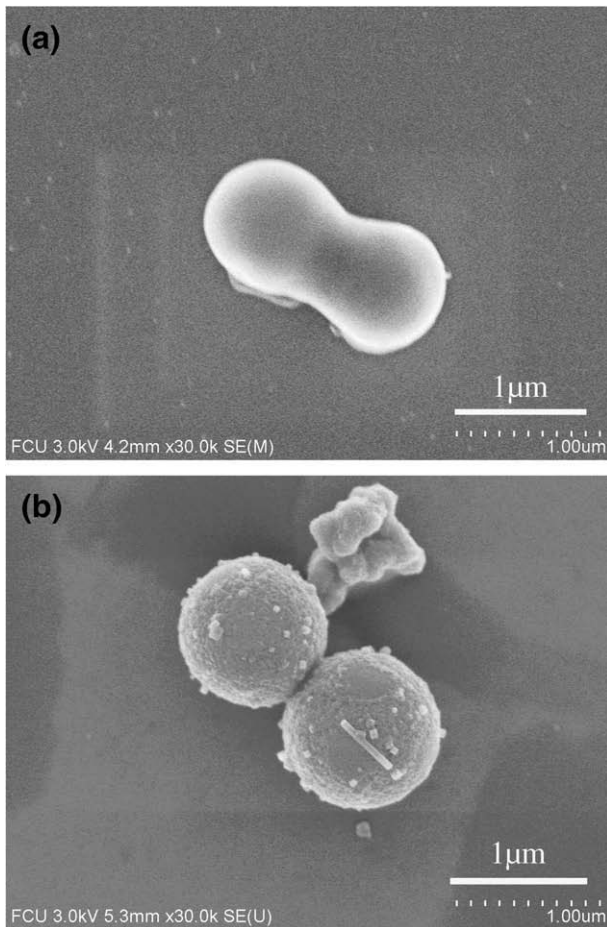


Fig. 3. FESEM images of (a) HP1 hollow spheres baked at 120  $^{\circ}\text{C}$  and (b)  $\text{TiO}_2\text{A-HP1}$  hollow spheres baked at 140  $^{\circ}\text{C}$ .

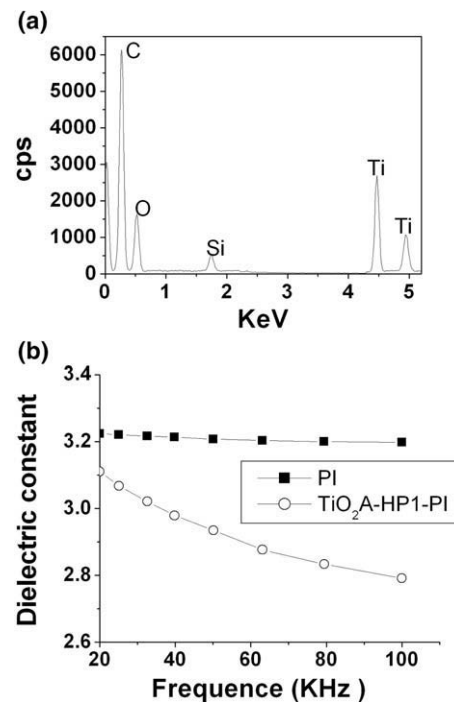


Fig. 5. (a) EDX spectrum of  $\text{TiO}_2\text{A-HP1-PI}$  film (b) dielectric constants of the polyimide film and the  $\text{TiO}_2\text{A-HP1-PI}$  film.



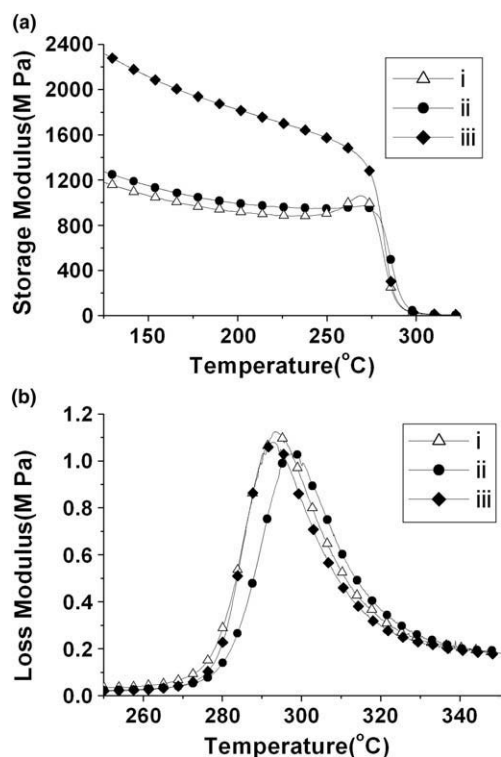


Fig. 6. (a) Storage modulus and (b) loss modulus of (i) TiO<sub>2</sub>A-HP1-PI film (ii) TiO<sub>2</sub>B-HP2-PI film (iii) pristine PI film.

and chemical resistance. They are not dissolved by DMF or collapsed during the heating process.

Qualitative identification of the cross-sectional area of the TiO<sub>2</sub>A-HP1-PI film was done by energy-dispersive X-ray (EDX) spectrometry (Fig. 5a). The small peak of Si element results from the glass substrate. In addition to C and O peaks, Ti peaks are also found on the EDX spectrum. It confirms that the round pores are the cross-cut TiO<sub>2</sub>A-HP1 hollow sphere. Fig. 5(b) shows the dielectric constants of pristine polyimide film and TiO<sub>2</sub>A-HP1-PI composite film measured at different frequency. The dielectric constants turn lower as the hollow spheres are incorporated.

The storage modulus of the porous TiO<sub>2</sub>A-HP1-PI and TiO<sub>2</sub>B-HP2-PI polyimide is lower than that of the nonporous polyimide (Fig. 6a). Introducing the pores reduces the elastic modulus of the material. The storage modulus of the pristine polyimide decreased with increasing temperature. For the TiO<sub>2</sub>A-HP1-PI film, enhancement of the storage modulus between 225 °C and T<sub>g</sub> (275 °C) suggests that the close pore also occurs densification during the dynamic tensile test. When the temperature is higher than the T<sub>g</sub>, the polymeric matrix begins to transit from glassy to elastic state, and the storage modulus falls rapidly. Jiang [13] reported that the storage modulus peak of microcellular poly(aryl ether ketone) foams accompanies micropore rearrangement during tests. When the celled-wall reciprocally contacts by tensile action, the densification will lead to rapid stress increase. The property of TiO<sub>2</sub> shell would have some influences on the storage modulus peak. The micropore is more difficult to

densificate when the shell/hollow core ratio is larger. Compared with the TiO<sub>2</sub>A-HP1-PI film, the storage modulus of the TiO<sub>2</sub>B-HP2-PI film is higher, and the storage modulus between 225 °C and T<sub>g</sub> remains almost the same. Jiang et al. [13] reported that the loss modulus of the porous poly(aryl ether ketone) prepared by the batch foaming process is lower than that of the poly(aryl ether ketone) matrix. It is attributed to the reason that the microinertia of micropores endows micropores with higher elasticity in very small strain range. The strain of micropores in the porous poly(aryl ether ketone) is easier to elastic rebound and the loss modulus turns smaller. However, the loss modulus of the porous polyimide film with TiO<sub>2</sub>/polymer double shell hollow spheres is nearly the same as that of the nonporous polyimide matrix (Fig. 6b). Pores formed by TiO<sub>2</sub>/polymer double shell hollow spheres were different from those prepared by the batch foaming process.

#### 4. Conclusion

In summary, by using the polymeric hollow spheres as template instead of traditional polymeric microspheres, TiO<sub>2</sub> encapsulated double shell hollow spheres were prepared without the template removal process. TiO<sub>2</sub> encapsulated hollow spheres can be added in the PAA solutions to prepare the low dielectric porous polyimide films. TiO<sub>2</sub> shell exhibits good chemical and thermal resistance to prevent the hollow sphere from collapsing during mixing with the PAA solution and the imidization procedures. Porous textures of the films mainly depend on the as-doped arrangement of the hollow spheres. Addition of PVP and controlling the TTIP/HP1 ratio are important to fabricate redispersible double-shell hollow spheres and porous PI films. Incorporation of hollow spheres lowered the dielectric constant of the composite film. In the dynamic mechanical test, the storage modulus of the porous TiO<sub>2</sub>A-HP1-PI film exhibited a peak near T<sub>g</sub>. It may be attributed to the effects of densification. However, the loss modulus of the porous polyimide film with double shell hollow spheres is nearly the same as that of the nonporous polyimide matrix.

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