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RESEARCH ARTICLE

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Preparation, structure and properties of porous polyimide films via PAA/PU alloy

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Abstract A new route to porous polyimide (PI) films with pore sizes in the nanometer regime was developed. A polyamic acid (PAA)/polyurethane (PU) blend with PU as the disperse phase was first prepared via *in situ* polymerization of pyromellitic dianhydride and 4,4-oxydianiline in PU solutions. Porous PI films were obtained from PAA/PU films by thermolysis of PU at 360°C and imidization of PAA at 300°C, respectively. Fourier transform infrared spectroscopy and thermal gravimetric analysis were used to detect the imidization and thermolysis processes of PAA/PU blends under thermal treatment. The microporous structure of the PI films was observed by transmission electron microscopy. It was found that the size and content of pores increased with an increase in the PU mass fraction in the PAA/PU blend up to 20%. Because of the existence of nanopores, the dielectric constant of PI films decreased by a wide margin and was less than 2.0 at a PU mass fraction of 20%. It implies that this is an effective means to reduce the dielectric constant of PI, but it also causes the decrease of tensile strength and the rise of water absorption.

Keywords polyimide, polyurethane, porosity, dielectric constant

Polyimides (PIs), aromatic heterocyclo-polymers containing imide groups in their backbone, have been widely used as dielectric and packaging material in the microelectronics industry because of their excellent thermal, dielectric, mechanical and optical properties [1–6]. However, the miniaturization of the ultra-large scale integration circuits has increasing demands for the low dielectric constant (ε) PIs to greatly reduce the resistance–capacitance time delays, cross-talks, and power dissipation in the high-density and high-speed integrated circuits [7–10]. Most PIs are insufficient in meeting these requirements because of their high ε value of about 3.4.

In recent years, many studies have been contributed to reduce the ε of PIs, such as the incorporation of fluorinated substituents [11,12] and low ε block or aliphatic chains [13]. However, these approaches merely reduce the ε to 2.6. Moreover, the fluorinated PIs are expensive. Several groups have reported that the reduction in dielectric constant can be simply achieved by replacing a significant part of the PIs with air, which has a dielectric constant of 1. The approaches to the porous PI films include microwave processing, incorporation of foaming agents and/or hollow microspheres. Most of the porous PIs prepared via the above methods have fairly large pore sizes and open pore structures. Fine works on the preparation of nanoporous PI films with low-ε by thermal decomposition of the thermal labile components in block or graft copolymers have also been reported [14]. In this process, microphase-separated block or graft copolymers were prepared, and the morphology consists of a matrix of the thermal stable polymers (PIs) with thermal labile polymers (PS [15], PAAc [16], and PU [17]) as the dispersed phase. Upon thermal treatment, the thermally unstable polymers thermolysis, and the decomposition products diffuse out of the film leaving pores embedded in the PI matrix.

Herein, we reported a simple method for preparing low-ε porous PI films from poly(amic acid)/polyurethane (PAA/PU) polymer alloy. A PAA/PU polymer alloy was first prepared via *in situ* polymerization of PAA in PU solution, with the PU constituting the dispersed phase. The PU phase was subsequently decomposed and taken away by thermal treatment, leaving the pores of same size and shape duplicating the PU phase distribution in the PI matrix. The morphology, dielectric constants, thermal and mechanical properties of porous films were investigated.

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1 Experimental

1.1 Materials

Pyromellitic dianhydride (PMDA) and 4,4-oxydianiline (ODA) from Shanghai Research Institute of Synthetic Resins,

were dehydrated prior to use. *N*,*N*-Dimethylacetamide (DMAC) from Tianjin Fu Chen Chemicals Reagent Co. was used as received. Polyurethane (PU, M_n = 22000) from Luoyang Liming Chemical Plant was used as received.

Fourier-transformed infrared spectroscopy (FTIR) measurements were made on a Nexus 670 spectrometer with a mercury cadmium telluride detector. The thermal properties of PU were investigated by thermal gravimetric analysis (TGA) from room temperature to 500°C at a heating rate of 10°C/min in a flowing air atmosphere. Transmission electron microscopy (TEM) observation was performed on a HITACHI H-800 TEM instrument at 100 kV. The films were cut into 4 mm × 25 mm pieces to measure the mechanical properties of films with an Instron-1185 system at room temperature. Dielectric properties of well-dried film samples were measured using a WY2851 Q instrument at 1 MHz. The water absorption of porous PI films was measured according to the GB 1034-70.

1.2 Preparation of porous PI films

The preparation of porous films is shown in Scheme 1. In a 250 mL three-necked round-bottomed flask fitted with a mechanical stirrer certain amounts of PU and 3.661 g (0.0183 mol) of ODA were dissolved in 60 ml of DMAC. PMDA powder 4.030 g (0.0184 mol) was then introduced into the solution stepwise. After the dissolution of all PMDA, a PAA/PU solution was formed. The calculated content of PU (weight percentage) in the PAA/PU alloy films was 5, 10, 15, 20, and 25 wt% respectively. The mixture was cast subsequently on quartz wafers, which were cleaned using distilled water and acetone, and heated with the curing procedure: 80°C (for 1 h), 120°C (for 1 h), 180°C (for 1 h), 250°C (for 1 h), 300°C (for 1 h), 360°C (for 4 h) in an air circulating oven. Thermal curing gives a porous PI film with about 50 µm thickness, and it was retrieved from the wafer by immersing in water for a few minutes.

2 Results and discussion

2.1 Preparation and characterization of the porous PI films

The porous PI films were prepared via the thermal treatment of PAA/PU alloy films. In this thermal treatment process, the PAA was imidized to PI, and the PU was decomposed, leaving pores where the PU was placed. The temperature at which thermal decomposition of the PU occurs is crucial; it should obey the following equation: $T_i < T_d < T_f < T_g$ (T_i is the imidization temperature, T_d is the decomposition temperature, T_f is the foaming temperature and T_g is the glass transition temperature) [15]. It has been reported that the imidization degree of the PMDA/ODA polyimide is nearly 99% at 300°C, and increasing temperature would not have an effect on the imidization degree [18–20]. In this study, the foaming temperature should be the temperature at which the rate of the decomposition reaction of the PU is maximal. TGA was used to evaluate the thermal properties of PU (Fig. 1). It can be seen from Fig. 1 that the PU begins to decompose at 310°C, and the rate of the decomposition reaction is maximal at 360°C. Because the T_g of PMDA/ODA polyimide is about 383°C, the foaming temperature was selected as 360°C to decompose the PU thoroughly and decrease the thermal treatment time.

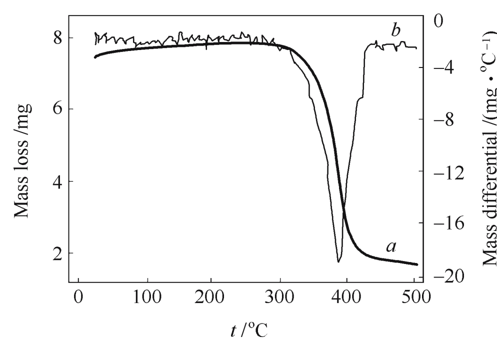


Fig. 1 TGA curves of PU
(a) Mass loss; (b) Mass differential

The FTIR spectra of pure PI film (Fig. 2a), pure PU film (Fig. 2b), PU/PI film (Fig. 2c) and porous PI film (Fig. 2d) are shown in Fig. 2. It can be seen from the figure that the FTIR spectrum of PU/PI film includes the characteristic peaks of pure PI and PU, and the FTIR spectrum of porous PI film is similar to that of pure polyimide. These results confirm that only polyimide remains in the porous film and PU has been decomposed completely and diffused out of the PI matrix.

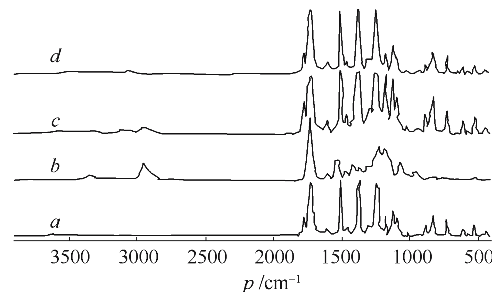
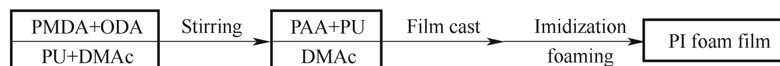


Fig. 2 FTIR spectra of PI (a), PU (b), PI/PU (c) and porous PI (d)



Scheme 1 Schematic diagram for preparing the porous polyimide films

2.2 Effect of PU content on the morphology of porous PI films

To investigate the distribution and morphology of the pores in the PI matrix, the morphology of the porous films was investigated by TEM. Figure 3 shows the TEM images of porous films prepared with different PU mass fraction: (A) 0%, (B) 5%, (C) 10%, (D) 15%, (E) 20%, and (F) 25%, respectively. It can be seen from Fig. 3 that prolate and close pores are well distributed in the PI matrix, and the dimension of pores increases with increasing the PU content. These results may imply that the rigid PAA chains are oriented in the casting process. By increasing the PU content the width and length of the pores increase from 40 nm to 300 nm and from 400 nm to 1.5 μm, respectively. Moreover, the amount and density of pores in the PI matrix also increase with an increase in the PU content. However, when the PU content reaches 25%, the amount and density of pores become lower. This might result from the collapse of pores caused by the excessive large size of pores and the orientation of polymer chains.

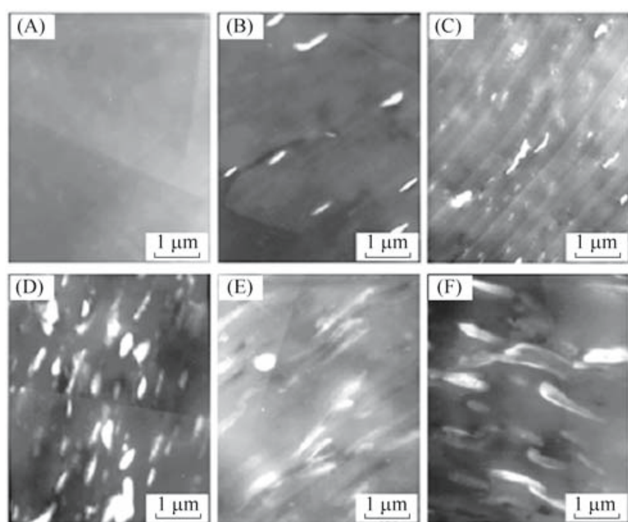


Fig. 3 TEM images of porous PI films with different mass fractions of PU

(A) 0%; (B) 5%; (C) 10%; (D) 15%; (E) 20%; (F) 25%

2.3 Effect of PU content on the properties of porous PI films

2.3.1 Dielectric properties

The dielectric constant of the porous films is governed by the intrinsic dielectric constant of the PI matrix and the morphology of the porous structure. Figure 4 shows the dependence of the dielectric constant of the porous PI film on the PU content of the original PI/PU films. The dielectric constant of the pure PI film is about 3.2 under ambient conditions. As anticipated, all the porous PI films exhibit considerably lower dielectric constants and the dielectric constants of the porous

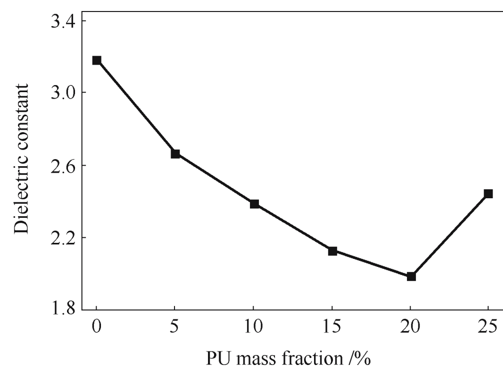


Fig. 4 Dielectric constants of porous PI films vs. PU mass fraction

films steadily decreased as the mass fraction of PU increased. When the content of the PU in the PI matrix is 20%, a dielectric constant of 1.994 is achieved, which is much lower than that of the pure PI films. The drop in the dielectric constant is a natural result of the introduction of air that possesses a dielectric constant near unity. The abnormal increasing of the dielectric constant at a PU content of 25% results from the collapse of the pores in the PI matrix.

2.3.2 Water absorption property

The incorporation of pores into the PI matrix would have an effect on the water absorption property of PI films. Figure 5 shows the water absorption property of porous PI film with different PU contents. The water absorption of porous films increases as the PU content increases, and has a maximum at a PU mass fraction of 20%. The reduction of water absorption of porous PI film again is caused by the collapse of large pores.

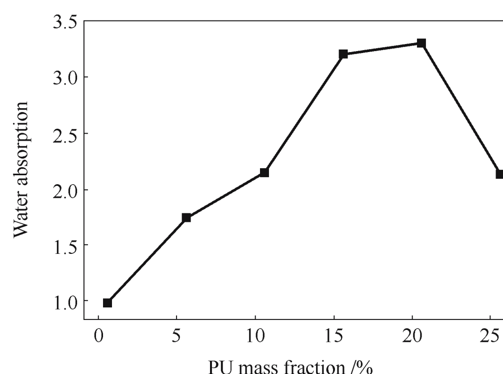


Fig. 5 Water absorption of porous PI films vs. PU mass fraction

2.3.3 Mechanical properties

Figure 6 shows that the tensile strength and modulus of the porous films decrease gradually as PU content increases up to about 20% followed by a slight increase at higher PU fractions. This is naturally attributed to the stress concentration caused by the pores in the porous film and the reduced section

area of the samples. The collapse of the pores causes the increase of the tensile strength and modulus of porous films at a PU content of 25%.

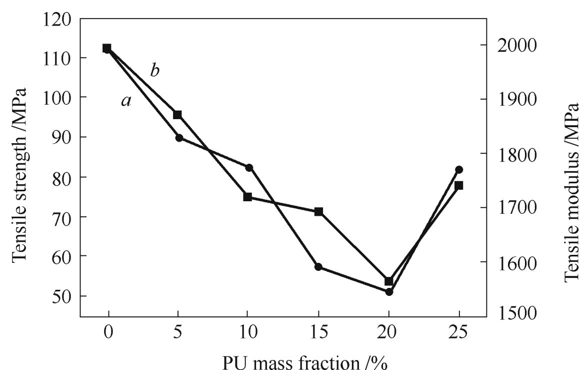


Fig. 6 Curves of tensile strength (a) and modulus (b) of porous PI films vs. PU mass fraction

In conclusion, in situ polymerization of PAA/PU alloy provides a novel method for preparing porous polyimide films of ultra-low dielectric constant. This is a simple, versatile approach for the production of porous materials. Additionally, the flexibility of PI chains may have a great effect on the morphology and size of the pores; this can be resolved by improving the compatibility of the PI and PU phases via introducing flexible groups (such as ether) into the PI chains.

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References

1. Jiang L Z, Liu J G, Feng Y Z, Luo N, Song F, Wu D Z. Preparation of PI/SiO_2 nanocomposite films by Sol-Gel process and its structure and properties. J Beijing University Chemical Technology, 2005, 32(1): 59−61 (in Chinese)
2. Jiang L Z, Liu J G, Wu D Z, Li H Q, Jin R G. A methodology for the preparation of porous polyimide films with low dielectric constants. Thin Solid Films, 2006, 510: 241−246
3. Wang J G, Shen Y Q. The synthesis and thermal stability of thioether sianhydride poly(amic acid). Chem J Chinese Universities, 2000, 21(6): 879−883 (in Chinese)
4. Sun J P, Wu H C, Li B M, Ying Z J. Preparation, third-order nonlinear optical property and optical information storage of polyimide attached with azobenzene chromophore side-chain. Chem J Chinese Universities, 2004, 25(2): 372−375 (in Chinese)
5. Pan X X, Sui Y, Xu H J, Yin J, Liu Y G, Gao J, Zhu Z, Huang D Y, Wang Z G. One-step synthesis of high Tg organo-soluble side-chain fluorinated polyimides containing a triazine-azo chromophore. Chem J Chinese Universities, 2002, 23(7): 1433−1436 (in Chinese)
6. Feger C, Franke H. Polyimides: Fundamentals and Applications. Marcel Dekker Press, New York, 1996, 7
7. Muruganand S, Varayandass S K, Mangalaraj D, Vijayan T M. Dielectric and conduction properties of pure polyimide films. Polym Int, 2001, 50(10): 1089−1094
8. Maier G. Low dielectric constant polymers for microelectronics. Prog Polym Sci, 2001, 26(1): 3−65
9. Hawker C J, Hedrick J L, Miller R D, Voklsen W. Supramolecular approaches to nanoscale dielectric foams for advanced microelectronic devices. MRS Bull, 2000, 25: 54−57
10. Martin S J, Godschalx JP, Mills M E, Shaffer EO, Townsend P H. Development of a low-dielectric-constant polymer for the fabrication of integrated circuit interconnect, Adv. Mater., 2000, 12(23): 1769−1778
11. Hedrick J L, Carter K R, Richter R, Miller R D, Russell T P. Polyimide nanofoams from aliphatic polyester-based copolymers. Chem Mater, 1998, 10(1): 39−49
12. Simpson J O, Clari A K S. Fundamental insight on developing low dielectric constant polyimides. Thin Solid Films, 1997, 308/309: 480−485
13. Dai J Y, Liu D S. Structure and properties of fluoro-containing polyimides. Journal of Functional Polymer, 1999, 12(3): 337−343 (in Chinese)
14. Qiu J, Takashi Y. Horie KJ. Polyimides with alicyclic diamines. II. Hydrogen abstraction and photocrosslinking reactions of benzophenone-type polyimides. J Polym Sci: Part A, Polym Chem, 1997, 32(3): 503−511
15. Hedrick J L, Russell T P, Labadie J, Lucas M, Swanson S. High temperature nanofoams derived from rigid and semi-rigid polyimides. Polymer, 1995, 36(14): 2685−2697
16. Hedrick JL, Hawker CJ, Dipietro R. The use of styrenic copolymers to generate polyimide nanofoams. Polymer, 1995, 36(25): 4855−4866
17. Wang W C, Rohitkumar H V, Kang E T, Neoh KG, Ong C K, Chen L F. Nanoporous Ultra-Low- Films Prepared from Fluorinated Polyimide with Grafted Poly(acrylic acid) Side Chains. Adv Mater, 2004, 16(1): 53−57
18. Santhana G K P, Cheng C Z, Cheng Y S, Cheng J W C. Preparation of Nanoporous Polyimide Films from Poly(urethane-imide) by Thermal Treatment. Macro Mater Eng, 2003, 288(9): 730−736
19. Xie Q, Yang W, Chang A M, Kang J. Study on imidization process of polyamic acid for humidity sensor. Applied Chemical Industry, 2003, 3(26): 20−22(in Chinese)
20. Wang X Q, Wu Z T, Bian J H, Zhu F T, Li S J. Study on the synthesis and properties of a new polyimide end-capped with maleic anhydride I: Synthesis of amic acid and its kinetics of imidization. Journal of Functional Polymer, 1994, 7(3): 279−291 (in Chinese)
21. Ding M X, He T B, Zhou J. Polyimide New Materials. Science Press, Beijing, 1998