Desalination and Water Treatment
www.deswater.com

34 (2011) 344–348
October

1944-3994/1944-3986
doi: 10/5004/dwt.2011.2899

Fabrication of polyimide composite film with both magnetic and surface conductive properties

Jiayu Zhan[a,b], Dezhen Wu[b], Cuixian Chen[a], Jiding Li[a,*], Fusheng Pan[a], Jian Chen[a], Xia Zhan[a]

[a]*Department of Chemical Engineering, Membrane Technology & Engineering Research Center, Tsinghua University, Beijing 100084, P.R. China*
Tel. +86-10-62782432; Fax: +86-10-62770403; email: lijiding@mail.tsinghua.edu.cn
[b]*State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China*

Received 3 September 2010; Accepted 3 January 2011

ABSTRACT

Bilayer polyimide film with superparamagnetic response and conductive surface has been exploited as an important candidate for electromagnetic interference shielding material. Polyimide matrix was derived from 4,4′-oxydianiline and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride. Iron (III) 2,4-pentanedionate ($Fe(acac)_3$) and (1,1,1-trifluoro-2,4-pentadionato) silver(I) (AgTFA) were chosen as magnetic nanoparticles precursor and silver source, respectively. At magnetic polyimide layer, in situ method allowed the $Fe(acac)_3$ to decompose to γ-Fe_2O_3, exhibiting typical superparamagnetic response. The conductive surface-silvered polyimide layer was prepared via in situ single-stage self-metallization technique by thermal curing of the AgTFA-contained poly(amic acid). The reduction of silver(I) and further aggregation of silver atoms gave the conductive polyimide surface. The surface square resistance for the bilayer film of 0.1 Ω/square could be obtained. The structure and the properties of final bilayer film were characterized by X-ray diffraction, scanning and transmission electron microscope, magnetic and conductive measurements.

Keywords: Polyimide; Bilayer; Film; Conductive; Superparamagnetic; In situ method

1. Introduction

Electromagnetic interference (EMI), such as radio noise, electronic noise, radio-frequency interference, etc., has been invisible electron pollution with the increasing use of electronic products and communication instruments. Polymer composites with conducting fillers, such as metal particles, metal flakes, carbon particles, and carbon fibers, because of their light weight and easy processing, have been extensively studied to provide EMI prevention [1–4]. However, the dispersion of nanosize fillers is always challengeable. In order to develop versatile and effective EMI shielding materials, the ideal combination would be to have a magnetically or electrically tunable microwave material, the properties of which can be obtained by adjusting the composition and microstructure. Intrinsically conductive polymers such as polyaniline and polypyrrole/magnetic particles nanocomposites have been identified as candidates for EMI-shielding materials [5,6]. However, the application was restricted because the intrinsically conducting polymers bear a high cost of preparation and have unstable conductivity. Another novel approach is to develop bilayer structures of magnetic polymer nanocomposites with a conductive surface layer. Such a structure would ensure that the topmost layer has a high conductivity, resulting in a large shielding effectiveness, while the magnetic nanocomposite bottom layer can

*Corresponding author.

Presented at the AMS6/IMSTEC10, The 6th conference of the Aseanian Membrane Society in conjunction with the 7th International Membrane Science and Technology Conference, Sydney Australia, November 22–26, 2010

be used to assist in improving device characteristics by providing better impedance matching and tenability [7].

Polyimide offers many advantages such as high thermal stability, superior chemical resistance, and excellent mechanical property [8,9]. In recent years, in attempt to present materials with electrical and/or magnetic properties, polyimide films containing metal or metal oxide particles have been prepared respectively [10–13]. Typically, various synthetic routes have been applied to obtain metal/metal oxide modified polyimides: deposition, sol-gel, and in situ method [14–16]. Among these methods, the in situ method is considered as a most prospect one because of its processing simplicity and outstanding adhesion at the polymer-metal or polymer-metal oxide interface compared with external deposition methods. For example, the highly reflective and conductive silvered polyimide films have been fabricated through the in situ single stage self-metallization method. More than 90% reflective 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA)/4,4′-oxydianiline (4,4′-ODA) based polyimide films were fabricated with a surface electrical resistivity less than 0.1Ω/sq [17]. Taylor's group also reported that iron oxide polyimide composite films with magnetic properties had been synthesized by the in situ method [18]. Therefore, in situ method provides an effective way to realize the preparation of multifunctional polyimide film to meet the requirement of EMI-shielding application.

The work describes the preparation of bilayer polyimide composite films by in-situ technique. The bottom layer prepared by the incorporation of iron complex into a solution of poly(amic acid)(PAA) exhibited typical superparamagnetic response, while the topmost layer prepared by the incorporation of silver complex solution into the solution of PAA showed surface electrical conductivity with excellent silver-polyimide interfacial adhesion due to the mechanical interlocking mechanism. Therefore, both highly metallic electrical conductivity and superparamagnetism can be realized in the bilayer polyimide films.

2. Experimental section

2.1. Materials

3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) was purchased from Acros Organics and used without further purification. 4,4′-oxydianiline (4,4′-ODA) was obtained from the Shanghai Research Institute of Synthetic Resins and recrystallized in ethyl acetate prior to use. N,N-dimethylacetamide (DMAC, analytical pure, water content ≤0.1%) was purchased from Tianjin Fu Chen Chemicals Reagent Factory and used after distillation. Silver acetate(AgAC) (analytic pure, ≥99.0%) and 1,1,1-trifluoro-2,4-pentanedione (TFAH) (≥98%) were purchased from Shanghai Shiyi Chemicals Reagent Co. Ltd. and Acros Organics, respectively, and used as received. Iron (III) 2,4-pentanedionate ($Fe(acac)_3$) was provided by Shanghai Suocheng Chemical Co. Ltd. and used as received.

2.2. Film preparation

The following procedures were used to prepare bilayer polyimide composite film. PAA synthesis was performed in DMAC, 20% solids concentration. 4,4′-ODA was added to a flask with DMAC and stirred until dissolved. The dianhydride was added, and consequent pale yellow solution was mechanically stirred for 1 h. Iron complex incorporated PAA solution was made by adding $Fe(acac)_3$ and stirring for at least 0.5 h. Film was made by casting the solution onto a dust free glass substrate, and then cured under air atmosphere at 80°C for 20 min and at 100°C, 200°C, 300°C and 320°C for 1 h each.

The (1,1,1-trifluoro-2,4-pentadionato) silver(I) (AgTFA) complex was freshly produced by dissolving AgAC in a small volume of DMAC containing TFAH with three times mole equivalent to the AgAC. AgTFA complex was then added to PAA solution. Films were cast on the already thermally cured PAA/ $Fe(acac)_3$ films and stayed for 12 h at room temperature before thermal curing. The cure cycle involved heating to 135°C over 1 h and holding for 1 h, heating to 300°C over 2 h, and holding at 300°C for varying times.

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (D/Max2500VB2+/PC, Rigaku, Japan). Scanning electron microscope (SEM) was performed on a Hitachi S-4700 instrument. All the samples were coated with a ca. 5 nm platinum layer prior to measurement. Cross-sectional transmission electron micrograph (TEM) images were obtained with a Hitachi H-800 transmission electron microscope. The hysteresis loop of the film was determined with Model 4HF VSM from ADE Corporation. The surface square resistances were measured with a RTS-8 four point probes meter produced by Guangzhou Semiconductor Material Academic in China.

3. Results and discussion

Fig. 1 outlines the procedure for the bilayer polyimide film via in-situ method. The magnetic layer, that is the bottom layer, was prepared by incorporating

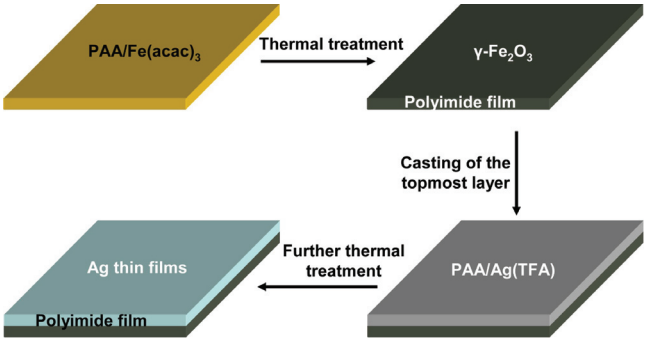

Fig. 1. Schematic illustration of the present process for the bilayer polyimide films.

$Fe(acac)_3$ into the solution of PAA, and then film was cast on the glass substrate. Thermal curing of the precursor film converted the PAA into its polyimide form with concomitant decomposition of $Fe(acac)_3$ to form magnetic nanoparticles. For clarity, the surface close to the substrate side was referred to as the substrate-side surface, and the other side close to the air was referred to as the air-side surface. The conductive layer, that is the topmost layer, was formed by incorporating of AgTFA into the solution of PAA, and then film was cast on the bottom layer. During the Thermal curing process, silver (I) was reduced to silver atoms and near-atomic silver clusters, which can diffuse and aggregate to give conductive surface. The conductive surface was marked air-side surface.

Fig. 2. shows the XRD patterns of PAA/$Fe(acac)_3$ precursor film cured at 320°C for 1 h and the final bilayer polyimide composite film. Five distinct diffraction peaks in Fig. 2a suggest that conversion of the $Fe(acac)_3$ to either γ-Fe_2O_3 or Fe_3O_4 has occurred. Fe_3O_4 can be oxidized to γ-Fe_2O_3 by heating Fe_3O_4 to 300°C for one hour in

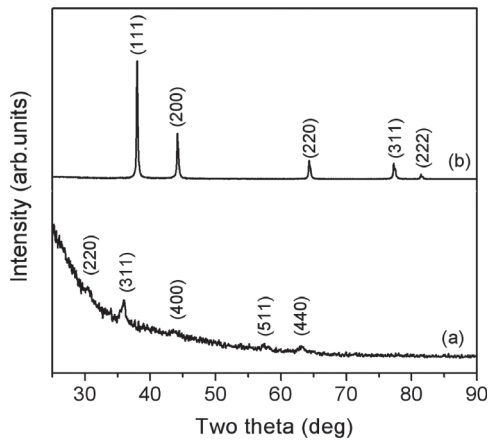

Fig. 2. XRD patterns of (a) γ-Fe_2O_3-contained polyimide film and (b) bilayer polyimide film.

the same atmosphere in which the films were cured [19]. Therefore, we believe that only γ-Fe_2O_3 is produced by the thermal decomposition of $Fe(acac)_3$ in the polyimide matrix. XRD pattern in Fig. 2b for the bilayer polyimide film exhibits five distinct diffraction peaks at 2θ=38.0°, 44.2°, 64.3°, 77.3° and 81.4°. The peaks can be indexed as the diffraction from the (111), (200), (220), (311) and (222) planes of the face-centered-cubic(fcc) silver metal, indicating the formation of metallic silver of zero-valent state and the crystallization of sliver in the film.

TEM was performed to detect the dispersion of formed γ-Fe_2O_3 nanoparticles as shown in Fig. 3a. Morphological image of sample cured at 320°C for 1 h shows that, upon thermal curing at this temperature, $Fe(acac)_3$ were decomposed to cubic γ-Fe_2O_3 nanoparticles which were uniformly dispersed in the particles contained region.

For the bilayer composite film thermally cured at 300°C for 7 h, Fig. 3b showed that a well-established continuous silver layer, about 400 nm thick, was formed on the air-side surface upon silver aggregation. The possible mechanism of the formation of silver layer on the polyimide film surface is that the initially generated silver(0) clusters are unstable as a result of their high surface free energy. Spontaneously, they start to aggregate to produce a thermodynamically stable silver layer [20]. Furthermore, the binding energy between silver particles is higher than that between silver and polyimide substrate. Therefore, silver layer would result at the polyimide surface [21]. SEM image in Fig. 3c exhibited that the aggregation of silver clusters formed a continuous "netlike" surface of the film.

The well-defined silver layer on the surface of bilayer polyimide film results in the excellent conductivity. The compact netlike morphology of film surface gives the surface square resistance of 0.1Ω/square due to the effect of silver aggregations at 300°C for 7 h.

Magnetic hysteresis loop for the bilayer polyimide film at iron content of 3 wt% is shown in Fig. 4 measured at room temperature. The magnetization loop does not

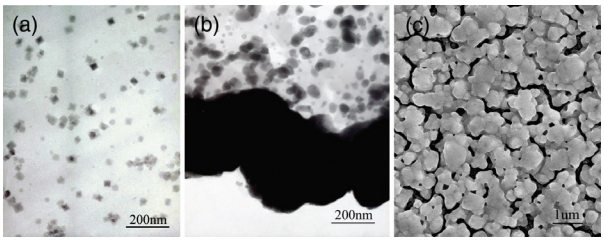

Fig. 3. Cross-sectional TEM images of (a) magnetic nanoparticles- contained polyimide films cured at 320°C, (b) bilayer polyimide film near the air-side surface, and (c) SEM image of bilayer polyimide film of air-side surface cured at 300°C for 7 h.

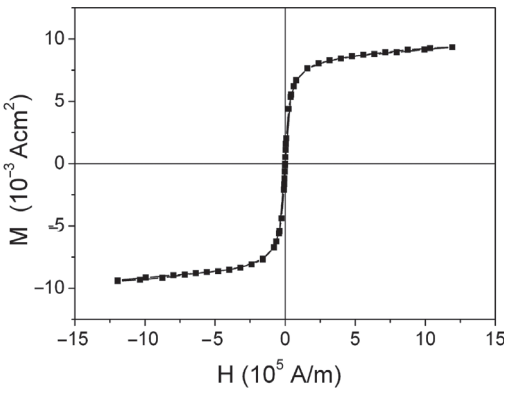

Fig. 4. Magnetic hysteresis loop of bilayer polyimide film.

show hysterethesis (zero coercivity and remanence), consistent with the characteristic behavior of superparamagnetic particles. Thus, the bialyer film contained iron oxide nanoparticles small enough to exhibit superparamagnetic response. Both the magnetism and resistance characterization results indicate that the bilayer films are highly conductive and superparamagnetic, which are the most important targets of our work.

4. Conclusion

In summary, bilayer polyimide film with both superparamagnetic and highly conductive property has been readily prepared via the in situ technique. The bottom layer containing γ-Fe_2O_3 nanoparticles was formed by the thermal decomposition of $Fe(acac)_3$ precursor in the polyimide matrix, exhibiting the typical superparamagnetic response. For the topmost layer, under thermal treatment circumstance, silver ions derived from the Ag(TFA) precursor was reduced to metallic silver. Further migration and aggregation of silver clusters with high surface free energy give rise to the formation of continuous silver layer. Optimum surface electrical resistance reaches to the value of 0.1Ω/square.

Acknowledgements

The authors greatly appreciate the financial supports of the Major State Basic Research Program of China (2009CB623404), National Natural Science Foundation of China (20736003, 20906056), National High Technology Research and Development Program of China (2007AA06Z317, 2008EG111021), Foundation of Ministry of Education of China (20070003130), and Foundation of the State Key Laboratory of Chemical Engineering (SKL-ChE-08A01).

References

[1] J.F. Feller, S. Roth and A. Bourmaud, Conductive polymer composites: Electrical, thermal, and rheological study of injected isotactic poly(propylene)/long stainless-steel fibers for electromagnetic interferences shielding, J. Appl. Polym. Sci., 100 (2006) 3280–3287.
[2] C.C.M. Ma, Y.L. Huang, H.C. Kuan and Y.S. Chiu, Preparation and electromagnetic interference shielding characteristics of novel carbon-nanotube/siloxane/poly-(urea urethane) nanocomposites, J. Polym. Sci. PartB: Polym. Phys., 43 (2005) 345–358.
[3] C.J. Huang and T.C. Chang, Studies on the electromagnetic interference shielding effectiveness of metallized PVAc-$AgNO_3$/PET conductive films, J. Appl. Polym. Sci., 91 (2004) 270–273.
[4] Z. Rimska, V. Kresalek and J. Spacek, AC conductivity of carbon fiber-polymer matrix composites at the percolation threshold, Polym. Compos., 23 (2002) 95–103.
[5] M.X. Wan, W.X. Zhou and J.C. Li, Composite of polyaniline containing iron oxides with nanometer size, Synth. Met., 78 (1996) 27–31.
[6] C.Y. Lee, D.E. Lee, C.K. Jeong, Y.K. Hong, J.H. Shim, J. Joo, M.S. Kim, J.Y. Lee, S.H. Jeong, S.W. Byun, D.S. Zang and H.G. Yang, Electromagnetic interference shielding by using conductive polypyrrole and metal compound coated on fabrics, Polym. Adv. Technol., 13 (2002) 577–583.
[7] J. Gass, P. Podda, J. Almand, S. Srinath and H. Srikanth, Superparamagnetic polymer nanocomposites with uniform Fe_3O_4 nanoparticle dispersions, Adv. Funct. Mater., 16 (2006) 71–75.
[8] C.T. Yen and W.C. Chen, Effects of molecular structures on the near-infrared optical properties of polyimide derivatives and their corresponding optical waveguides, Macromolecules, 36 (2003) 3315–3319.
[9] C.P. Yang, R.S. Chen, Organosoluble polyimides and copolyimides based on 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane and aromatic dianhydrides, J. Polym. Sci. Part A: Polym. Chem., 38 (2000) 2082–2090.
[10] K. Akamatsu, S. Ikeda, H. Nawafune and S. Deki, Surface modification-based synthesis and microstructural tuning of nanocomposite layers: monodispersed copper nanoparticles in polyimide resins, Chem. Mater., 15 (2003) 2488–2491.
[11] J.D. Rancourt and L.T. Taylor, Preparation and properties of surface-conductive polyimide films via in situ codeposition of metal salts, Macromolecules, 20 (1987) 790–795.
[12] M.M. Ellison and L.T. Taylor, Modifier and polymer interactions in metal-modified polyimide composites, Chem. Mater., 6 (1994) 990–998.
[13] K. Akamatsu, H. Shinkai, S. Ikeda, S. Adachi, H. Nawafune and S. Tomita, Controlling interparticle spacing among metal nanoparticles through metal-catalyzed decomposition of surrounding polymer matrix, J. Am. Chem. Soc., 127 (2005) 7980–7981.
[14] R.E. Southward and D.M. Stoakley, Reflective and electrically conductive surface silvered polyimide films and coatings prepared via unusual single-stage self-metallization techniques, Prog. Org. Coat., 41 (2001) 99–119.
[15] C.M. Chang, C.L. Chang and C.C. Chang, Synthesis and optical properties of soluble polyimide/titania hybrid thin films, Macromol. Mater. Eng., 291 (2006) 1521–1528.
[16] S.L. Qi, D.Z. Wu, Z.P. Wu, W.C. Wang and R.G. Jin, Reflective and conductive surface-silvered polyimide films prepared via in-situ technique using copolyimide as matrix, Polymer, 47 (2006) 3150–3156.
[17] R.E. Southward, D.S. Thompson, D.W. Thompson and A.K.S. Clair, Inverse chemical vapour deposition: A novel single stage synthesis of highly reflective and conductive silvered polymeric films, Chem. Mater., 11 (1999) 501–507.
[18] J.J. Bergmeister, J.D. Rancourt and L.T. Taylor, The synthesis and characterization of magnetic iron-modified polyimide films, Chem. Mater., 2 (1990) 640–641.

[19] J.J. Bergmeister and L.T. Taylor, Synthetic strategies in the formation of iron-modified polyimide films, Chem. Mater., 4 (1992) 729–737.
[20] G. Carotenuto, Synthesis and characterization of poly(*N*-vinylpyrrolidone) filled by monodispersed silver clusters with controlled size, Appl. Organomet. Chem., 15 (2001) 344–351.
[21] A. Heilmann, Polymer Films with Embedded Metal Nanoparticles, In: R.R. Hull, R.M.J. Osgood, J. Parisi, editors, Berlin Heideberg: Springer-Verlag, 2003.