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Characteristics and properties of polyimide/vanadium oxide hybrid membranes

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Abstract

A series of polyimide/vanadium pentoxide (PI/V_2O_5) hybrid film has been successfully fabricated through the in situ formation of V_2O_5 within a polymer matrix by sol–gel process. The polyamic acid (PAA) is prepared from 4,4′-diaminodiphenyl ether (ODA) and 3,3′,4,4′-benzophenonetetracarboxylic anhydride (BTDA) in *N*-methyl-pyrrolidinone (NMP) solvent. Then different amounts of Bis-(2,4-pentanedionato) vanadium oxide are incorporated into polyamic acid (PAA) matrix, respectively and then thermally imidized to form PI/V_2O_5 hybrid membranes. The imidization temperature and time are optimized by FTIR measurements through the observation of V_2O_5 absorption peak. The influence of V_2O_5 content on the thermal stability, morphology and mechanical properties of PI/V_2O_5 hybrid films are studied.

Keywords: Polyimide; Vanadium oxide; Hybrid; Sol–gel method

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1. Introduction

The preparation, characterization and applications of polymer/inorganic hybrid materials have become a fast expanding area of research in material science. The major driving forces behind the intense activities in this area are the new and different properties of the nanocomposite for the traditional macroscale composites and conventional materials do not have. Recently, new hybrid materials are prepared through chemical bonding formation between molecules, such as covalent or hydrogen or ionic bonds. From then on, this new hybrid material can conquer obvious phase separation between polymer and inorganic and possess mutual characteristics complementing each other.

The sol–gel method has been widely used to synthesize polymer/inorganic nanocomposite. There are many polyimide/inorganic hybrid materials prepared and applied in electronic and automobile industry due to their superior mechanical properties, thermal stability and low dielectric constants.

Vanadium oxide and their derivative compounds have attracted much attention due to their special physical and chemical properties, and potential applications in various fields such as catalysts [1], lithium-ion batteries [2], electrochromic [3,4], and chemical sensors [5,6]. This material possesses an outstanding structural versatility and can be manufactured into various one-dimensional (1D) nanostructures that have many useful physicochemical properties. In addition, the nanostructured vanadium oxide shows a good potential for completely novel applications such as nanoactuators [7] and nonlinear optical limiters [8].

The vanadium pentoxide (V_2O_5) films can be deposited by several techniques, such as reactive magnetron sputtering, ion beam evaporation, wet chemical coating and sol–gel deposition process [9–11]. While, the sol–gel method of preparation of metal oxide in the polyimide has been well-documented [12–16]. The organic/inorganic sol–gel methodology offers the advantages of large area deposition with controlled-film microstructure and production of films containing multiple cations [17]. However the inferior thermal stability of organics may restrict a composites application in the electronic and optoelectronic industries. Meanwhile, PI and hybrids are a well-known thermally stable polymer and mechanical stable for the high reliability of electronic and photoelectronic applications [18–20].

In this study, the PI/V_2O_5 hybrid films are prepared by sol–gel method. The $VO(acac)_2$ is introduced to the poly(amic acid) PI precursors, the composite is thermally imidized to form PI/V_2O_5 hybrid films. The effect of the V_2O_5 content and PI structure on the thermal, mechanical and morphology characteristics of the hybrid films are investigated.

2. Experiment

2.1. Materials

3,3′,4,4′-Benzophenonetetracarboxylicdianhydride (BTDA) from ACORS company is purified by recrystallization from acetic anhydride and then dried in a vacuum oven at 125°C overnight. 4,4′-diamino-diphenyl ether (ODA) from Lancaster is vacuum-dried for 3 h at 120°C prior to use. *N*-methyl-2-pyrrolidinone (NMP) from Tedia Company is dried over molecular sieves. (Bis(2,4-pentanedionato)vanadium-oxide) from TCI company is used as supplied.

2.2. Preparation of the PI/V_2O_5 hybrid films

The procedures for preparing poly(amic acid) (PAA) and PI/V_2O_5 hybrid film are shown in Fig. 1. The PAA solution is made by reacting equal amounts of BTDA and ODA in NMP solvent under a nitrogen atmosphere. Then the different amount of $VO(acac)_2$ is added into

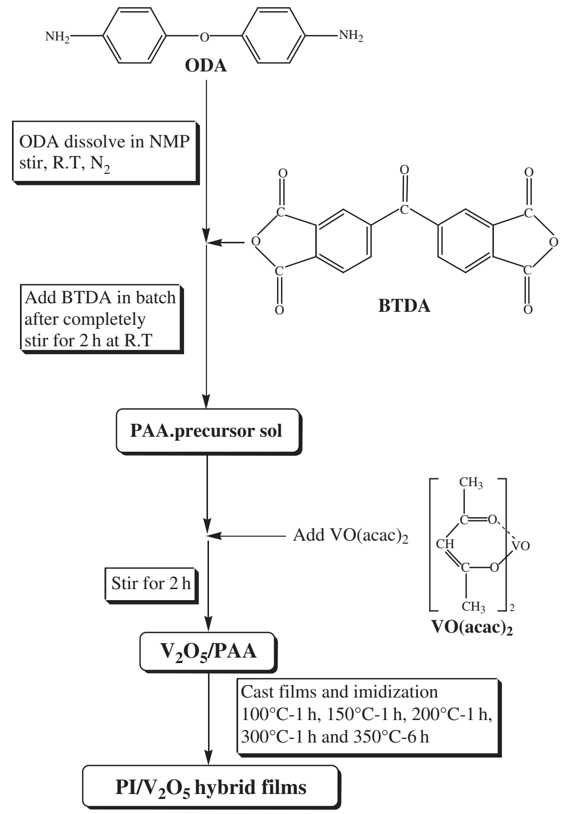

Fig. 1. The preparation procedures of PI/V_2O_5 hybrid films.

PAA to obtain PAA/V_2O_5 precursor. The PAA/V_2O_5 mixture is cast on glass plates and then step-heated in an oven through optimized imidization temperatures 350°C for 6 h. Sample abbreviation is named as PI/V_2O_5-X%. X denotes the weight percentage of V_2O_5 within polymer matrix.

2.3. Measurements

The functional groups and absorption peaks are measured with fourier transform infrared spectrophotometer (FTIR; Nicolet PROTÉGÉ-460). The decomposition temperature of the hybrid film is detected with Thermogravimetric analyzer (TGA; TGA-Q500) at a heating rate of 20°C min^{-1} from 100 to 800°C under nitrogen atmosphere. The storage modulus and T_g are measured by dynamic mechanical analyzer (DMA; DMA 2980) at a heating rate of 3°C min^{-1} from 100 to 425°C. The cross-section morphology is performed using a scanning electron microscopy (SEM; TESCAN 5136LS). X-ray diffraction (XRD) pattern is obtained with a MacScience MXP model using graphite-filtered Cu–Kα radiation. The diffraction pattern is taken at room temperature in the range of $10 < \theta < 60°$ at the scan rate of 6° min^{-1}.

3. Results and discussion

The optimum preparation of membrane is described as following: first, the coated PAA/V_2O_5 precursor is heated gradually at 100, 150, 200 and 300°C for each 1 h respectively and then further heated for 6 h at 350°C.

FTIR is used to identify the structure of PI/V_2O_5 hybrid film. Fig. 2 displays the FTIR absorption spectra of pure PI and PI/V_2O_5 hybrid film with various V_2O_5 content and are recorded between 4000 and 400 cm^{-1}. The characteristic absorption peak are 1780 cm^{-1} (C=O, asymmetric stretch), 1720 cm^{-1} (C=O, symmetric stretch), 1380 cm^{-1} of imide group (C–N) and 700–430 cm^{-1} (V–O–V stretching) are clearly presented. While hybrid film with

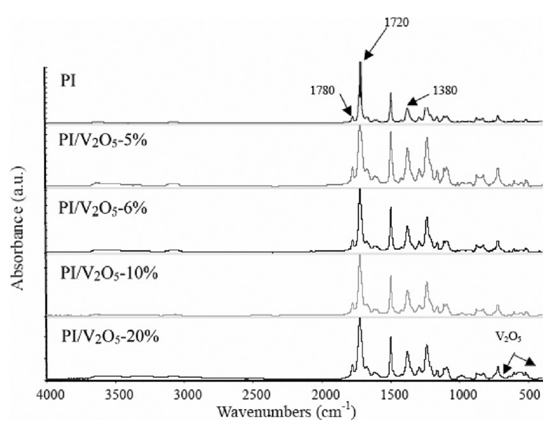

Fig. 2. FTIR spectra of PI/V_2O_5 hybrid film with different V_2O_5 content.

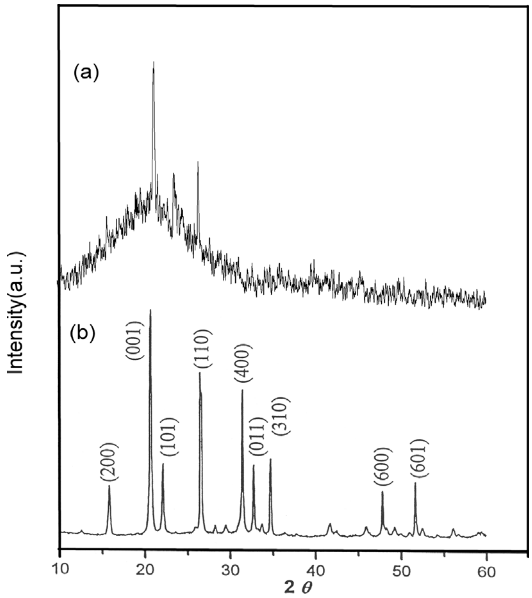

Fig. 3. X-ray of (a) PI/V_2O_5 10% hybrid film and (b) standard V_2O_5.

high V_2O_5 content (20 wt.%) has wide absorption peaks in the range of 650–450 cm^{-1}.

Owing to the ODA and BTDA with non-linear and amorphous structure, respectively, the X-ray spectra of BTDA/ODA hybrids cannot present obviously diffraction peaks as presented in Fig. 3. Therefore, the all hybrid films show amorphous properties. While the three peaks of PI/V_2O_5 hybrid film can be depicted that there are three (001), (101), (110) crystalline peaks presented and hence can be used to predict the existence of V_2O_5.

Fig. 4 shows the cross-section images of PI/V_2O_5 hybrid films with SEM. According to Fig. 4a, the hybrid film with 1% V_2O_5 is homogeneous and smooth as compared with other content of hybrid film. From Fig. 4a–e, it can be seen that the cross-section surface roughness increases as increasing the content of V_2O_5 in PI matrix. While the domain size of the V_2O_5 cannot be estimated with SEM analysis.

The thermal stability of the hybrid films are listed in Table 1. The dynamic thermogravimetric

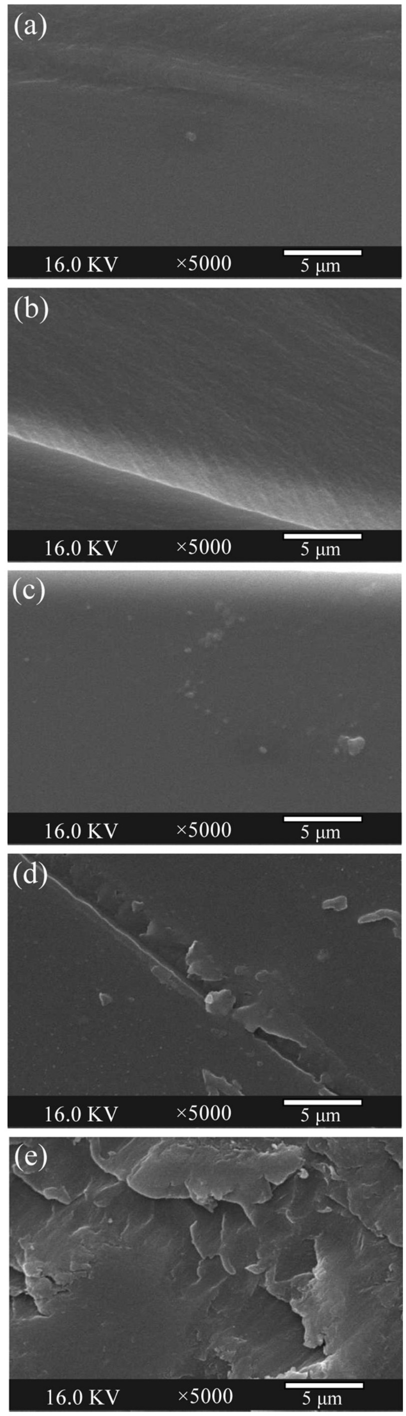

Fig. 4. SEM photograph of PI/V_2O_5 hybrid film with different V_2O_5 content. (a) 1%, (b) 2%, (c) 3%, (d) 4% and (e) 5%.

Table 1
Thermal weight loss of PI/V_2O_5 hybrid films

Compound code	Decomposed temperature[a] (°C)	800°C Char yield (%)
PI	580.26	59.72
PI/V_2O_5-1%	480.74	61.49
PI/V_2O_5-2%	478.31	60.77
PI/V_2O_5-6%	467.39	60.85

[a]Temperature at 5% weight loss.

curves of pure PI and PI/V_2O_5 hybrid film are shown in Fig. 5. The introduction of V_2O_5 causes a decrease in thermal stability of hybrid films, which could be attributed to the decomposition reaction of metal oxide occurred during the PI imidization reaction step [16,17]. And the ether group of ODA component possessing unpaired electron will induce the oxidation reaction of PI film and hence lower the thermal stability.

Fig. 6 is the storage modulus curves of pure PI and PI/V_2O_5 hybrid films changing with temperature. The storage modulus of hybrid films are all larger than pure PI and increased as the V_2O_5 content is with 6 wt.%, while the storage modulus decreases as the V_2O_5 content is with 10 wt.%.

The reason could be attributed to the 6 wt.% V_2O_5 content, which induces that the molecular structure to become more rigid. While as the V_2O_5 content increases up to 10 wt.%, the compatibility between polyimide and V_2O_5 decreased and the microstructure defected. This will induce the decrease of storage modulus. Fig. 7 and Table 2 show the effect of temperature on the Tan Delta curves. And the Tan δ values of pure PI and the T_g values are increased with the increase of V_2O_5 content. The reason is that the crosslinked structure formed by the addition of V_2O_5, which will hinder the rotation and mobility of polyimide

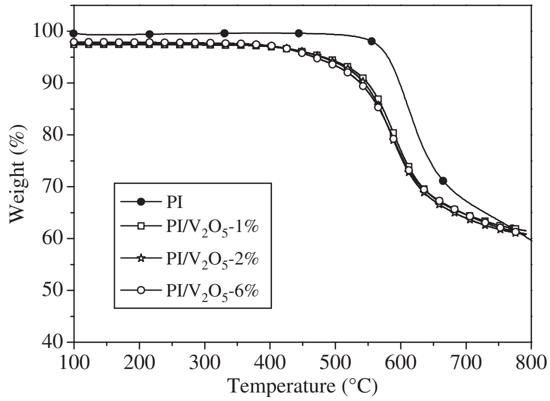

Fig. 5. Thermogram of pure PI and PI/V_2O_5 hybrid film with different V_2O_5 content.

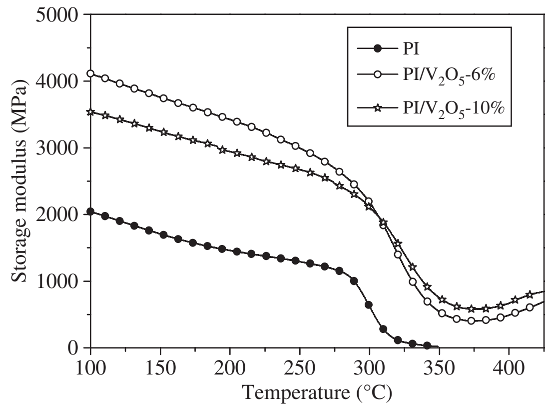

Fig. 6. Storage modulus curves of pure PI and PI/V_2O_5 hybrid films change with temperature.

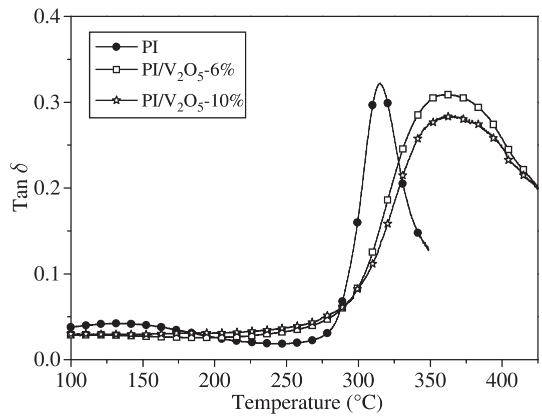

Fig. 7. Tan δ curves of pure PI and PI/V_2O_5 hybrid films.

Table 2
The glass transition temperature and storage modulus of PI/V_2O_5 hybrid films

Compound code	Storage modulus (MPa)	Temperature (°C) of Tan δ peak
PI	2042	314.6
PI/V_2O_5-6%	4107	361.8
PI/V_2O_5-10%	3548	364.0

molecular chain. And then induce the T_g values increase with the increase of V_2O_5 content for PI/V_2O_5 hybrid polymer.

4. Conclusions

Polyimide containing V_2O_5 has been successfully prepared by sol–gel method. There is an obvious absorption peaks of V_2O_5 in the range of 700–430 cm^{-1}. The intensity of absorption peak is increased with V_2O_5 content. Based on SEM result, the fractured cross-section surface roughness of the hybrid film also increases with V_2O_5 content. The incorporation of V_2O_5 causes a decrease in thermal stability of hybrid films. However, the hybrid films still possess good thermal property. According to the results of DMA study, the storage modulus of the hybrid films is reinforced with addition of V_2O_5. It also points that the addition of V_2O_5 shows higher T_g as compared with pure PI. Besides, the existence of V_2O_5 and amorphous morphology of hybrids can be indicated by X-ray detection.

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References

[1] M. Ponzi, C. Duschatzky, A. Carrascull and E. Ponzi, Obtaining benzaldehyde via promoted V_2O_5 catalysts, Appl. Catal. A, 169 (1998) 373–379.
[2] P. Poizot, S. Grugeon, L. Dupont and J.M. Tarascon, Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries, Nature, 407 (2000) 496–499.
[3] C.G. Granqvist, Handbook of inorganic electrochromic materials, Elsevier Science, Amsterdam, 1995.
[4] A. Talledo and C.G. Granqvist, Electrochromic vanadium-pentoxide-based films: structural, electrochemical, and optical properties, J. Appl. Phys., 77 (1995) 4655–4666.
[5] J. Livage, Vanadium pentoxide gels, Chem. Mater., 3 (1991) 578–593.
[6] G. Micocci, A. Serra, A. Tepore, S. Capone, R. Rella and P. Siciliano, Properties of vanadium oxide thin films for ethanol sensor, J. Vac. Sci. Technol. A, 15 (1997) 34–38.
[7] G. Gu, M. Schmidt, P.W. Chiu, A. Minett, J. Fraysse, G.T. Kim, S. Roth, M. Kozlov, E. Munoz and R. Baughman, V_2O_5 nanofibre sheet actuators, Nat. Mater., 2 (2003) 316–319.
[8] J.F. Xu, R. Czerw, S. Webster, D.L. Carroll, J. Ballato and R. Nesper, Nonlinear optical transmission in VO_x nanotube composites, Appl. Phys. Lett., 81 (2002) 1711.
[9] A. Talledo, A.M. Anderson and C.G. Granqvist, Electrochemically lithiated V_2O_5 films. An optically passive ion storage for transparent electrochromic devices, J. Mater. Res., 6 (1990) 1253–1256.
[10] N. Gharbi, S. Sanches, J. Livage and J. Lemerle, Mixed-valence polyvanadic acid gels, Inorg. Chem., 21 (1982) 2758–2765.
[11] N. Ozer, Electrochemical properties of sol–gel deposited vanadium pentoxide films, Thin Solid Films, 305 (1997) 80–87.
[12] X. Wang, X. Chen, L. Gao, H. Zheng, M. Ji, T. Shen and Z. Zhang, Citric acid-assisted sol–gel

synthesis of nanocrystalline $LiMn_2O_4$ spinel as cathode material, J. Cryst. Growth, 256 (2003) 123–127.
[13] P.C. Chiang, W.T. Whang and M.H. Tsai, Physical and mechanical properties of polyimide/titania hybrid films, Thin Soild Films, 447 (2004) 359–364.
[14] P.C. Chiang, W.T. Whang, S.C. Wu and K.R. Chuang, Effects of titania content and plasma treatment on the interfacial adhesion mechanism of nano titania-hybridized polyimide and copper system, Polymer, 45 (2004) 4465–4472.
[15] M.H. Tsai, S.J. Liu and P.C. Chiang, Synthesis and characteristics of polyimide/titania nano hybrid films, Thin Soild Films, 515 (2006) 1126–1131.
[16] M.H. Tsai and C.J. Ko, In situ formation, surface characteristics, and interfacial adhesion of poly(imide siloxane)/tantalum oxide hybrid films, Surf. Coat. Technol., 201 (2006) 4367–4371.
[17] C.J. Brinker and G.W. Sherrer, Sol–gel science, the physics and chemistry of sol–gel processing, Academic Press, San Diego, 1990.
[18] M.H. Tsai and W.T. Whang, Low dielectric polyimide/poly(silsesquioxane)-like nanocomposite material, Polymer, 42 (2001) 4197–4207.
[19] M.H. Tsai, P.C. Chiang, W.T. Whang, C.J. Ko and S.L. Huang, Synthesis and characteristics of polyimide/siloxane hybrid films for reliability adhesion, Surf. Coat. Technol., 200 (2006) 3297–3302.
[20] S.C. Hsu, W.T. Whang, C.H. Hung, P.C. Chiang and Y.N. Hsiao, Effect of the polyimide structure and ZnO concentration on the morphology and characteristics of polyimide/ZnO nanohybrid films, Macromol. Chem. Phys., 206 (2005) 291–298.