

Polyimide/silica/titania nanohybrids via a novel non-hydrolytic sol–gel route

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Abstract

Polyimide/silica/titania hybrid films were prepared via a non-hydrolytic sol–gel route. Silicic acid and titanium tetrachloride were used as the precursors of silica and titania, respectively. The absorption band of Si–O–Ti bonds in FTIR spectra of the hybrid films revealed the formation of the hybrid inorganic network between SiO₂ and TiO₂. Scanning electron microscopy results indicated that the nanometer-scaled inorganic domains were homogeneously dispersed in polyimide matrix due to the introduction of silica-stabilized TiO₂ and the interactions between organic and inorganic phases. The studies on the optical properties of the hybrid films indicated the red-shift of the absorption band increased with increasing TiO₂ content, while all the hybrid films maintained their transparencies. The surface resistances of the hybrid samples decreased with increasing TiO₂ content. The thermal decomposition temperature of the ternary hybrid films decreased slightly with increasing TiO₂ content. This kind of hybrid materials may have potential application in the preparation of opto-electronic devices.

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1. Introduction

Currently, many research efforts have been focused on the organic/inorganic nanocomposites with unique mechanical, photoelectric and thermal properties [1–11]. There are plenty of literatures on polymer/silica hybrid materials with improved mechanical and thermal properties [12–15]. On the other hand, polymer/titania nanohybrids have also attracted lots of interests due to their adjustable refractive indices and good UV shielding properties which have application in the photoelectric fields [1,2,7–11,16–20]. However, the reports on polyimide/titania nanohybrid materials are limited though the polyimides (PI) have excellent thermal and photoelectric properties [16–20]. There lies some problems for the preparation of PI/titania nanohybrids: first, the decrease of thermal stabilities of

the hybrids caused by the decomposition catalytic activity of TiO₂ and the incomplete imidization of polyamic acid (PAA), the PI precursor, induced by TiO₂ and second, the difficulty with the control of the hydrolytic reaction of TiO₂ precursors due to their high reactivity, which often results in the accumulation of inorganic particles [17,18,20]. It is necessary to use some chelating agents such as allyl acetylacetone to stabilize the fast condensation of titanium alkoxides, the titania precursor, and the addition of overmuch chelating agents may do harm to the resulting hybrids because the chelating agents are found difficult to be completely removed from the titanium center [21,22].

Recently, Liu and Qiu prepared PI/silica/titania hybrid materials via a sol–gel process using tetraethoxysilane and tetrabutyl titanate as precursors for silica and titania, respectively [19,23]. Liu's results indicated that the introduction of TiO₂ led to a decrease in the thermal stability of PI hybrid materials, and these results are in accordance with some previous reports [1,12]. But they found that this adverse effect could be compensated by the addition of SiO₂. However, Qiu's results showed that the thermal stabilities

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of all the obtained PI hybrids containing SiO₂, TiO₂ and SiO₂/TiO₂ are better than pure PI samples.

In this paper, we present a new non-hydrolytic sol-gel method to prepare the PI/silica/titania nanohybrids in which the reactivity of titania precursors can be well controlled without using any chelating agents. The more abundant and affordable titanium tetrachloride and silicic acid are used as titania and silica precursors, respectively. Meanwhile, the interactions between PAA main chains and TiO₂ components decrease, which is favorable for the complete imidization of PAA. Further more; the addition of SiO₂ components can also compensate the decrease of the thermal stabilities of the nanocomposites because of the introduction of TiO₂. The structure, and thermal, optical and electrical properties of the resulting ternary nanohybrids have been studied. The results show that PI/SiO₂/TiO₂ nanocomposites have potential application in the opto-electronic devices [7–11,15–20].

2. Experimental part

2.1. Materials

4,4'-Oxydianiline(ODA, chemical reagent grade), pyromellitic dianhydride (PMDA, chemical reagent grade), *N,N*-dimethylacetamide (DMAc, chemical reagent grade), sulfuric acid (analytical reagent grade), tetrahydrofuran (THF, analytical reagent grade), titanium tetrachloride (TiCl₄, analytical reagent grade) and ethanol (analytical reagent grade) were all purchased from Shanghai Chemical Reagents Company, Shanghai, China and used without further purification. Water glass (highly purified, containing 9.15 wt% Na₂O and 28.55 wt% SiO₂) was a gift from Jiading Water Glass Factory, Shanghai, China and was used as received.

2.2. Preparation of silica/titania precursor

Silicic acid was prepared by the extraction from water glass according to the procedure described previously [24]. A silicic acid-THF solution and a TiCl₄-ethanol solution were mixed and stirred at room temperature for 2 h and then refluxed at 100 °C for another 4 h.

2.3. Preparation of polyimide/silica/titania hybrid films

The PI prepolymer, polyamic acid (PAA) was prepared by solution polycondensation between PMDA and ODA in DMAc at room temperature for 8 h. Appropriate amounts of silica/titania precursors were introduced to a PAA solution and the mixture was mechanically stirred at room temperature for 4 h to obtain a uniform and transparent solution. Then the solution was cast on a glass substrate and dried at 60 °C for 3 h, 100 °C for 1 h, 200 °C for 1 h and 300 °C for 4 h, respectively. The preparation procedure

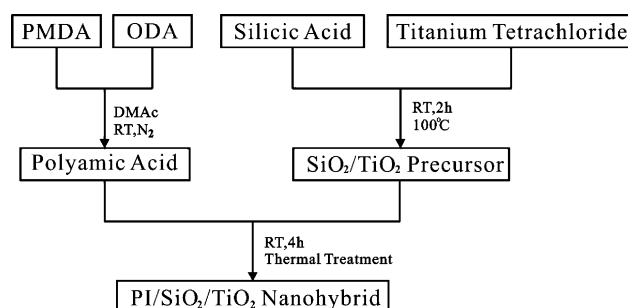


Fig. 1. Procedure of the preparation of PI/SiO₂/TiO₂ nanohybrid.

of PI/SiO₂/TiO₂ hybrids is depicted in Fig. 1 and the recipe is listed in Table 1, respectively.

2.4. Measurements

FTIR spectra of the hybrid films were recorded on a Nicolet Nexus 470 FTIR spectrophotometer. UV-vis spectra were measured on a Perkin-Elmer Lambda 35 UV/vis spectrometer using the wavelength from 200 to 1100 nm. The morphologies of the liquid nitrogen fractured surfaces of the PI/SiO₂/TiO₂ hybrid films were observed with a JSM-5600LV scanning electron microscope. Thermal gravimetric analyses (TGA) were performed on a Perkin-Elmer Pyris 1 thermal gravimetric analyzer at a heating rate of 10 °C/min in air and the temperature range was from 50 to 700 °C. The surface resistances of PI/SiO₂/TiO₂ nanocomposites were measured on a ZC43 ultrahigh resistance meter (Shanghai No. 6 factory for electricity meters, China) with a voltage of 1000 V.

3. Results and discussion

3.1. FTIR spectra

The FTIR spectra of PI and PI/SiO₂/TiO₂ nanohybrid films are shown in Figs. 2 and 3. The characteristic peaks of symmetric and asymmetric C=O stretching and C–N stretching of the imide group at 1720, 1780 and 1380 cm⁻¹ are observed in Fig. 2 [25]. After the introduction of the inorganic components, it can be observed that the broad and strong absorption bands in the range of 400–850 cm⁻¹ corresponding to Ti–O–Ti network, and 920–1100 cm⁻¹ corresponding to Si–O–Ti and Si–O–Si network are enhanced with increasing TiO₂ and SiO₂ content [26,27]. This proves the formation of the chemical bonds between SiO₂ and TiO₂ moieties. The band near 3400 cm⁻¹ is the characteristic band of the residual Ti–OH and Si–OH groups in the hybrid films [8]. For sample d–f having the same TiO₂/SiO₂ molar ratio, it can be seen from Fig. 2 that the intensity of this band increases with increasing inorganic content. There is no absorption near 1650 cm⁻¹ for the carbonyl group of PAA appears in the spectra of all the hybrid films.

Table 1
Recipe and properties of PI/SiO₂/TiO₂ nanocomposites

Samples	TiO ₂ /SiO ₂ (molar ratio)	Total inorganic content (wt%) ^a	Ash (wt%) ^b	Decomposition temperature (°C) ^c	TiO ₂ content (wt%) ^d	Surface resistances (Ω)
PI-0	–	0	0	533	0	7 × 10 ¹⁴
PI-1	9.0	5	4.3	456	4.0	1 × 10 ¹²
PI-2	6.5	5	4.4	461	3.9	1 × 10 ¹³
PI-3	4.5	5	4.4	473	3.8	5 × 10 ¹³
PI-4	4.5	10	9.2	444	7.9	N/A
PI-5	4.5	15	13.4	436	11.5	N/A

^a The total inorganic contents of the hybrids were calculated according to the inorganic and PI concentration in their respective solution.

^b The residual ash determined by thermal gravimetric analysis (TGA).

^c Temperature at 5 wt% loss in weight of the hybrids.

^d Calculated from the molar ratio of TiO₂/SiO₂ and the inorganic content in the nanocomposites.

This indicates the complete imidization and hence we can say that the inorganic moieties do not interfere with the imidization reaction of PAA.

3.2. SEM photographs

It was amply documented that in PI/silica binary hybrid system, the micron-sized SiO₂ particles are dispersed inhomogeneously within PI matrix due to the poor compatibility between organic and inorganic phases [12]. So in order to prepare PI/silica nanohybrids, coupling agents should be used to introduce some kinds of linkage between the two phases. For PI/titania binary hybrid system, it has been reported that there is interactions between PI and titania domains induced by the chelating ligands between the amic acid and titania, but this interaction is not enough to restrain titania from aggregating because of the too fast condensation rate of Ti–OH groups [9,23]. We have already studied the preparation of transparent PI/silica nanohybrids using silicic acid as silica precursor [24]. Since the existence of a small amount of nano-sized silica particles may not do

harm to the thermal and optical properties of PI/titania hybrids. Here we tried to use silicic acid to co-condense with titanium chloride, the titania precursor, in order to control the total condensation rate.

In the prepared PI/silica/titania ternary hybrid films, the inorganic particles show a homogeneous dispersion in polymer matrix and smaller inorganic domain, it suggests that the aggregation of silica and titania is restricted by the formation of Si–O–Ti bonds and there exist interactions between polymer and inorganic phases as shown in Fig. 4. From Fig. 4a–c, it can also be seen that for the same inorganic content, the edges of the inorganic particles become dimmer and the particle sizes decrease with the increasing amount of TiO₂.

There might be two reasons for the formation of nano-sized inorganic particles in PI/silica/titania ternary hybrid films. First, silanol groups with lower reactivities from silicic acid co-condense with Ti–OH on the surfaces of TiO₂ nano-sized domains so as to prevent the accumulation of titania particles; second, the chelation between titania and PI main chains enhances the adhesion between organic and inorganic phases.

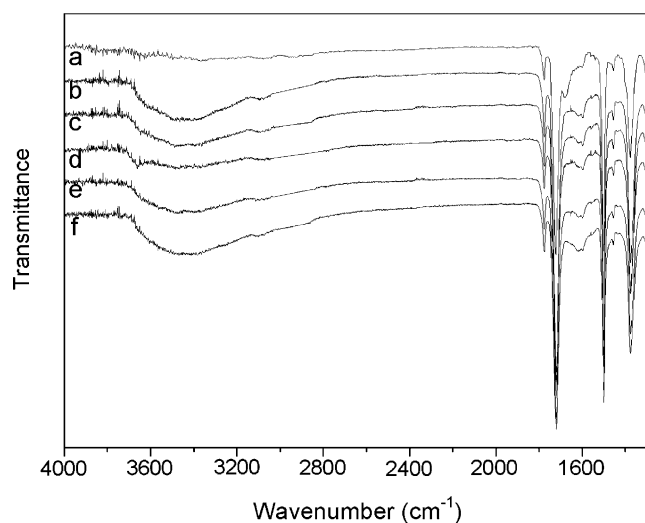


Fig. 2. FTIR spectra of PI and PI/SiO₂/TiO₂ hybrid films in the wavenumber range of 1300–4000 cm⁻¹: (a) PI-0; (b) PI-1; (c) PI-2; (d) PI-3; (e) PI-4; (f) PI-5.

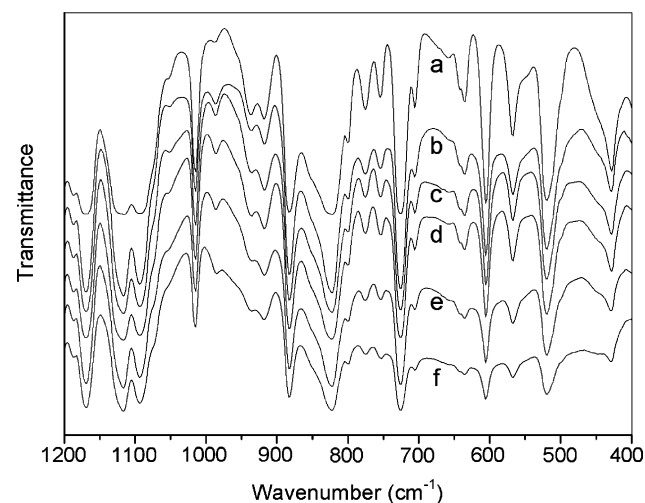


Fig. 3. FTIR spectra of PI and PI/SiO₂/TiO₂ hybrid films in the wavenumber range of 400–1200 cm⁻¹: (a) PI-0; (b) PI-1; (c) PI-2; (d) PI-3; (e) PI-4; (f) PI-5.

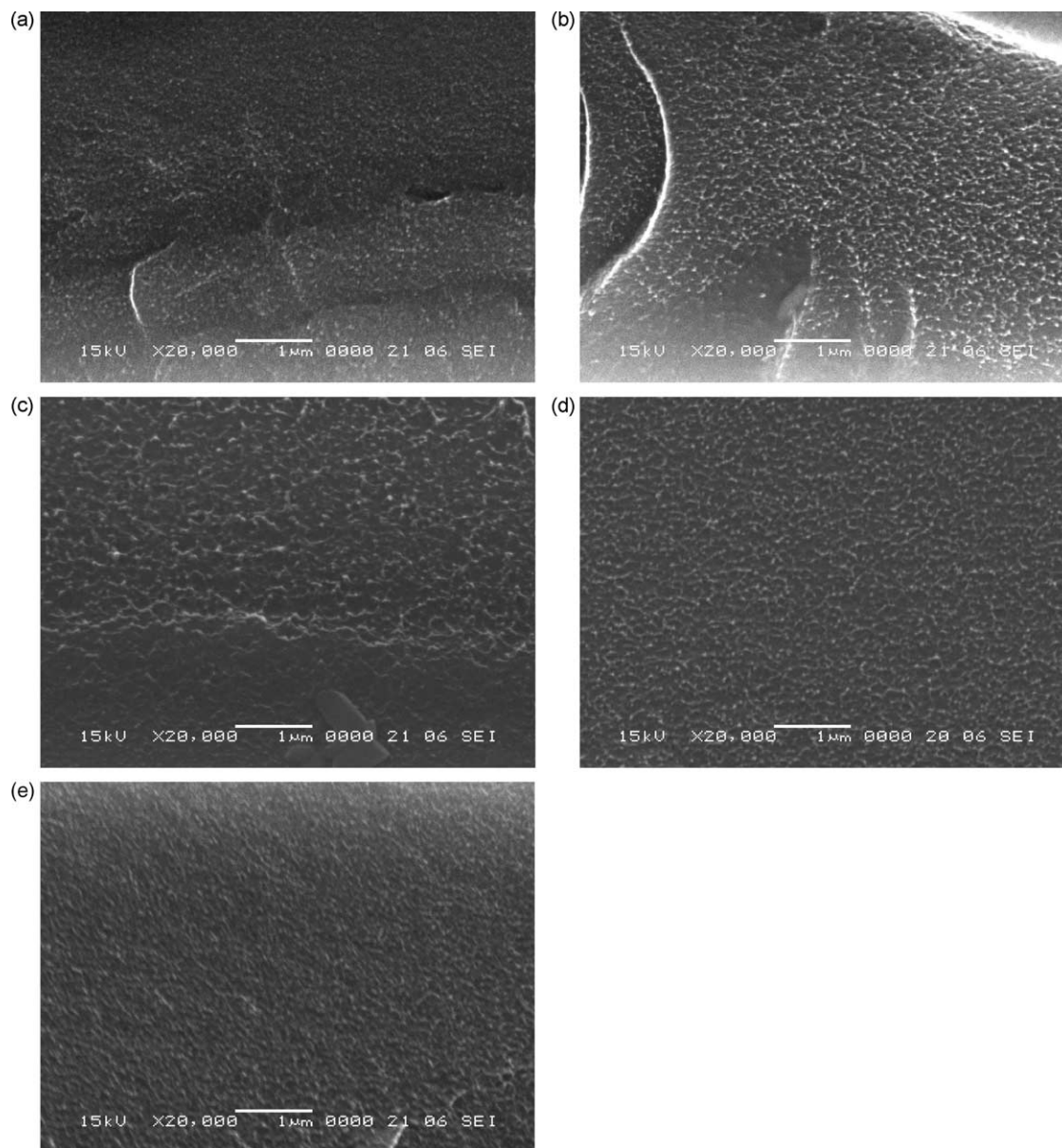


Fig. 4. SEM photographs of PI/SiO₂/TiO₂ hybrid films: (a) PI-1; (b) PI-2; (c) PI-3; (d) PI-4; (e) PI-5.

3.3. UV–vis spectra

UV–vis spectra of the prepared hybrid films with different inorganic content are shown in Fig. 5. With the increasing inorganic content, the absorption band moves toward longer wavelength. By appearance, all the hybrid films are transparent but become darker and darker. It can be concluded that the red-shift of the absorption band in visible region can be easily controlled by adjusting the TiO₂ content in the hybrids while the transparency can still be maintained.

3.4. Surface resistances

The surface resistances of PI/SiO₂/TiO₂ nanocomposite films were measured and the results are listed in Table 1.

The surface resistances of PI dramatically decrease from about 10^{15} to 10^{12-13} Ω by the addition of 5 wt% SiO₂/TiO₂ inorganic moiety. Further more, for the nanocomposites with similar inorganic content; their surface resistances also have a few differences. It decreases with increasing TiO₂ content in the inorganic component. All of the above results show that the surface resistance of PI/SiO₂/TiO₂-nanocomposites can be accurately controlled by adjusting either the total inorganic content or the ratio of SiO₂/TiO₂.

3.5. Thermal stabilities

The TGA curves of PI and PI/SiO₂/TiO₂ hybrid films are shown in Fig. 6 and the temperature at 5 wt% weight loss and the residual ashes at 700 °C are also listed in Table 1.

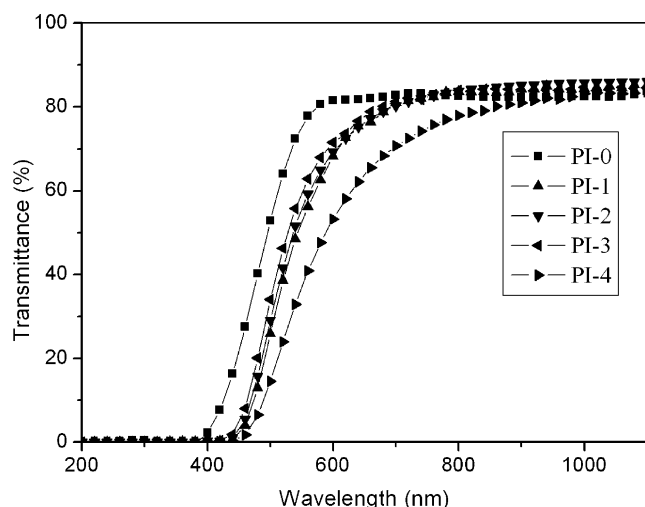


Fig. 5. UV-vis spectra of PI and PI/SiO₂/TiO₂ hybrid films.

The introduction of TiO₂ causes only a slight decrease in thermal decomposition temperatures of the hybrid films compared to pure PI, which is in accordance with the results of Liu's [19]. One reason for the decrease in thermal stability of hybrid films containing TiO₂ may be the metal-catalyzed oxidative decomposition [28,29]. The other reason reported for the decrease in the decomposition temperature of PI/TiO₂ hybrids is the chelating ligands between the amic acid and titania which lead to incomplete imidization [9]. There is no significant incomplete imidization found in our study according to the FTIR results mentioned above. So the catalysis characteristic of TiO₂ should be the main reason for the decrease in thermal stabilities of the PI ternary hybrids in this case. According to Liu's results, to some extent, the introduction of SiO₂ can compensate the decrease on the thermal stability of PI/titania hybrids. However, they did not discuss about the reason for this compensation effect. In our opinion, the increase of the decomposition temperatures of the ternary hybrids probably results from the covering of the active

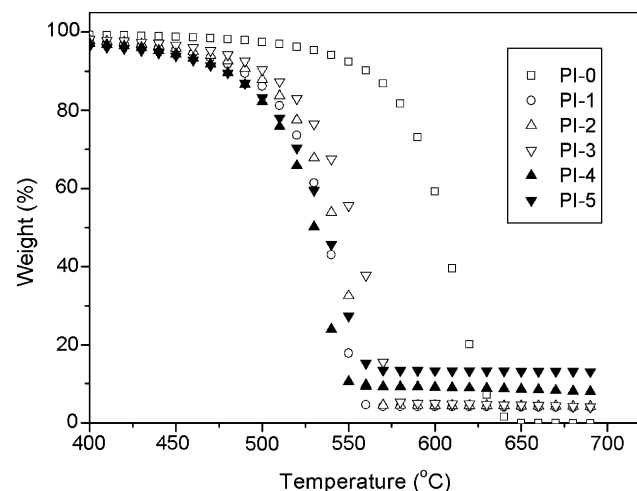


Fig. 6. TGA curves of PI and PI/SiO₂/TiO₂ hybrid films.

catalytic sites of TiO₂ by silicic acid. Since Liu et al. only reported the results of one ternary hybrid sample having equal amount (10 wt% each) of silica and titania. So it can be expected that the thermal stabilities of the hybrids can probably be improved by the addition of more silica. Some optical applications, like high refractive-index materials need high titania content nanohybrids. In this study, we have proved that PI/titania nanohybrid materials can be achieved by adding a small amount of silica. People can easily adjust the recipe of the ternary hybrids to make a balance between the optical property and thermal stability.

4. Conclusion

PI/SiO₂/TiO₂ nanohybrid films have been prepared successfully by a novel non-hydrolytic sol-gel route using silicic acid and titanium chloride as silica and titania precursors, respectively. The nanometer-scaled inorganic domains disperse homogeneously in PI matrix without macro phase separation because there are interactions between the two phases and the aggregation behavior of TiO₂ was restricted by the introduction of SiO₂. The prepared hybrid films have fairly good optical transparency in visible region and good thermal stability. The surface resistances of the hybrid samples decreased with increasing TiO₂ content. The obtained hybrids may have potential application in the preparation of optical devices.

Acknowledgements

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