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Morphology and size control of inorganic particles in polyimide hybrids by using SiO_2–TiO_2 mixed oxide

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Abstract

Polyimide/inorganic hybrids were prepared by sol–gel reaction starting from tetraethoxysilane (TEOS), and tetrabutyl titanate (TBT) in the solution of polyamic acid in *N*,*N*-dimethylformamide. The hybrid films were obtained by the hydrolysis-polycondensation of TEOS and TBT in polyamic acid solution, followed by the elimination of solvents and imidization process. Binary polyimide/SiO_2 and polyimide/TiO_2 hybrids, as well as ternary polyimide/SiO_2–TiO_2 hybrids (with varied ratio of SiO_2 to TiO_2) were prepared to study the effects of the recipes and inorganic components on the morphologies of the polyimide hybrids. Transparent films with much higher inorganic content can be obtained in ternary polyimide hybrids, while lower inorganic content in binary hybrids. The results also indicate that the inorganic particles are much smaller in the ternary systems than in the binary systems, the shape of the inorganic particles and the compatibility for polyimide and inorganic moieties are varied with the ratio of the inorganic moieties in the hybrids. The completely imidization temperature of the polyamic acid was delayed, and furthermore, the thermal stability of polyimide was enhanced through the incorporation of the inorganic moieties in the hybrid materials.

Keywords: Polyimides; Hybrid; Morphology

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1. Introduction

In recently years, increasing attention has been paid to the organic/inorganic hybrid materials that comprise organic and inorganic components intimately dispersed on the nanometer scale. The hybrid materials with high performance can be obtained through the controlling of morphology and functional segment size [1]. These materials can be formed by several different approaches. One of the successful is the in situ polymerization of metal alkoxides in organic polymer matrix via the sol–gel process, which is a process for preparation of inorganic metal oxides under mild conditions in low temperature, the inorganic phase were generated from the alkoxide precursor through hydrolysis and condensation reactions. The most common hybrid is the silica systems. Many hybrid silica/organic polymeric materials have been prepared in sol–gel method. Some examples are poly(dimethyl silane) and poly(methylphenylsiloxane) [2–4], poly(methyl methacrylate) and (poly(vinyl acetate) [5–7], poly(tetramethylene oxide) [8–10], poly(oxyethylene) [11], poly(ether ketone) [12], polyoxazoline [13], epoxy resins [14], and others.

Polyimides are considered to be one of the most important super-engineering materials due to their thermal stability as well as the superior mechanical properties at elevated temperature [15,16]. Of the organic/inorganic hybrids investigated, polyimide/silica hybrid films are of particular interest [17–19]. Since polyimide/silica hybrid materials has been prepared successful by Kakimoto et al. through sol–gel process [20], more attentions were given to the field [21–24]. Recently, metal-containing hybrid polyimide/titania hybrids were also prepared [25]. The key challenge for preparation of the hybrid materials is how to control the phase separation between the organic and inorganic moieties. The phase behavior is connected with the interaction between the organic segment and the inorganic network in the hybrids. Hydrogen bonding or covalent bonding is usually used to prevent phase separation [26,27]. In our early works, inorganic metal moieties were chemically bonded into the main chains of the polymers by

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using the metal-containing diamines, through which metal-containing polyimides were prepared [28–30]. Previous studies about polyimide/inorganic hybrids through sol–gel method were concentrated on the binary systems, in which exists one kind of inorganic portion, the size and morphology was controlled usually by introducing of chemical bonds between polyimides and SiO_2 particles, such as by using aminoalkoxysilane [31]. In this work, we investigated the possibility of control of SiO_2 particles by introduce a third portion of TiO_2 particle, through the interaction between SiO_2 and TiO_2 to control the size and morphology of the inorganic particles. The binary hybrids of polyimide/silica (PI/SiO_2), polyimide/titania (PI/TiO_2) as well as ternary hybrids of polyimide/silica–titania (PI/SiO_2–TiO_2) were prepared through sol–gel process, and presented herein was focused on effects of the ratio of SiO_2 to TiO_2 on the morphologies as well as thermal properties of the resultant hybrids.

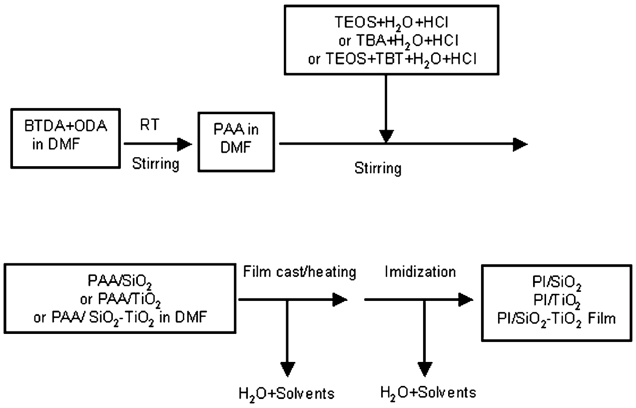
2. Experimental

2.1. Materials

3,3′-4,4′-benzophenone tetracarboxylic dianhydride (BTDA) was purchased from Aldrich. Bis(4-aminephenyl) ether (ODA), tetraethoxysilane (TEOS), tetrabutyl titanate (TBT), and *N*,*N*-dimethylformamide (DMF) were all analytical grade, used as received.

2.2. Preparation of PI/SiO_2, PI/TiO_2, and PI/SiO_2–TiO_2 hybrid films

Preparation of PI/SiO_2, PI/TiO_2, and PI/SiO_2–TiO_2 hybrid films by Sol–Gel process is shown in Scheme 1. A certain amount of ODA was dissolved in DMF completely with stirring, then BTDA (with the same molar ratio of ODA) was added into the solution in three times within 0.5 h. The viscosity increased quickly over 0.5 h. The reaction was continued for another 2.5 h at room temperature under stirring. Polyamic acid (PAA) solution was obtained, and the solid content of PAA is 10 wt%.



Scheme 1.

A calculated quantity of TEOS ethanol solution, and deionized water as well as HCl (or TBT solution, H_2O and HCl; or TEOS and TBT solution, H_2O and HCl) was added into the PAA solution by droplets under stirring. The molar ratio was fixed at 0.01 for HCl/TEOS (TBT, or TEOS + TBT), and 1 for H_2O/TEOS (TBT, or TEOS + TBT). After the mixture was stirred at room temperature for another 6 h, a film of the PAA/SiO_2 (or PAA/TiO_2, or PAA/SiO_2–TiO_2) mixture was prepared by casting the solution onto a glass plate, and was dried at 60 °C for 8 h, at 150 °C for 1.5 h in vacuo. Finally, the film was treated at 300 °C for 2.5 h in vacuo to convert the PAA into polyimide (PI), and the PI/SiO_2 (or PI/TiO_2, or PI/SiO_2–TiO_2) hybrid film was obtained.

2.3. Analysis

FT-IR analysis was performed with the films of the hybrids with a MAGNA-560 spectrometer, using a resolution of 4 cm^{-1}. The morphology were observed by scanning electron microscopy (SEM) using a Hitachi S-530 electron microscopy and the cryogenic fractured surfaces of polyimide hybrids were sputter-coated with gold before viewing. Thermogravimetric analysis (TG) was investigated with the Perkin–Elmer 7 instrument under a flow of N_2, at a heating rate of 20 °C/min.

3. Results and discussion

3.1. Preparation of the hybrid films

Since the polyimide is insoluble in organic solvents, the Sol–Gel reaction was carried out in the solution of polyamic acid, the PAA and HCl works as the acid catalyst of the hydrolysis. After the hydrolysis carried out for 6 h, the resultant homogeneous mixture solution was cast onto the glass plate to prepare PAA hybrid film. The PAA hybrid film was obtained by drying the cast film at 60 °C, to evaporate the solvent, unreacted TEOS (and TBT), ethanol, and water, etc. In the process of drying, the siloxane network of silica between PAA and TEOS molecules and among TEOS molecules was developed [17], for the titania systems, the network between PAA and TBT molecules and among TBT molecules may be developed, particularly, in the ternary hybrids of polyimide/silica–titania systems, a network between TEOS and TBT molecules may also be expected. The PI hybrid film was obtained by thermal-treating the precursor film at higher temperature. Binary PI/SiO_2 and PI/TiO_2 hybrid films with a varied amount of inorganic (SiO_2 or TiO_2) moieties were prepared, respectively. The inorganic portions in the hybrid films were the theoretical amount calculated by assuming that the Sol–Gel reaction proceeded completely. The solution is homogeneous and transparent to the eye for PAA/SiO_2 when the SiO_2 is lower then 25 wt%, while for PAA/TiO_2 solution is lower than 8 wt%. The hybrid films of both PI/SiO_2 and PI/TiO_2 were transparent in which the inorganic content is lower than 5 wt%, semitransparent at the inorganic content is 8 wt%, and opaque while the inorganic content beyond 10 wt%.

The ternary hybrids films of PI/SiO_2-TiO_2 were prepared with varied inorganic (SiO_2-TiO_2) contents, and three serious ternary hybrids were synthesized in the ratio of SiO_2/TiO_2 at 2/1, 1/2 and 1/1 by weight, respectively. The transparent PAA/SiO_2-TiO_2 solution was obtained when inorganic portion is no more than 30 wt% for the SiO_2/TiO_2(2/1) systems and SiO_2/TiO_2(1/2) systems, while 50 wt% for the SiO_2/TiO_2(1/1) systems. The PI/SiO_2-TiO_2 hybrid films reveal transparent at an inorganic portion is no more than 10 wt% for SiO_2/TiO_2(2/1) systems, 25 wt% for SiO_2/TiO_2(1/2) systems, and 30 wt% for SiO_2/TiO_2(1/1) systems, respectively. Compared with PI/SiO_2 and PI/TiO_2 systems, the critical transparent values increased in SiO_2/TiO_2 systems.

3.2. FT-IR spectra

The absorption of Si–O–Si bonds hydrolyzed from TEOS appears at around 1000–1100 cm^{-1} [20,32], while Ti–O–Ti bonds from TBT at around 600 cm^{-1} [33,34]. However, the transparent PI/SiO_2 and PI/TiO_2 films did not show any obvious difference from the neat polyimide film. This is due to the very lower inorganic content in the binary hybrid films, and was overlapped with the absorptions of polyimide matrix. Fig. 1 shows the FT-IR spectra of polyimide and the ternary hybrids. In Fig. 1(a), the absorption bands at 1778, 1720 and 720 cm^{-1} is characteristic of imide group, no absorption at 1650 cm^{-1} indicating the completely imidization of PAA to PI. Different from the spectrum of the neat PI, in Fig. 1(b)–(d), a broadening of the bands in the range of 1200–850 cm^{-1} was found, furthermore, appeared an absorption at about 940 cm^{-1}, which may be assigned as Si–O–Ti bonds [35,36]. This indicates that the chemical bonds formed between silica and titania moieties, and yields a Si–O–Ti network in the hybrids. Moreover, appears a weak broad absorption around 3200–3700 cm^{-1} in the FT-IR spectra of samples with higher inorganic content (not shown in Fig. 1), the absorptions are assigned to the –OH residue, formed in the hydrolysis of alkoxy groups of TEOS and TBT [27,31], indicating the uncondensed Si–OH and Ti–OH groups remains in the hybrids with a higher inorganic contents.

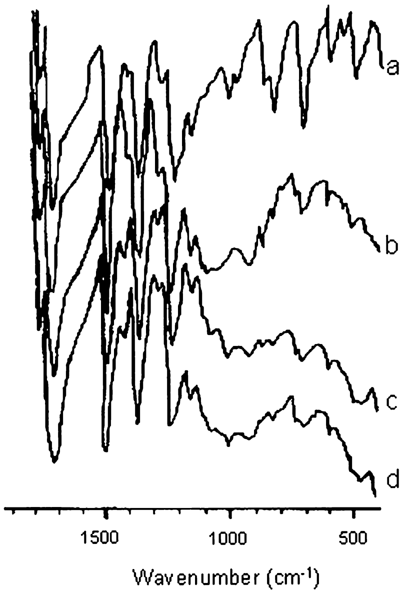


Fig. 1. FT-IR spectra of (a) PI, and PI/SiO_2-TiO_2 hybrids (30% inorganic moiety) of (b) $SiO_2/TiO_2 = 2/1$; (c) $SiO_2/TiO_2 = 1/2$; and (d) $SiO_2/TiO_2 = 1/1$.

3.3. Morphology of the hybrid films

The water in the inorganic sol solution may lead the hydrolysis of the PAA and thus causes the decrease in chain length of PAA, and the ethanol in the solution may affect the hydrolysis and condensation reactions. Although, these effects are supposed to influence the phase separation, accordingly, the morphology and particle size in the hybrids. However, it seems that in this study, the effect of the recipes and the component of inorganic portions is dominant. Fig. 2 shows the SEM micrograph of the hybrid films. It can be observed from Fig. 2(a) that the large spherical silica particles dispersed in the polyimide matrix, and the average diameter of the particles is ca.1 μm. The voids and gaps suggest that the lack of adequate compatibility between polyimide matrix and SiO_2 particles. The same micrographs were also observed in a no compatibilized polyimide-silica hybrids [19]. In Fig. 2(b), TiO_2 particles are poor dispersed as spherical particles or ellipsoid particles, with the diameter of 0.5–2.0 μm, the distinct phase separation indicating the poor adhesion in the interface.

Different from the morphology of binary systems, in the ternary hybrid films, the inorganic particles show a much more homogeneous distribution and a very fine interconnected domains, the particle size reduced significantly. That the variation of the ratio SiO_2 to TiO_2 in the hybrids, not only change the size of the inorganic domains, but also the shape as well as the phase compatibility. A bar-like particles with an estimated size of smaller than 100 × 300 nm, corresponding to the SiO_2/TiO_2 (2/1) hybrids, were observed in Fig. 2(c), whereas the spherical particles smaller than 100 nm in SiO_2/TiO_2 (1/2) system were seen in Fig. 2(d). It is noted that in SiO_2/TiO_2 (1/1) hybrids (Fig. 2(e)), an improved compatibility for the organic and inorganic components was observed, very small inorganic particles are well dispersed in the polyimide phase.

In the polyimide hybrid films, the morphology is strongly influenced by the recipes and component of the inorganic

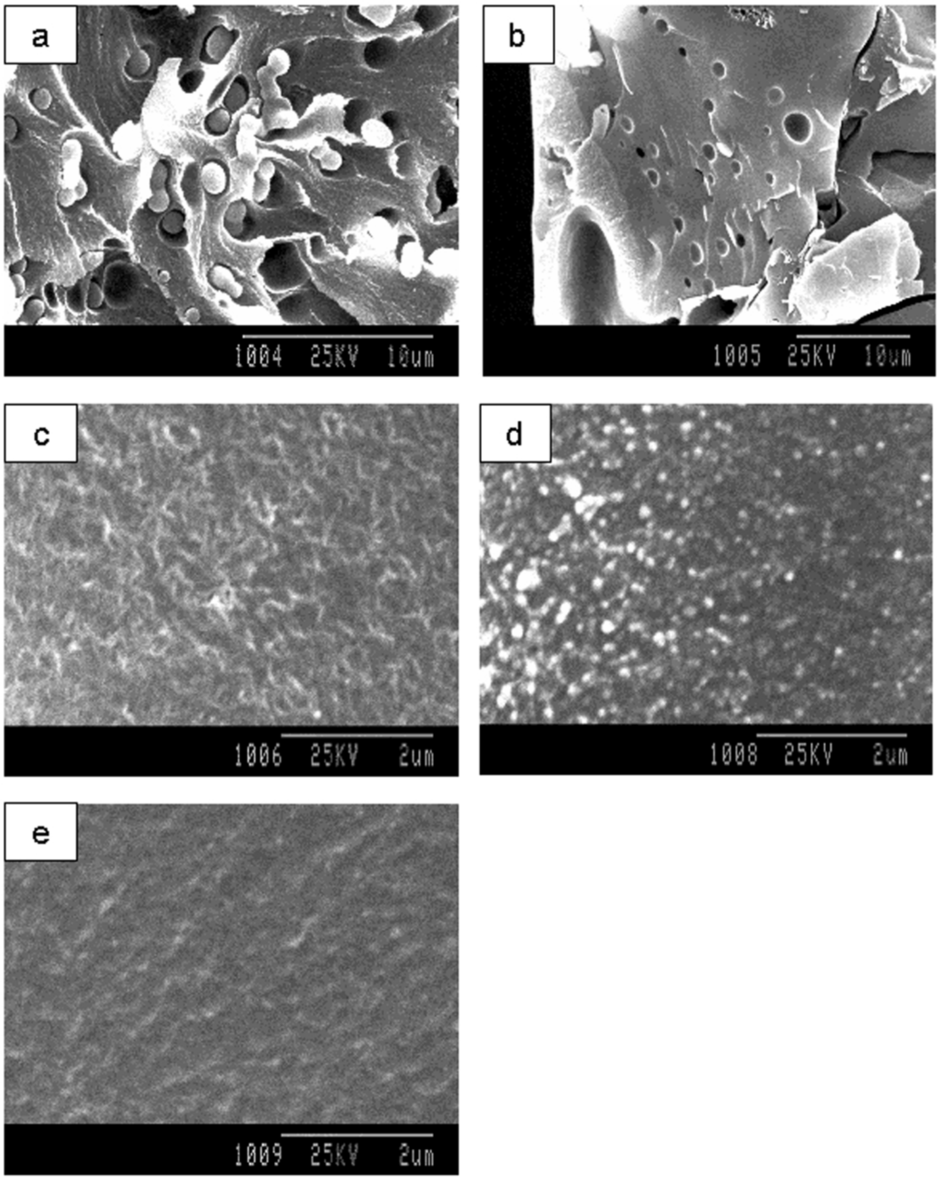


Fig. 2. SEM photographs of the hybrid films (10 wt% inorganic moiety): (a) PI/SiO_2; (b) PI/TiO_2; (c) PI/SiO_2–TiO_2 (SiO_2/TiO_2 = 2/1); (d) PI/SiO_2–TiO_2 (SiO_2/TiO_2 = 1/2); (e) PI/SiO_2–TiO_2 (SiO_2/TiO_2 = 1/1).

portions (SiO_2 or TiO_2), and the ratio of the inorganic component (SiO_2 to TiO_2). Unlike in binary systems, in the ternary systems, the inorganic particles are well distributed, and the size of particles decreased significantly, moreover, the interaction between the particles and the matrix increased intensively, particularly in the hybrid of SiO_2/-TiO_2 (1/1) systems.

3.4. Thermal stability

The pre-dried specimens were analyzed by the TG analysis in an inert nitrogen atmosphere, to investigate the effect of the inorganic moieties on the imidization temperature of PAA as well as the thermal stability of polyimide component of the hybrids. Fig. 3 shows the TG curves of the samples. The imidization temperatures (T_i) and the thermal decomposition temperatures (T_d) of the prepared films are shown in Table 1, both of which were taken from the cross-point of the tangent lines of the TG curve. There are two main weight losses in all the samples. The first one started at about 150 °C is associated primarily with the elimination of water during the imidization and the loss of residual solvents, whereas, the second one started at about 500 °C is associated with the degradation of the polymer. In the binary hybrids of SiO_2 systems, the increase in the initial T_i and the decrease in the ended T_i indicates that the introduction of SiO_2 facilitates the imidization of PAA to PI as well as the removal of the residual solvents. Compared with the neat PI, the initial degradation temperature (T_d) of PI increased with the increase of SiO_2

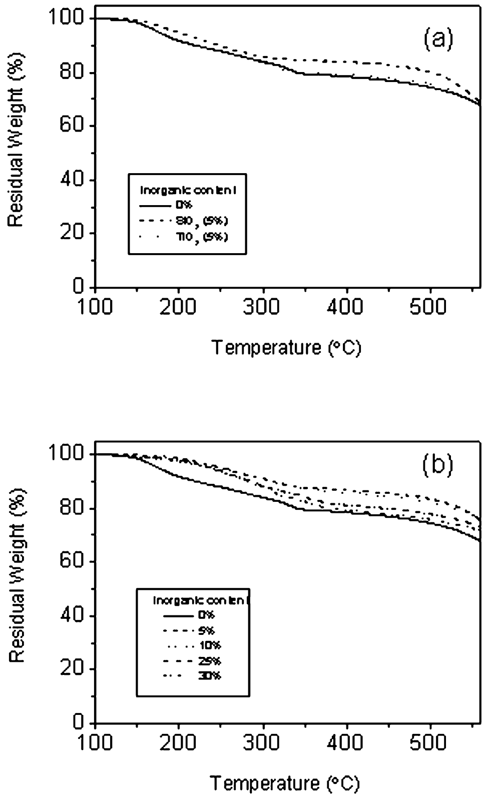


Fig. 3. TG curves of (a) binary hybrids, and (b) ternary hybrids ($SiO_2/TiO_2 = 1/1$).

moiety in the hybrids. In the binary hybrids of TiO_2 systems, the ended T_i was delayed. Although, the T_d of TiO_2 systems increased in the hybrids, however, the improvements are smaller than that in SiO_2 systems. In the ternary systems, the initial T_i and particularly the ended T_i increased in the hybrids, and the range of T_i were broadened. This suggests the successful incorporation of the inorganic moiety ($SiO_2–TiO_2$) in the hybrid materials. The T_d of the PI/$SiO_2–TiO_2$ hybrids increased, shown a maximum with the increase of the inorganic moiety at a certain inorganic content, which varied upon the ratio of SiO_2 to TiO_2. The enhanced thermal stability of polyimide in the hybrids is due to the formation of network of polyimide and the inorganic moieties, whereas the decreased T_d of the ternary hybrids at higher inorganic content maybe results from the Si–OH and Ti–OH residual groups in hybrid thin films, which increases with the inorganic content because of the incomplete condensation reaction. Another possibility is probably due to the lower molecular weight PI segments in the hybrid materials.

Table 1
TG data of the polyimide hybrids

Specimens (inorganic moiety, wt%)	T_i (°C)	T_d (°C)
Binary hybrids	(SiO_2 systems)	
0	150–305	500
1	156–285	509
5	153–288	510
8	161–295	516
15	162–300	525
	(TiO_2 systems)	
0	150–305	500
1	150–346	505
5	156–332	507
8	160–338	510
15	163–338	514
Ternary hybrids	($SiO_2/TiO_2 = 2/1$)	
0	150–305	500
5	143–337	508
10	154–342	517
25	163–370	511
30	160–387	506
	($SiO_2/TiO_2 = 1/2$)	
0	150–305	500
5	198–332	520
10	210–357	522
25	193–363	523
30	197–360	516
	($SiO_2/TiO_2 = 1/1$)	
0	150–305	500
5	187–329	512
10	193–349	522
25	215–375	514
30	208–370	507

T_i : the temperature range of imidization of PAA to PI as well as the elimination of the solvents, T_d : the initial degradation temperature of polyimide.

4. Conclusions

Polyimide/SiO_2, polyimide/TiO_2, as well as polyimide/$SiO_2–TiO_2$ hybrids were successfully prepared through the in situ sol–gel process. Morphologies can be controlled through varying the recipe and inorganic component in the hybrids. The silica and titania moiety forms an inorganic phase through Si–O–Ti network in the ternary hybrids. The hybrid films are transparent at much higher inorganic content for ternary systems, whereas lower for binaries. The inorganic particles are much smaller and homogeneous in the ternary systems than in the binary systems, and the shape of the inorganic particles as well as the compatibility for polyimide and inorganic moieties are varied with the ratio of the inorganic moieties in the hybrids. The completely imidization temperature of the polyamic acid was delayed, and the thermal stability of polyimide was enhanced in the hybrid materials.

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