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Templated Silica Tubes with High Aspect Ratios as Effective Fillers for Enhancing the Overall Performance of Polyimide Films[†]

Shao-Yun Fu* and Bin Zheng

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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Silica tubes (T-silica) with uniform size and large aspect ratios were synthesized by hydrolyzing tetraethyl orthosilicate using D,L-tartaric acid as a template. The prepared silica tubes have a diameter of about 200–400 nm and a length of about 40−100 μm; hence, their aspect ratios range from 100 to 500. The inner shape of the silica tubes is rectangular, and their wall thickness is 100–150 nm. T-silica/polyimide (PI) composite films were prepared from a solution of a PI precursor (polyamic acid) and silica tubes modified by a coupling agent (γ-aminopropyltriethoxy silane, KH-550). The overall performance including tensile strength, ductility, tearing strength, thermal expansion and diffusivity, and volume and surface resistivities of the T-silica/PI composite films were examined as a function of the T-silica content. It is interesting to note that the tensile strength and ductility have been simultaneously improved; tearing strength has also been enhanced; thermal expansion and diffusivity have been simultaneously decreased; and both volume and surface resistivities have been dramatically enhanced by the introduction of T-silica in proper amounts into the PI matrix. Moreover, the composite films containing silica tubes have low densities that range from 1.408 to 1.447 g/cm^3. These suggest that templated silica tubes are very effective in enhancing the overall performance of the PI composite films that have a great potential to be used as electrical and thermal insulating materials in high tech areas such as aircraft and spacecraft manufacture and so forth, where high strength and ductility, high tearing strength, low thermal expansion and diffusivity, high resistivities, light weight, and so forth are desirable.

1. Introduction

Aromatic polyimides (PIs) have long been considered as one of the most useful superengineering plastics because of their excellent thermal stability, chemical resistance, mechanical properties, and low dielectric constant.[1–3] With the rapid development in modern electrical, electronic, and defense technologies, PI films are receiving increasing attention, and improved mechanical and physical properties are needed for PI films to meet the higher requirements. So, various combinations of PIs with inorganic fillers including silica,[4–20] carbon nanotubes,[21,22] layered silicate such as montmorillonite[2,23–28] or mica,[29] alumina,[30,31] titania,[32–34] and so forth have been reported. These composite films

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* Corresponding author. Phone/fax: +86-10-82543752. E-mail: syfu@mail.ipc.ac.cn.

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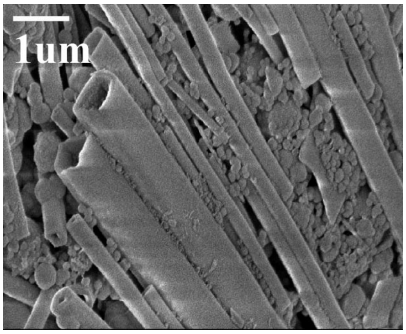

Figure 1. SEM photograph of the synthesized product,[5,7,9] showing that the relative percentage of silica particles is high and the size of the silica tubes is not uniform.

typically exhibited improved thermal stability, mechanical properties, gas barrier properties, dielectric properties, and water absorption retardation behavior in comparison with those of pure PI films when the proper amounts of fine inorganic fillers are incorporated into the PIs. PI films have also important applications as electrical and thermal insulating materials in high tech areas such as in aircraft and spacecraft manufacture and so forth,[35] where improved mechanical strength and ductility, enhanced tearing strength, decreased thermal expansion and diffusivity, increased resistivities, light weight, and so forth are desired for the PI films. Fine inorganic fillers such as silica particles and so forth can enhance the strength and ductility[4,6] and reduce the thermal expansion.[4,12] However, the addition of inorganic fillers to polymers generally increase the thermal diffusivity and decrease the resistivities because inorganic fillers have a higher thermal diffusivity and a lower resistivity than polymers.[32,36] Introduction of solid inorganic fillers, which have a higher density than polymeric materials, can also significantly increase the weight of the polymers. So far, no work has been reported on using any inorganic filler for enhancing the above mentioned overall performance of the PI films. Therefore, to improve the utility of the PI films in high tech areas such as in aircraft and spacecraft manufacture and so forth, the study and development of new inorganic/PI composite films with improved overall performance are of great importance.

In our early works,[5,7,9] novel silica tube (T-silica)/PI composite films have been reported on mechanical and dielectric properties. The results showed that the increase of the mechanical properties and the decrease of the dielectric constant of the composite films were possible when the proper amounts of T-silica content were introduced into the PI film. However, in our previous works,[5,7,9] the relative percentage of silica particles was high in the synthesized products as shown in Figure 1. The silica particles are not competent as silica tubes with high aspect ratios in enhancing the mechanical and physical properties of the PI films, as pointed out in our theoretical works predicting the effects of fiber (filler) aspect ratio and orientation on mechanical and thermal properties.[37–43] Moreover, the synthesized silica tubes in our previous works[5,7,9] have broad aspect ratios from 10 to 500, but only those higher than 100 would be effective in enhancing the mechanical and thermal properties of polymers.[37–43] Therefore, in our recent work,[44] the effects of the synthetic condition on the formation of silica tubes have been examined in detail, and an optimal synthetic condition has been established for preparing a high yield of T-silica with high aspect ratios. Under the optimal synthetic condition, the relative percentage of silica tubes with a uniform size and high aspect ratios from 100 to 500 was high while the relative percentage of silica particles was low in the prepared products. The high aspect ratios of T-silica should be very effective in improving the mechanical and thermal properties of polymers.[37–43] To achieve an excellent composite performance, the load must be transferred effectively to the silica tubes, and a strong silica tube/matrix compatibility or bonding is required. Hence, γ-aminopropyltriethoxy silane (KH-550) as a common silane coupling agent with an amino group, which could react chemically with acid anhydride groups of polyamic acid (PAA) molecules, could be chosen to improve the interface adhesion and to thereby enhance the mechanical properties of the T-silica/PI composite films.

In the present investigation, the silica tubes with high aspect ratios were synthesized by a modified templating method under the optimal synthetic condition,[44] and their surfaces were modified by the KH-550 coupling agent. T-silica/PI composite films were prepared by an in situ polymerization process combined with a multistep curing. The prepared silica tubes and the composite films were characterized using various techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectrometry, and so forth. The mechanical and physical properties, including tensile strength, ductility, tearing strength, thermal expansion and diffusivity, and volume and surface resistivities, of the composite films are examined as a function of the T-silica content. It will be shown that the introduction of the silica tubes in proper amounts into the PI films can improve all these mechanical and physical properties. The developed T-silica/PI composite films with the high overall performance have a great potential to be used as electrical and thermal insulating film materials in high tech areas such as in aircraft and spacecraft manufacture, and so forth.

2. Experimental Section

2.1. Materials. Pyromellitic dianhydride (PMDA, industrial product) and 4,4′-oxydianiline (ODA, industrial product) were provided by Dongying Baotong Chemical Co. Ltd. (Shandong, China). γ-Aminopropyltriethoxy silane (KH-550, industrial product) was purchased from Shen Da Co. Ltd. (Beijing, China). *N,N*-

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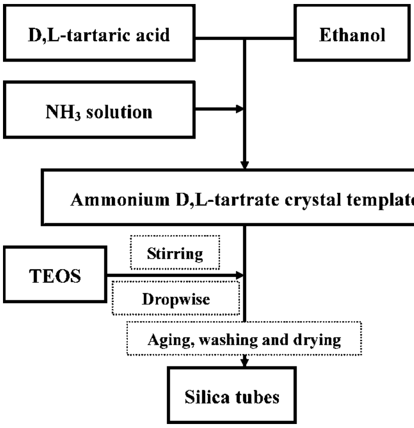

Figure 2. Flowchart for the preparation of silica tubes.

Table 1. Formulations for Preparation of T-silica/PI Composite Films

T-silica content (wt %)	silica weight (g)	KH550 (g)	DMAc (g)	PMDA (g)	ODA (g)
0	0	0	107.4	7.6342	7.0084
1	0.1352	0.0135	107.4	7.6342	7.0084
3	0.4139	0.0414	107.4	7.6342	7.0084
5	0.7043	0.0704	107.4	7.6342	7.0084
8	1.1636	0.1164	107.4	7.6342	7.0084
15	2.3615	0.2362	107.4	7.6342	7.0084

Dimethylacetamide (DMAc), D,L-tartaric acid, and tetraethyl orthosilicate (TEOS) in analytical grade were obtained from Tianjin Fine Chem. Co. Ltd. (China). Ammonia and ethanol were of analytical grade and were used without further purification.

2.2. Preparation of T-Silica. In our previous works,[5,7,9] the synthesis of T-silica by hydrolyzing the TEOS using D,L-tartaric acid as a template according to the literature has been reported .[45] This method was modified in our recent work,[44] and the effects of TEOS addition time, aging time after TEOS addition, ammonia concentration, and reaction temperature on the formation of silica tubes were investigated in detail. The flowchart for synthesizing silica tubes is shown in Figure 2. Preparation of silica tubes with a uniform size and large aspect ratios under the optimal condition is briefly described next. In a typical experiment, 0.04 g of D,L-tartaric acid was completely dissolved in 5 mL of ethanol; then, the resulting solution was added to 4 mL of aqueous ammonium to obtain an ammonium D,L-tartrate crystal template. Afterward, 1.57 mL of the TEOS was dropwise added to the above mixture for 1 h under vigorous stirring, and the resulting solution was aged for 10 h. The white products were washed with a large amount of water and dried at 80 °C for 2 h.

2.3. Preparation of T-Silica/PI Composite Films. Preparation of the T-silica/PI composite films has been described in detail in our previous works,[5,9] and a similar preparation process is presented here in brief. The compositions for preparing the pure PI and the composite films are shown in Table 1. The composite films were prepared using an in situ polymerization reaction followed by casting and multistep thermal curing. The flowchart for the preparation of the T-silica/PI composite films is shown in Figure 3.[5] First, PAA was prepared from PMDA and ODA with a molar ratio of 1:1; PMDA was then added into the solution three times within 0.5 h. The mixture was continuously stirred at room temperature under nitrogen for about 12 h to obtain the PAA precursor. On the other hand, the prescribed amount of silica tubes was added to the DMAc solvent, and the solution was ultrasonically treated for 5 min; then, the coupling agent KH-550 was added to the solution. After the solution was stirred for 12 h, the mixture was added to the prepared PAA solution with stirring. The resulting T-silica/PAA homogeneous solution obtained after stirring for 12 h was cast onto a glass plate using a glass bar. Two copper wires with tunable diameters were used at the two ends of the glass bar to control the film thickness. The films were heated for imidization at 80, 120, 150, 180, 210, 240, 270, and 300 °C for 1 h each, and finally, a series of pure PI and composite films containing 0, 1, 3, 5, 8, and 15 wt % of silica tubes were obtained. The thickness of the films was controlled in the range of about 47−52 μm.

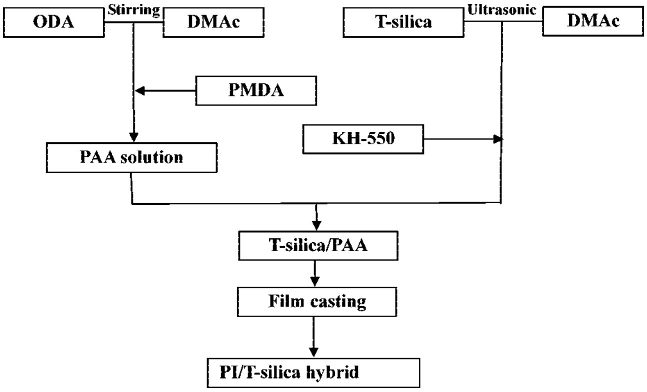

Figure 3. Flowchart for the preparation of T-silica/PI composite films.[5]

2.4. Characterization. SEM photographs of silica tubes and tensile fracture surfaces of T-silica/PI composite films were taken using a HITACHI S-4300 scanning electron microscope. TEM photographs of silica tubes were performed with a HITACHI 800 transmission electron microscope at an accelerating voltage of 20 kV. The density of the films was measured at room temperature (23 °C) according to the recommendation of GB1033-86. $Ca(NO_3)_2$ was selected as the impregnating solution whose density range is suitable for the measurement of the film density. FT-IR spectra of the pure PI and composite films were recorded at room temperature in the range of 400−4000 cm^{-1} using a Perkin Elmer FTIR 16PC spectrometer. X-ray diffraction (XRD) patterns of the films were recorded at a scanning range of 10°−70° on a Bruker D8 Advance X-ray diffractometer with graphite monochromatized Cu Kα radiation. The transmittance spectra of the films were scanned in the range of 300–900 nm with a 1 nm interval using a UV–vis spectrophotometer (Secoman Uvikonxs). Atomic force microscopes (AFM; Nanoscope IIIa, Digital Instruments Co.) were used to investigate the surface morphology of the pure PI and T-silica/PI composite films. AFM images were taken with a 5 × 5 μm scan area from 1 × 1 cm films.

The tensile properties of pure PI and T-silica/PI composite films were measured using an RGT-20A universal tester at the loading rate of 2 mm/min. The dimensions of the film specimens were 10 mm × 150 mm, and the gauge length was 50 mm as shown in Figure 4a. The tearing testing was performed at a tearing rate of 200 mm/min using an RGT-2A universal tester. The dimensions of the film specimens were 40 mm × 120 mm, and the cutting was made along the central line from one end to the center of the specimen as shown in Figure 4b. The specimens were cut from free films, and more than six samples were tested for each composition for both tensile and tearing testing.

The charge coupled device (CCD) technique was employed for the measurement of the thermal expansion (TE) of the T-silica/PI composites films as done for the silica particle/PI composite films prepared using a novel sol–gel route.[4] The samples of the T-silica/PI composite films for the TE measurement with length × width,

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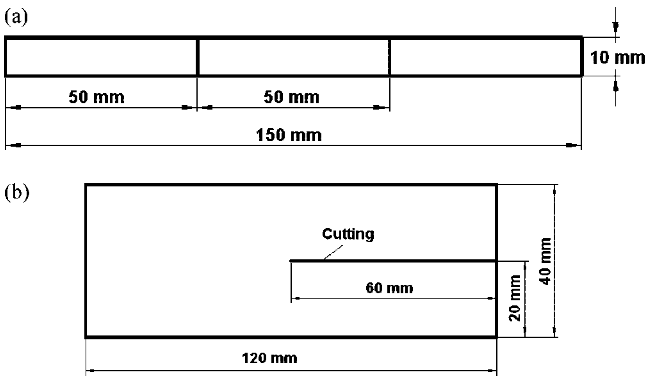

Figure 4. Film sample geometries for (a) tensile and (b) tearing testing.

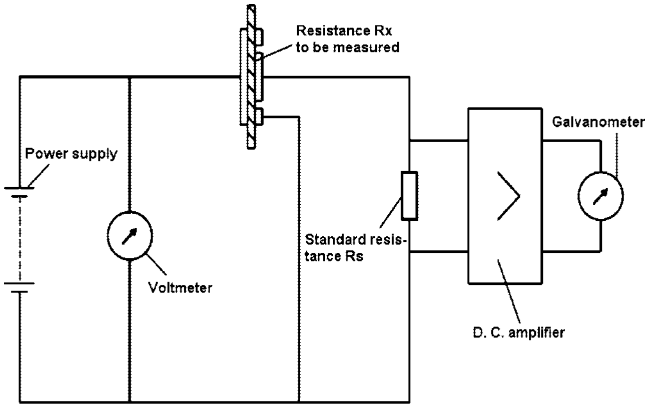

Figure 5. Schematic diagram for the measurement of the volume and surface resistivities of the films.

9.7–9.8 mm × ~14 mm, were cut from the original samples with a razor blade. After cleaning the samples with a silk cloth to remove the dust and measuring their lengths with an Abbe optical comparator with the precision of 1 μm, the samples were put in the sandwich sample assembly; then, the TE measurement was carried out using the CCD technique. The thermal diffusivity of the films was also measured using the CCD technique according to the flash method of determining thermal diffusivity, thermal capacity, and thermal conductivity.[46] The volume and surface resistivities of the films with a thickness of 47–52 μm were measured on a ZC36 megohmmeter (Shanghai, China) according to the recommendation of GB1410-89. The schematic diagram for the measurement of the volume and surface resistivities using the ZC36 megohmmeter is shown in Figure 5. Thermogravimetric analyses (TGA) were conducted in the temperature range of 30–850 °C with a Netzsch STA 409 C calorimeter, working at 10 °C min^{-1} in a nitrogen atmosphere.

3. Results and Discussion

3.1. Characterization of Silica Tubes. Silica tubes with uniform size and high aspect ratios, as shown in Figure 6, were obtained by hydrolizing the TEOS in the presence of ammonium D,L-tartrate crystal templates. In the modified process,[44] the effect of the synthetic condition on the formation of silica tubes has been studied in detail, and an optimal condition was achieved for obtaining the high yield of silica tubes with high aspect ratios in the prepared product. The main conditions in the improved process are described here: (1) ~1 h of TEOS addition time is most advantageous to the formation of silica tubes, (2) the aging time of ~10 h is favorable for the formation of T-silica, not only can the TEOS be fully hydrolyzed but also a high yield of uniform sized silica tubes with small diameters can be obtained, and (3) the ammonia concentration and reaction temperature have little effect on the formation of silica tubes. Therefore, a minimum amount of aqueous ammonium is good for the preparation of the T-silica at room temperature. Figure 6 shows that the prepared silica tubes have a diameter of 200−400 nm and a length of about 40−100 μm; then, the corresponding aspect ratios are about 100−500. The inner shape of the silica tubes is rectangular (Figure 6b) because the templating tartrate crystals have a rectangular outer shape,[44] and the wall thickness of T-silica is about 100−150 nm (Figure 6c). Although there are some silica particles around the tubes, their number is much less than in our previous works[5,7,9] as shown in Figure 1 that followed the reported process.[45]

3.2. Characterization of T-Silica/PI Composite Films. Table 2 and Figure 7 show that the prepared T-silica/PI composite films have a low density from 1.408 to 1.447 g/cm^3. The density of the T-silica can be derived from Figure 7 at 100 wt % of T-silica, and the density of T-silica is evaluated to be 1.67 g/cm^3. Because the density of T-silica is low, the density of the obtained composite films is relatively low. This is beneficial to the application of composite films to aircraft and spacecraft areas where light weight is critical to reduce costs.

The chemical structures of the PI and T-silica/PI composite films were characterized by FT-IR spectroscopy as shown in the Supporting Information Figure S1. The characteristic peaks of the symmetric C−O stretching and the asymmetric C−O stretching of the imide group are clearly visible near 1720 and 1780 cm^{-1}, respectively. The assignment of the stretching of the imide ring is at about 1380 cm^{-1}. As the T-silica content increases, the absorption band intensity of the Si−O stretching at 1060 cm^{-1} increases. A broad Si−O−Si band is observed around 1030–1080 cm^{-1} in the spectra as shown by the boxed range in the Supporting Information Figure S1, and the intensity of the absorption band also increases with increasing T-silica content. The characteristic absorption of the amide carbonyl at 1660 cm^{-1} does not appear in the spectra, indicating that the imidization reaction is complete.[19] This also reveals that the introduction of the T-silica has no noticeable effect on the thermal imidization process of the PAA precursor.

The XRD patterns for the pure PI, the composite films, and the T-silica are given in the Supporting Information Figure S2. The patterns for all the samples do not show any sharp peaks that are for the crystalline structure, indicating that the silica tubes in the samples are amorphous. The broad characteristic peak of the silica tubes was centered at ~24°. The XRD patterns of the pure and the composite films exhibit only a very broad hump centered at $2\theta = 18°$, originating from the amorphous phase of the aromatic PI. Moreover, the patterns of the composite films do not appear near 24°, indicating that the silica tubes do not form sufficiently large aggregates in the PI matrix.

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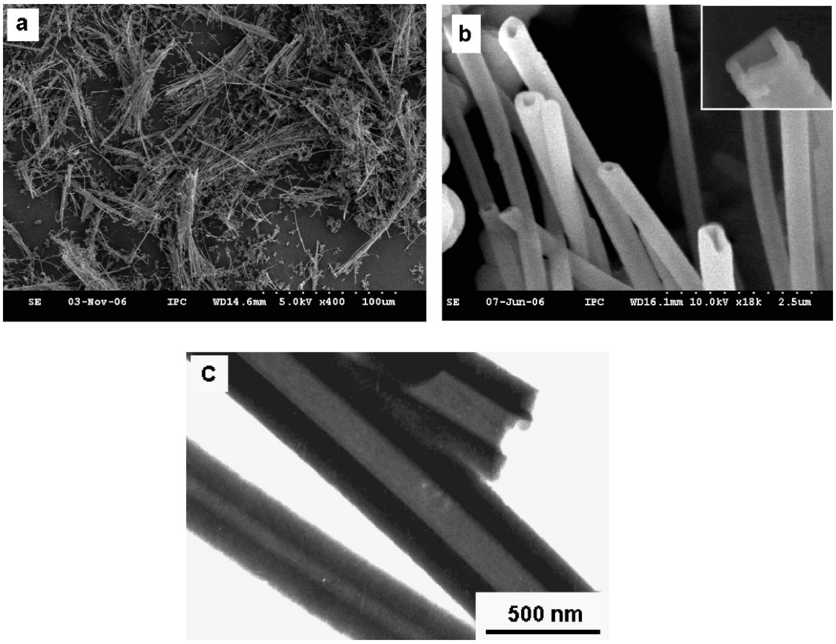

Figure 6. (a) Low and (b) high magnification SEM and (c) TEM photographs of the prepared silica tubes.[44]

Table 2. Densities of Pure PI Film and T-silica/PI Composite Films

T-silica content (wt %)	0	1	3	5	8	15
density (g/cm^3)	1.408	1.412	1.417	1.423	1.434	1.447

Figure 8a shows the effect of the T-silica content on the transmittance and the transparency of the pure PI and the composite films. It can be seen that the transmittance of the composite films decreases dramatically as the T-silica content increases. The corresponding transparency shown in Figure 8b confirms this tendency. This is because the introduction of the silica tubes will cause light scattering when the light transmits through the film samples, and higher T-silica content leads to more severe light scattering. As a result, as the content of the silica tubes increases, the transmittance and the transparency decrease.

The 2D and 3D AFM images of the surface topography obtained for the pure and composite films with different amounts of silica tubes are shown in the Supporting Information Figure S3. It can be seen that the film surfaces are quite smooth for most of the film samples except for the composite film containing 15 wt % silica tubes. Thus, the light scattering due to the effect of the surface roughness would be small for the cases of the T-silica content up to 8 wt %. For the 15 wt % of T-silica case, the surface is lightly rough, and the surface roughness would have an additional effect on the light scattering, leading to the very low transmittance of the corresponding composite film.

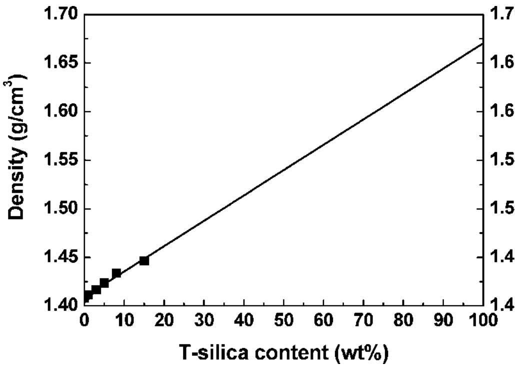

Figure 7. Densities of pure PI and composite films as a function of T-silica content.

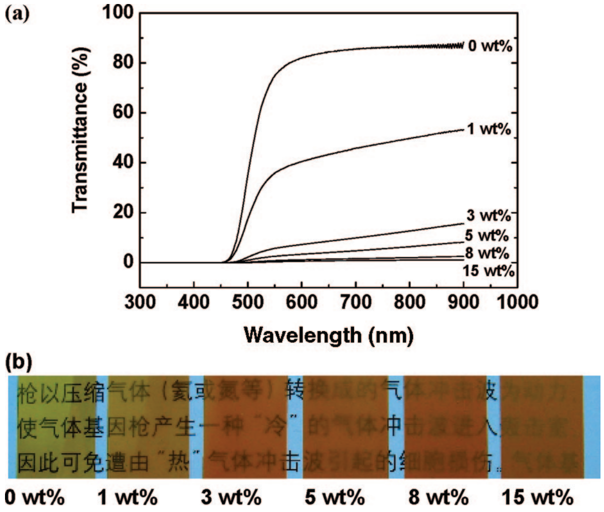

Figure 8. (a) UV–vis transmittance and (b) transparency of pure PI and T-silica/PI composite films.

3.3. Mechanical and Thermal Properties. The effects of the silica tube content on the tensile strength and the elongation at the break of the T-silica/PI composite films at room temperature are shown in Figure 9. It shows that the tensile strength and the elongation at the break of the T-silica/PI composite films with low T-silica contents are higher than those of the pure PI film. The tensile strength of the composite films exhibits the maximum value of 128.0 MPa with a 10.8% increase at 1 wt % of silica tubes and then decreases with the further increase of the T-silica content. This increase at the maximum value compared to that of the pure PI film is higher than the corresponding increase of 7.4% in our previous work,[5] where the previously synthe-

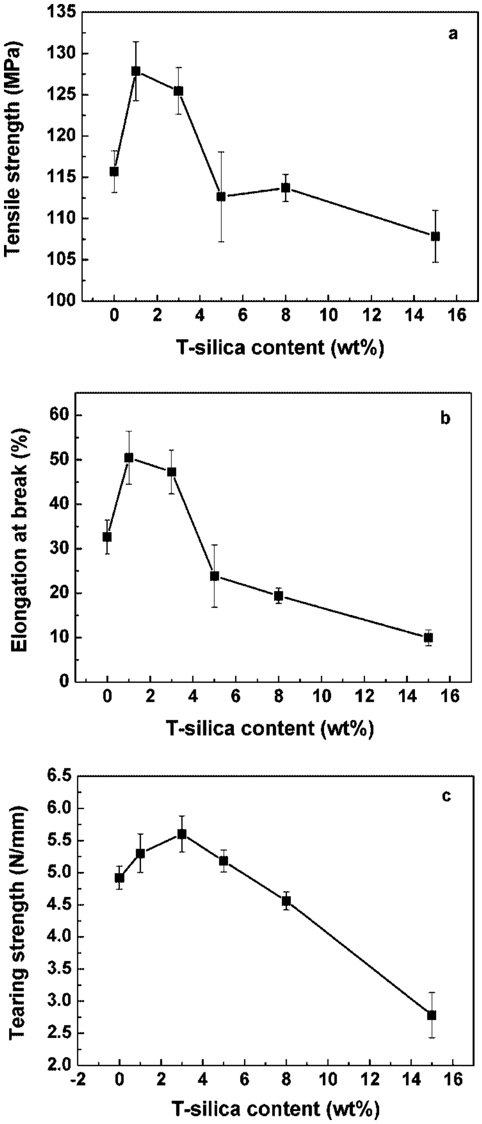

Figure 9. Effects of T-silica content on the tensile and tearing properties of the composite films. (a) Tensile strength, (b) elongation at break, and (c) tearing strength.

sized products contained more silica particles and the silica tubes have broader aspect ratios from 10 to 500. Also, the elongation at the break reaches the maximum value of 50.8% with a 55.4% increase at 1 wt % of T-silica compared to that of the pure PI film and then decreases with the increase of the T-silica content. This increase is also higher than the corresponding increase of 39.2% in our previous work.[5] According to our previous theoretical works, short fibers with aspect ratios higher than 100 would be very effective in stress transfer,[47] leading to higher mechanical properties.[37–42] This is the case in the present work in which silica tubes with aspect ratios of 100−500 have been employed as effective fillers to reinforce the PI matrix.

The improvements in the tensile strength and elongation at the break of the T-silica/PI composite films at low silica contents is attributed to the fact that the load can be effectively transferred to the silica tubes to reinforce and toughen the PI matrix because of the strong bonding between the KH-550 treated-silica tubes and the PI matrix. As shown in Figure 10, only fractured silica tubes are observed because of the strong interface adhesion. Moreover, it can be clearly seen from Figure 10 that dispersion of the T-silica is quite good at low contents while the T-silica dispersion becomes worse at high T-silica contents. The decrease of tensile strength and elongation at the break at high T-silica contents is very likely caused by the worse dispersion of the silica tubes in the PI matrix as shown in Figure 10. In the circled areas, small aggregates of a few silica tubes are observed. A similar observation has been noticed for carbon nanotube/polymer composites, and the agglomerates reduce the reinforcing effects of the carbon nanotubes (CNTs) because they are acting as flaws in the resin.[48,49] Comparatively, dispersion of silica tubes is better than that of CNTs in a polymer matrix. In the present study, a high content of up to 15 wt % of T-silica has been successfully incorporated into the PI matrix with a low degree of agglomeration of T-silica using an in situ polymerization method with ultrasonic treatment as shown in the present work (see Figure 10). On the other hand, carbon nanotubes have a strong tendency to form bundles and aggregate together because of their high surface area and the strong van der Waals interaction; thus, it was naturally observed that the carbon nanotubes were poorly dispersed in the polymer matrix at a low content of 1.5 wt %.[49] Some researchers have chemically modified the nanotube surface to obtain better carbon nanotube dispersion in polymer matrices.[50,51] However, the chemical modification may destroy the pristine structure of the carbon nanotubes and decrease the modulus and strength.[52]

Figure 9c shows that the tearing strength has been enhanced by the addition of T-silica at low contents and reached the maximum with an improvement of 14% at 3 wt % and then decreases with further increase of the T-silica content. Similar fracture surfaces to that of the tensile testing have been observed. For simplicity, they are not shown here. For the cases of low T-silica contents, T-silica with high aspect ratios can effectively resist crack propagation within the PI matrix. At high T-silica contents, agglomerates would reduce the strengthening effects because the agglomerates of T-silica would act as flaws for CNTs in the polymeric matrices.[48,49]

Figure 11 shows the results for the thermal expansion ($\Delta L/L_0$) of the pure PI film and the T-silica/PI composite films, where L_0 is the original length of the sample at room temperature (RT = 20 °C) and ΔL is the length change at a given temperature caused by thermal expansion (at a higher temperature than RT) or contraction (at a lower temperature than RT) relative to the original length of the sample. It can be seen from Figure 11a that the thermal expansion of the pure PI film has been significantly reduced by the introduc-

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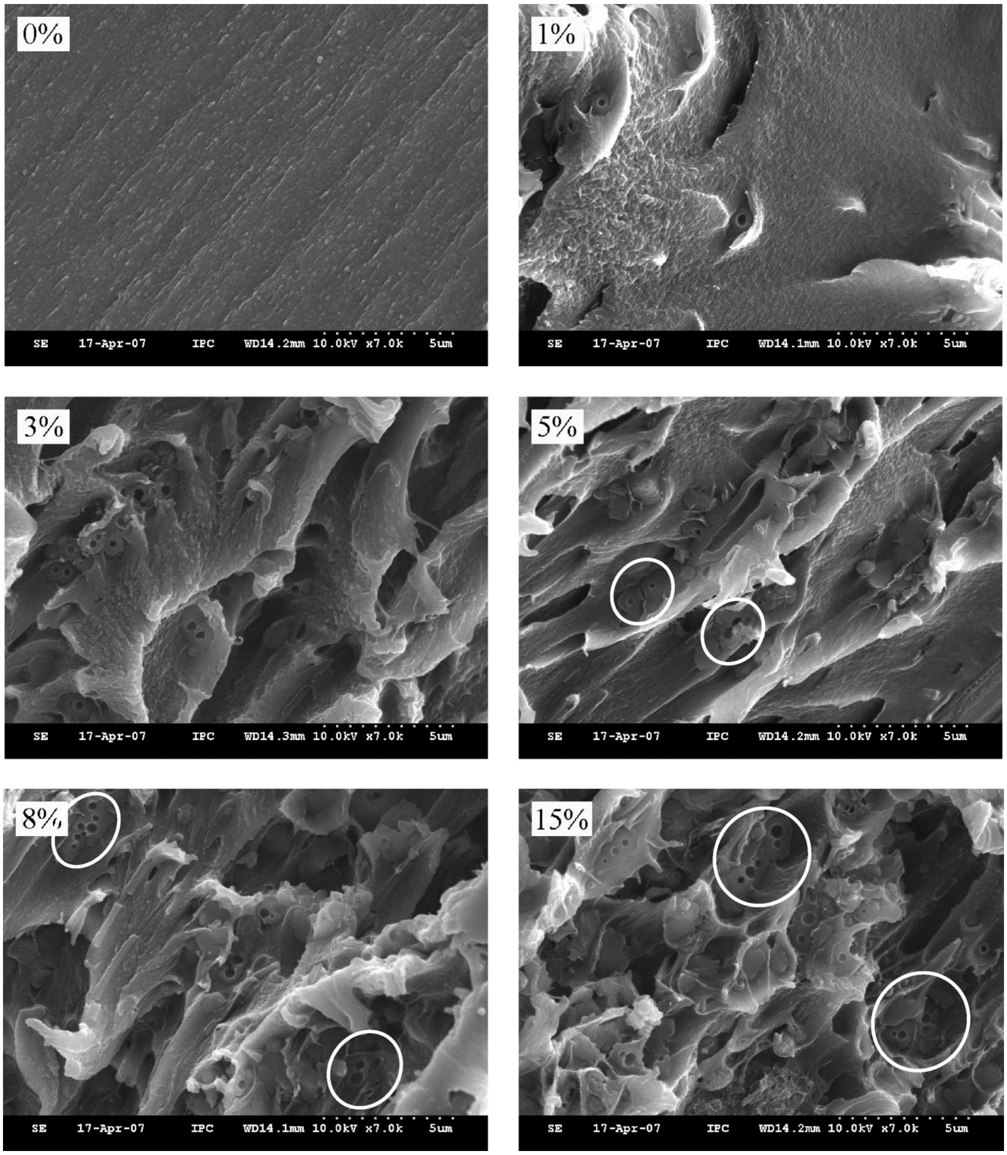

Figure 10. SEM pictures of the tensile fracture surfaces of pure PI and of T-silica/PI composite films (×7000).

tion of silica tubes. This is attributed to the very low thermal expansion and the high aspect ratio of T-silica. Moreover, the thermal expansion ($\Delta L/L_0$) is a function of the temperature (T), and the data can be approximately fitted by least-squares method; hence, their fitting equations can be easily obtained.[4] Using these equations, the coefficient of thermal expansion (CTE) of the films can be estimated in terms of the differentiation of $\Delta L/L_0$ with respect to the temperature (T). The results for the CTE of the pure PI film and the T-silica/PI composite films are exhibited in Figure 11b. It shows that the CTE has been significantly reduced by the addition of a small amount (1 wt %) of silica tubes. This is desirable in practical application of PI films. Moreover, the CTE decreases slightly with the further increase of the silica content. This can be explained as follows. It is well-known that in traditional polymer composites reinforced by micro-sized short fibers, with a diameter of about 10 μm or larger, the thermal expansion of the polymer matrix can be dramatically reduced by the addition of short fibers. This is because of the constraint effect of the reinforcing fibers on the dimensional change caused by the thermal expansion. However, when the fiber content is high enough such as 20 wt %, the thermal expansion and the resulting dimension change will decrease slowly with the further increase of the fiber content.[53] This is because the fiber number at any arbitrary cross section of the specimen has been already large enough at a high fiber content to constrain the dimension change due to the thermal expansion, leading to the slow decrease of the thermal expansion with further increasing fiber content. Next, we calculated the number of silica tubes in the specimen (9.7 mm × 14 mm) used for the measurement of the thermal expansion. The diameter of the T-silica ranged from 200 to 400 nm, and the medium value of 300 nm was used for the calculation of the T-silica numbers. The length of the T-silica was between 40 to 100 μm, and the medium value was 70 μm. An approximate estimation of the T-silica number (N) was made by N = T-silica volume fraction × (9.7 mm × 14 mm)/(0.3 μm × 70 μm). When 1 wt % (0.84 vol %) of the T-silica is incorporated into the PI

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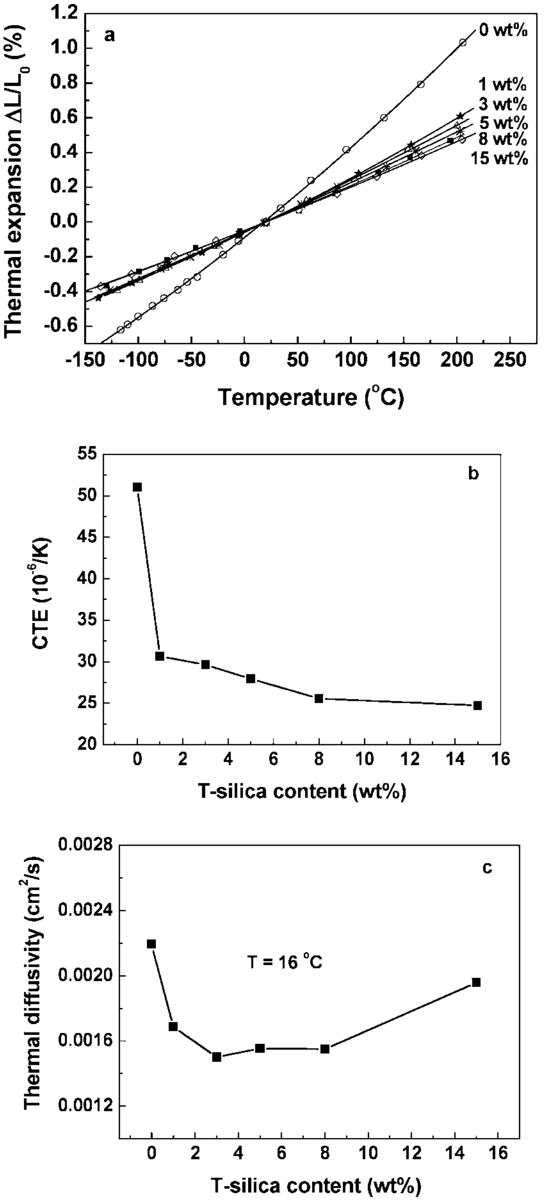

Figure 11. Effects of T-silica content on (a) thermal expansion, (b) CTE, and (c) thermal diffusivity of T-silica/PI composite films.

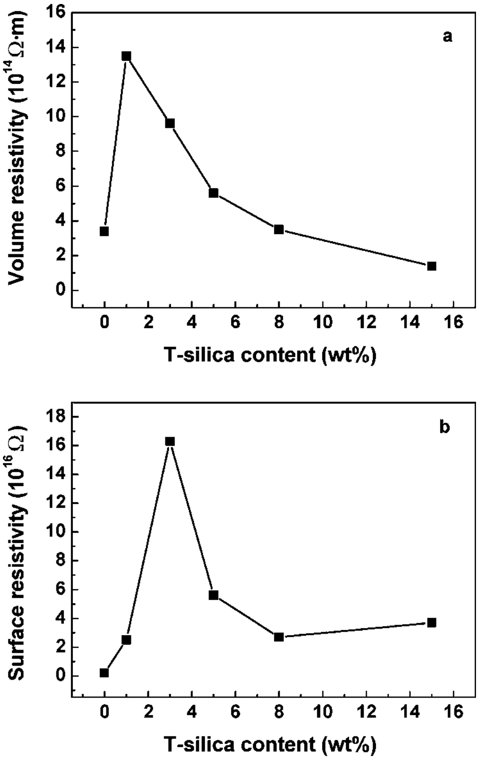

Figure 12. Effects of T-silica content on (a) volume and (b) surface resistivities of T-silica/PI composite films.

matrix, it can be obtained that there will be over 54 thousands of the T-silica in the specimen. Assuming that the silica tubes are uniformly dispersed in the matrix, there will be about 272 silica tubes crossing an arbitrary section (9.7 mm) in the specimen calculated in terms of our previous work.[37] This is a large number of reinforcing fillers in a composite, equivalent to the case of the traditional microcomposites reinforced by 28 vol % of short fibers with a diameter of 10 μm and a length of 1 mm. Moreover, the thermal expansion coefficient of silica is very low ($\sim 5 \times 10^{-7}$ K^{-1})[4] while the CTE of the PI matrix is obtained to be 51.3×10^{-6} K^{-1}. Therefore, the addition of 1 wt % silica tubes will considerably constrain the dimensional change of the PI film caused by the temperature change. It is then not difficult to understand why the CTE can be significantly reduced by the addition of only 1 wt % of T-silica. As the T-silica content increases further, the constraint degree will not be high as the first silica tubes constrain the dimensional change. Consequently, higher loading of silica tubes has relatively small additional effect on the thermal expansion.

Figure 11c exhibits that the thermal diffusivity of the composite films decreases gradually to the minimum value with the increase of the T-silica content, with a decrease of 32% compared to that of the pure PI film at 3 wt % T-silica, and then increases with increasing silica content. At low T-silica contents, the silica tubes are isolated from each other, and the decrease of the thermal diffusivity is mainly caused by the thermal insulating effect of the inert air (gas) in the tubes as the glass beads did.[54] This effect is beneficial to the use of PI composite films as thermal insulating materials in aircraft and spacecraft areas and so forth. At high T-silica contents, the silica tubes would easily approach or even contact each other, leading to the increase of the thermal diffusivity with the increase of the T-silica content.

Volume and surface resistivities of composite films are shown in Figure 12. It is interesting to note that the volume resistivity of the composite film has been dramatically enhanced from 3.39 to 13.53 ($\times 10^{14}$, $\Omega \cdot m$) with an increase of 299% by addition of 1 wt % T-silica. Also, the surface resistivity has been significantly raised from 0.199 to 16.37 ($\times 10^{16}$, Ω) with an increase of 8126% by addition of 3 wt % T-silica. Thus, it is clear that silica tubes are appropriate fillers for producing electrically insulating polymer composites. On the other hand, carbon nanotubes are suitable fillers for producing electrically conducting polymer composites. This is the major difference between silica tubes and carbon nanotubes. The high resistivities of the T-silica/PI composites are attributed to the inert air (gas) in the silica tubes, as reported in the literature on the high volume resistivity of

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the printed Ag tracks caused by the porosities in their films.[55] Afterward, both the volume and the surface resistivities decrease with further increase of the T-silica content. This normal tendency has also been observed for titania/PI composite films.[32]

The effect of T-silica content on the thermal stability of PI composite films is studied. Thermogravimetric curves of the pure PI and T-silica/PI composite films are shown in Supporting Information Figure S4. TGA curves indicate that water or solvent has been successfully removed from the pure PI and composite films because there is no weight loss below 100 °C. It is clearly displayed in the Supporting Information Figure S4 that the thermal stability of the PI is increased by the incorporation of the silica tubes in terms of the weight residues above 800 °C. The increase in the weight residues above 800 °C suggests the successful incorporation of the silica tubes into the PI composite films, leading to increases in thermal stability. The improvements in the thermal stability of the T-silica/PI composite films mainly derive from the high thermal stability of the silica tubes because inorganic components such as silica have inherently good thermal stability.[56]

4. Conclusions

In summary, the T-silica with uniform size and large aspect ratios have been successfully synthesized from D,L-tartaric acid and the hydrolysis of TEOS by a modified templating method. T-silica/PI composite films were successfully prepared by the incorporation of the as-prepared silica tubes modified with a coupling agent (KH-550) into the PI matrix. The effects of T-silica content on the overall performance of the composite films were studied. It was interesting to observe that the tensile strength and the ductility were simultaneously enhanced with an improvement of 10.8% and 55.4%, respectively, by introduction of a low T-silica content (1 wt %). The tearing strength was increased by 14% by addition of 3 wt % T-silica. On the other hand, the thermal expansion and the diffusivity were simultaneously reduced by the addition of a small amount of silica tubes. Moreover, the volume and surface resistivities of the PI films have been significantly enhanced with the increase of 299% and 8126%, respectively, by addition of T-silica at low contents of 1 wt % and 3 wt % T-silica. Furthermore, the T-silica/PI composite films have low densities in the range of 1.408−1.447 g/cm^3. Finally, a comparison of the results for the mechanical, thermal, and electrical properties obtained for the composite films containing the 1 wt % and 3 wt % T-silica shows that the 3 wt % T-silica would be more advantageous for enhancing the overall performance of the PI film.

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Supporting Information Available: FT-IR spectra, AFM images, and TGA curves for pure PI and T-silica/PI composite films; XRD patterns of pure PI, T-silica/PI composite films, and silica tubes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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