

Novel Polyimide/Silica Nanohybrids from Water Glass

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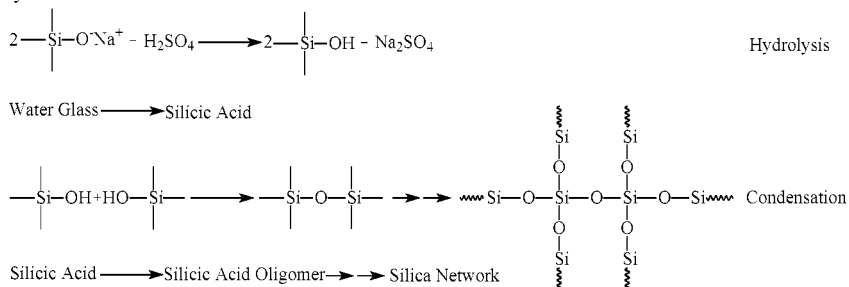
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Summary

Polyimide/silica hybrid materials were prepared via a novel sol-gel route using silicic acid oligomer (SAO) extracted from water glass. The decomposition temperatures of the hybrid samples were higher than pure polyimide. The transparency of the hybrid films could be maintained at up to 40 wt.-% silica content with the addition of γ -aminopropyltriethoxysilane (APTES). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) results confirmed the formation and dispersion of nanometer-scale size of inorganic particles within polyimide matrix with APTES. The coefficients of thermal expansion (CTEs) of the hybrid films were lower than pure polyimide and decreased with the increasing content of silica.

Introduction

Aromatic polyimides (PIs) are already widely used in aerospace, electrical and microelectronics industries because of their outstanding dielectric and mechanical properties at elevated temperatures [1-5]. However, some of their microelectronic applications like insulating layers in multichip semiconductor packaging are limited by their relatively high water sorption and CTE. On the other hand, inorganic materials such as silica exhibit very low water sorption and CTE, but high brittleness and poor film-forming characteristics [6]. The incorporation of well-dispersed silica particles into PI matrix has been proved an effective way to improve the thermal and mechanical properties of PI [7]. For some special applications like optical and optoelectronics, nanohybrids of polyimide/silica are in extreme need, not only for the transparency but the improved electrical, electro-optical, non-linear optical and other properties [8]. One promising approach for the preparation of the organic/silica hybrid materials is sol-gel process, which normally consists of two steps: first, the hydrolysis of alkoxy silane, and second, the polycondensation of the hydrolysis products [9]. Nevertheless, there still remain some drawbacks of the conventional sol-gel process such as using expensive alkoxy silane precursors, demanding adsorbent water and acid. In this communication, we present a convenient and economic sol-gel route for the preparation of polyimide/silica hybrid materials using SAO, which is extracted from water glass, as an abundant and more affordable silica precursor. The procedure of water glass to silica network via silicic acid was depicted in scheme 1. Abe et al. first studied the preparation of polysiloxane from silicic acid and the polycondensation of silicic acid in tetrahydrofuran (THF) [10-11]. Habsuda et al. prepared the composites from poly (silicic acid) and 2-hydroxyethyl methacrylate [12]. To the best of our knowledge, there is no report on the fabrication of PI/silica hybrid materials from SAO.



Scheme 1. The reaction process of water glass to silica network via SAO

Experimental

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) and γ -aminopropyltriethoxysilane (APTES, analytical reagent grade) were all purchased from Shanghai Chemical Reagents Company, China National Medicines (Group), Shanghai, China and used without 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.

Instruments

The picture showing the transparency of the PI and PI/silica hybrid films (Figure 1) was scanned with a Microtek X6 flat platform scanner. The molecular weight of SAO was monitored by a Perkin-Elmer Series 200 GPC equipped with 2 PL-gel columns using polystyrene as calibration standard. The morphologies of the silica particles within SAO solution and the hybrid films were observed with a Hitachi H-600 transmission electron microscope (TEM) and a JSM-5600LV scanning electron microscope (SEM). The SAO specimen for TEM was prepared by depositing a drop of SAO-THF solution onto carbon-coated copper grids and drying *in vacuo*. PI/silica hybrid specimens for TEM were encapsulated with epoxy resin followed by ultra-thin sectioning. The hybrid film samples for SEM were fractured at liquid nitrogen temperature. The CTEs of the PI and PI/silica hybrids were measured on a NETZSCH TMA 202 cell at a heating rate of 10°C/min. 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 30 to 800°C.

Preparation of silicic acid precursor

The silicic acid precursor was prepared according to the method slightly modified from Abe's in ref. 11. Briefly, a 3.2mol/l water glass solution was adjusted to PH 2.0 with 1.0mol/l H₂SO₄ aqueous solution under stirring at ambient condition. This solution was saturated with NaCl. And then an equal volume of THF was added with stirring. Before the organic layer was separated and dried over 4 Å molecular sieve, the mixture was stored at 10°C for half an hour. The silica content of the SAO-THF solution was determined to be 12.7wt.-% by TGA, assuming that all the silicic acid was transformed into silica at 800°C, the end point of the test. And the number average molecular weight (M_n) of SAO was 290, determined by GPC.

Preparation of polyamic acid (PAA)

PAA was prepared by stirring 0.7496mol pyromellitic dianhydride (PMDA) and 0.7491mol 4, 4'-oxydianiline (ODA) in DMAc under nitrogen atmosphere and room temperature for 10 hours. The final concentration of the viscous and clear PAA solution was 10wt.-%.

Preparation of PI/silica hybrid films

The PI/silica hybrid films were obtained by the imidization of PAA in the presence of SAO. A mixture of PAA-DMAc solution and SAO-THF solution was stirred at room temperature for 5 hours and then cast on a glass substrate. After thermal treatment at 60°C for 3 hours, 100°C for 1 hour, 200°C for 1 hour and 300°C for 4 hours in air, the imidized films were removed from the glass substrates and their thickness was around 20µm. The recipes for the PI/silica hybrid films are listed in table 1.

Results and discussion

Figure 1 shows the optical properties of PI and some typical PI/silica hybrid films. Other samples' results are summarized in Table 1. Generally, PI and PI/silica hybrid films with silica content lower than 10wt.-% are transparent. While the hybrid films become opaque with silica content above 20wt.-% because of the phase separation during the forming of the Si-O-Si inorganic network. This result is consistent with Kakimoto's result of PI/silica hybrids using TEOS as silica precursor and the same type of PAA [13]. It has been reported that the critical point of the

transparency of PI/silica hybrid films from alkoxy silane precursors can be shifted to 20wt.-% or even 30wt.-%, by using APTES or γ -glycidyoxypropyltrimethoxysilane (GPTMS) as the coupling agent between the PI backbone and SiO₂ network, respectively [8,14]. Here we succeed in preparing a transparent PI/silica hybrid film with 40wt.-% silica content using SAO as new silica precursor and APTES as coupling agent, which indicating the improved compatibility between PI and inorganic phase and a better dispersion of the silica particles in PI matrix. Because the amino group of APTES can react with the carboxyl end group of PAA because of excessive PMDA, and the other end of APTES can hydrolyze to afford silanol groups that can polycondense with SAO, thus after the imidization reaction there exist some covalent linkages between the PI backbone and the silica network. Because of this, the aggregation of the silica particles can be limited to a considerable extent, and a much better dispersion in PI matrix can be achieved.

From table 1, it can also be found that like previously reported silica-containing polyimide hybrids from alkoxy silane precursor the decomposition temperature of the hybrid samples are higher than pure polyimide [15], and even higher by the addition of APTES.

Table 1. The recipe for the PI/silica nanocomposites

Sample ^a	Silica Content ^b (wt.-%)	APTES Content (wt.-%)	Decomposition Temperature ^c (°C)	Ash ^c (wt.-%)	Remarks ^d
PI 0/0	0	0	551.3	0	T
PI 5/0	5	0	563.6	4.8	T
PI 10/0	10	0	564.0	9.6	T
PI 20/0	20	0	555.6	19.8	O
PI 20/2	20	2	566.2	19.5	T
PI 30/0	30	0	552.1	29.2	O
PI 40/0	40	0	554.8	38.5	O
PI 40/8	40	8	557.0	37.1	T

^a The number before the slash denotes the silica weight content in the hybrids and the number after denotes the APTES weight content; ^b Silica content was calculated from the silica content of the SAO-THF solution and the additive quantities of APTES; ^c Temperature at 10 wt.-% loss in weight of the samples and the residual ash determined by TGA; ^d Abbreviation: T, transparent; O, opaque

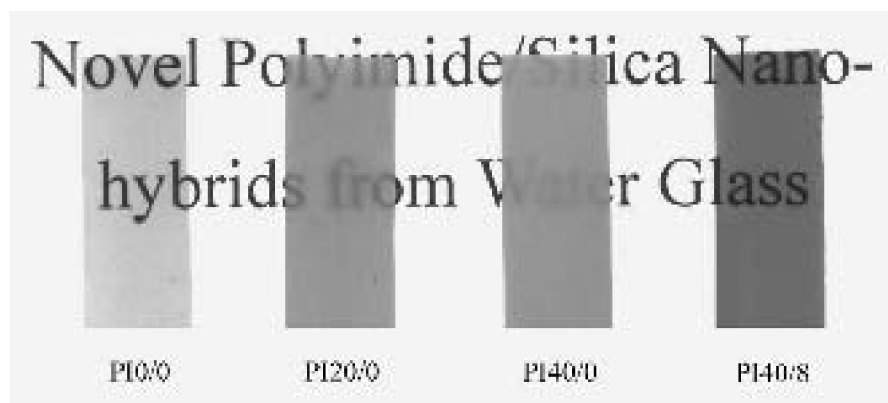
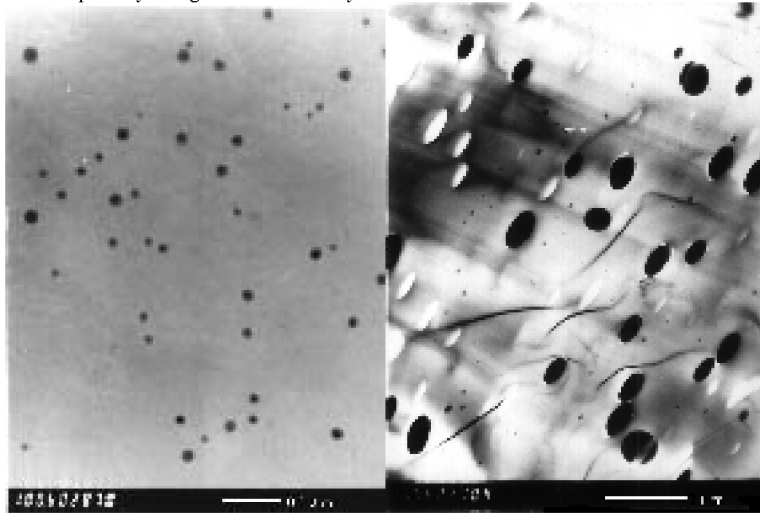


Figure 1. The optical properties of PI film and PI/silica hybrid films

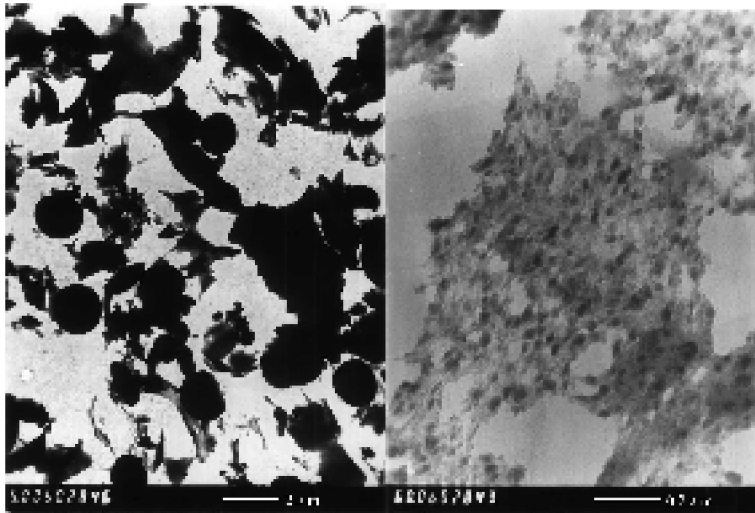
TEM images of the SAO solution and PI/silica hybrid films are shown in Figure 2. Figure 2a shows that the silica particle size with SAO solution is about 10 nm indicating the condensation degree of silicic acid is quite low in fresh prepared SAO solution. This consists with the low M_n results of SAO from GPC analysis. The hybrid film sample with lower silica content has smaller particle size. The silica particle size of the hybrid sample with 10 wt.-% silica is about 0.2-0.4 μm , while that of the sample with 40 wt.-% silica is increased to nearly 2 μm (Fig. 2b and 2c).

However, with the addition of 8 wt.-% of APTES, The silica particle size is greatly reduced to about 30 nm (Fig. 2d) which is much less than the wavelength of the visible light and close to the original silica particle size in the original SAO solution. This is the reason of the improvement of the transparency at high silica content by APTES.



a)

b)

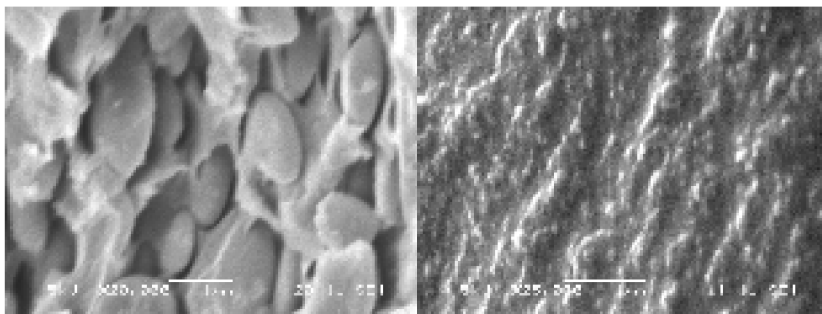


c)

d)

Figure 2. TEM images of the SAO-THF solution (a) and PI/silica hybrid films PI 10/0(b), PI 40/0 (c) and PI 40/8(d)

The results of SEM studies on the morphological structures of the hybrid films are consistent with the TEM results. Figure 3 shows the SEM images of the fracture surfaces of PI/silica hybrid films with 40 wt.-% silica without and with APTES (PI 40/0 and PI 40/8). It can be observed that the phase separation between PI and silica is greatly restricted with the addition of APTES and the compatibility is remarkably improved.



a)

b)

Figure 3. SEM images of the fracture surfaces of PI/silica hybrid films PI 40/0(a) and PI 40/8(b)

For the electronic packaging application, the thermal expansion of PI should be reduced. The influence of silica content on CTEs of the PI/silica hybrid films was studied at various temperatures and the results are illustrated in Figure 4. The CTEs of all the hybrid samples are lower than that of the pure PI at the full temperature range studied, whereas this reduction effect on CTEs tends to a certain limitation when the silica content is high enough (The CTEs of PI 30/0 and PI 40/0 being almost equal). The CTE of the sample with 5 wt.-% silica increases with increasing temperature, which is characteristic for pure PI. But this trend reverses on the samples with higher silica content. The reason of this phenomenon is perhaps that the inorganic particles dispersed in PI matrix restrict the thermal expansion of PI effectively, especially at elevated temperatures.

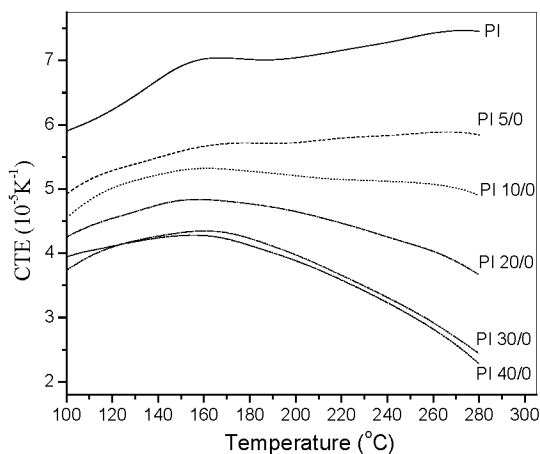


Figure 4. Effect of temperature on CTEs of PI/silica hybrid films

Conclusions

We have presented in this communication the synthesis of polyimide/silica hybrid films via a novel sol-gel route using silicic acid oligomer extracted from water glass as silica precursor. The decomposition temperature of the hybrid samples are higher than pure PI. By using APTES as coupling agent, the hybrid films keep their transparency at up to 40wt.-% silica content due to the formation of nanometer scale size of inorganic particles and their better dispersion in polyimide matrix. The coefficients of thermal expansion (CTEs) of the hybrid films are lower than pure polyimide and decrease with increasing silica content.

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