

Preparation and characteristic of a new class of silica/polyimide nanocomposites

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A new class of silica/polyimide nanocomposites was successfully prepared by the sol-gel reaction, tetraethoxysilane, (TEOS), was hydrolyzed by the water released from imidization at low and high temperature. Silica particles with diameter of around 30–50 nm were observed in the hybrid films by scanning electron microscopy. The flame retardance, decomposition temperature and glass transition temperature of the film increased with increasing silica content. The tensile strength increased slightly while the elongation at break of the films decreased with increasing silica content.

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1. Introduction

Polyimides with outstanding characteristics are used widely in various fields as matrix resins, adhesives, coatings, and so on. Especially, polyimide is one of a variety of thermoplastic polymers used in high temperature environment [1]. A requirement for flame resistance is very essential [2–4]. Fire resistant agents are commonly used to improve flame resistance of polyimides, but the addition of the fire-resistant agents may affect the mechanical properties of the composites, and most of them might emit toxic gas and smoke when polyimides are burned. Particularly at high temperature the fire-resistant agents could be decomposed. Silicon oxide and polymer hybrid materials can be made with uniquely low dielectric constants, low thermal expansion coefficients and high flame retardancy, without sacrificing their high-temperature characteristics and may exhibit advantages over them [5–8]. The key problem is how to make small silica particles and disperse them homogeneously.

In recent years, the sol-gel process has been employed; not only can it prepare organic/inorganic composites, but also can provide high-performance materials at lower temperature and lower cost [9–12]. Polyimide-silica composites have been synthesized [13], but the diameter of the silica particles is around 5 μm . Tetraethoxysilane (TEOS) was hydrolyzed by adding water.

In this paper, we report the first successful preparation of silica-polyimides nanocomposites with diameter of silica 30–50 nm, and the TEOS is hydrolysed by the water released from imidization at low and high temperature. The mechanical properties, thermal behavior and flame-retardance of the above-mentioned silica/polyimide nanocomposites were studied.

2. Experimental

2.1. Materials

Benzophenone tetracarboxylic acid dianhydride (BTDA) was vacuum dried, 4, 4'-oxyphenyl diamine (4-aminophenyl ether, 4ODA) was recrystallized twice from acetone prior to use. Tetraethoxysilane (TEOS) was used without further purification. *N,N*-dimethylacetamide (DMAc) was purified by stirring with calcium hydride for 8 h and distilling under reduced pressure.

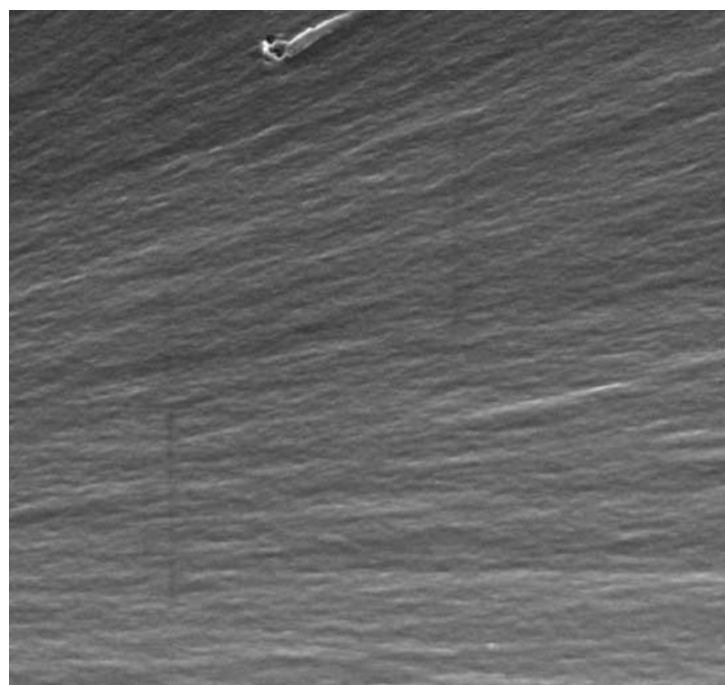
2.2. Synthesis

2.2.1. Preparation of BTDA-4ODA polyimide

To a 250 ml flask were added 12.26 g 4ODA and 19.53 g BTDA. The system was purified, alternating nitrogen and vacuum, several times before fresh DMAc was added. Solid concentration was kept at about 20%. The mixture was stirred at room temperature under nitrogen for about 8 h to allow the viscosity to increase. A film was prepared by casting the solution on a glass plate. After the film had been dried at 100°C for 1 h, the film was heated at 200°C and 300°C for 1 h respectively.

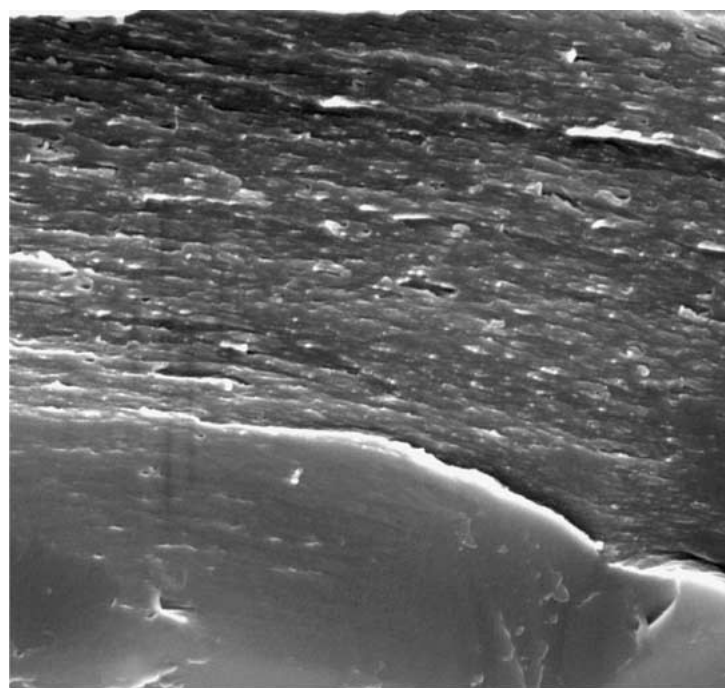
2.2.2. Preparation of polyimide/silica nanocomposite

In a flask, 1.55 g of tetraethoxysilane (TEOS) was added to 20.00 g of 10 wt% solution of polyamic acid in DMAc. The heterogeneous solution was stirred for 8 h until the solution became homogeneous. A film was prepared by casting the solution on a glass plate. After the film had been dried at 100°C for 1 h, the film was heated at 200°C and 300°C for 1 h, respectively.



DJ0 98-05-05
20 KV X 4 K WD:7 mm 6 um

(a)



DJ16 98-05-05
20 KV X4 K WD:7 mm 6 um

(b)

Figure 1 Scanning electron micrographs of polyimide-silica hybrid films. (a) and (b) polyimide films containing 0, 16%.

2.3. Characterization

2.3.1. Infrared analysis

The IR spectra were recorded in thin polymer films on a JASCO FT/IR-5000 spectrophotometer. Sample preparation of thin polymer films was carried out as above mentioned.

2.3.2. Mechanical experiments

The mechanical experiments were conducted with a Shimadzu AG-2000A mechanical tester to determine the elongation at break and tensile strength as a function of the content of silica in polyimide-silica hybrid films. Microdumbbells 10 mm in length were the designated

TABLE I Preparation of polyimide-silica hybrid films^a

Code	PAA (g)	TEOS (g)	Silica ^b (wt%)	Remarks ^c
1	12	0	0	T
2	12	0.21	3	T
3	12	0.78	10	T
4	12	1.21	15	T
5	12	1.68	19	HT

^a20 wt% DMAc solution.

^bCalculated silica content in the hybrid films.

^cT, transparent; HT, half transparent.

sample size and a 20%/min initial extension rate was utilized.

2.3.3. Thermogravimetric analysis

Thermogravimetric analysis measurements were carried out using Shimadzu-DT30 apparatus, the conditions used were as follows: sample weight, Ca 10 mg; heating rate, 10 K min⁻¹ in static air atmosphere.

2.3.4. Morphological evaluations

Cured samples were fractured just after being removed from liquid nitrogen. The fracture surfaces were gold plated (about 20 nm by sputtering) and examined in a scanning electron microscope (ISI MSM-5 "min SEM").

2.3.5. Flammability measurements

Flammability was measured using Stanton Redcroft Critical Oxygen Index equipment designed to meet ASTM D2863 Specifications.

3. Results and discussion

The mechanism of poly(amide-acid) degradation has not been discussed in detail, but appears to entail hydrolysis. Since the sol-gel reaction requires water to hydrolyze TEOS, there might be a possibility that polyamic acid is also susceptible to hydrolysis by the added water. When a solution of polyamic acid in DMAc is stirred in the presence of the same amount water as in the case of the sol-gel reaction, the silica particles form heterogeneously and with a large diameter of around 5 μm [13]. If the water released from imidization at low and high temperature is employed, the tendency for reduction of molecular weight could be inhibited. Especially, since the water is released slowly by the imidization, the silica particles could form homogeneously and small.

The results of preparation of polyimide-silica nanocomposites are summarized in Table I. The silica content in the table denotes the values calculated by assuming that the sol-gel reaction proceeded completely.

The polymers of codes 1, 2, 3 and 4 gave pale yellow, clear, and flexible films by casting from the DMAc solution, and the films containing silica 19 wt% (code 5) were half transparent. It showed that the diameter of

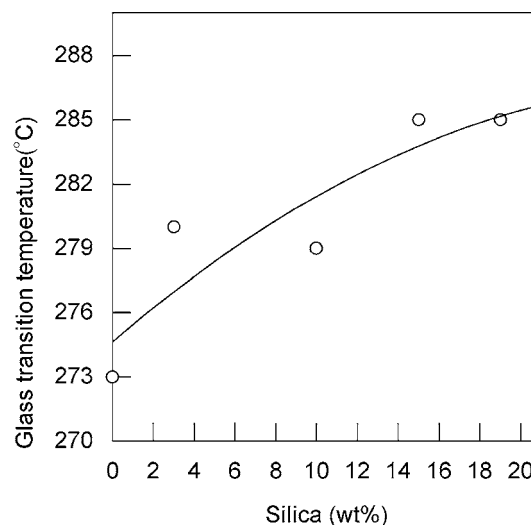


Figure 2 Relationship between T_g and silica content in polyimide-silica hybrid films.

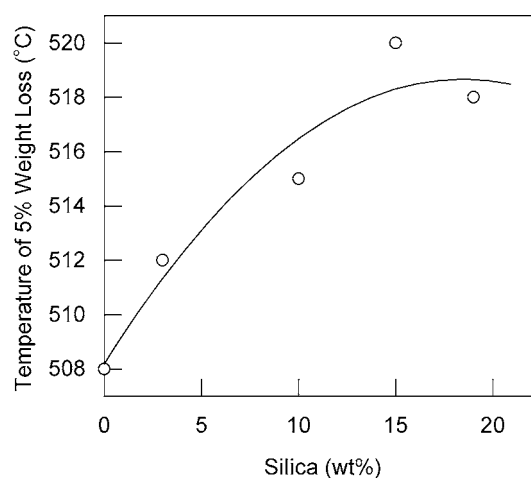


Figure 3 Relationship between temperatures of 5% weight loss and silica content in polyimide-silica hybrid films.

silica particles was smaller than the wavelength (400–700 nm) of visible light.

The size and distribution of silica particles were confirmed by means of the scanning electron microscopic (SEM). Fig. 1 shows the SEM photographs of the cross section of the hybrid films. The silica particles could be seen as white beads having a diameter of 30–50 nm, and dispersed homogeneously.

The chemical structure of the matrix polymer was confirmed by means of IR spectroscopy. The conversion was confirmed to be 100% by the disappearance of the infrared band amide carbonyl at 1650 cm⁻¹ and the appearance of the characteristic cyclic imide carbonyl bands at 1720 and 1780 cm⁻¹.

Fig. 2 shows the glass transition temperatures of five silica/polyimide nanocomposites. The T_g increased slightly as a function of silica content. This suggested that macromolecular chains in silica/polyimide nanocomposites had similar flexibility as those in polyimides.

Fig. 3 shows the thermogravimetric analysis of the five composites. The temperatures for 5% weight loss in silica/polyimide nanocomposites were higher than that

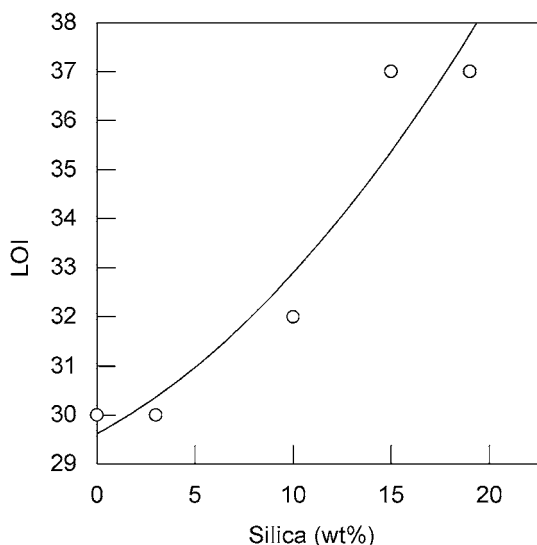


Figure 4 Relationship between LOI and silica content in polyimide-silica hybrid films.

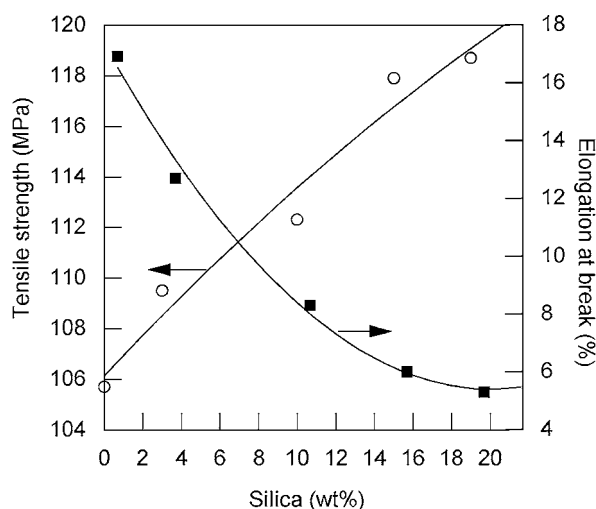


Figure 5 Relationship of tensile strength and elongation at break with silica content in polyimide-silica hybrid films.

for the polyimide, and changed slightly with increasing silica content. It indicated that the stabilization was higher for nanocomposites containing silica than that for polyimide alone.

The relationship between silica content and flame retardancy has been discussed. The flame-retardant properties of these composites were examined by measuring the limiting oxygen index (LOI). As can be seen from Fig. 4, the polyimide had LOI value of about 30, the LOI values of silica/polyimide nanocomposites were higher than that of polyimide, and an increase in LOI values with the increase of silica contents was observed.

Polyimides are commonly used in high temperature environments, in which the common fire resistant agents would be decomposed and, even emit toxic gas and smoke. The silica in composites not only can produce a siloxane network in organic matrices but also may be formed on the surface [14], and could delay the transmission of the flame and heat; moreover, volatilization of degradation products was avoided. So the sol-gel process for preparation of polyimide with nanosilica was a good method to improve fire resistance for polyimides.

Mechanical properties of silica/polyimide nanocomposites are shown in Fig. 5. It can be seen that the tensile strength changed slightly and elongation at break decreased gradually with increasing silica content. This phenomenon was probably explained by the incorporation of silica particles that would destroy the continuity of organic matrices. Another aspect, is that the silica particles are likely to adhere well to the polymer because of their nanosize.

In conclusion, silica/polyimide nanocomposites were successfully prepared by the sol-gel reaction starting from TEOS hydrolyzed by the water released from imidization at low and high temperature. The sol-gel process was an effective method to prepare organic-inorganic nanocomposites, which can provide high-performance materials at a relatively low temperature and easy process.

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