

Research on Heat Resistance of Hyperbranched Organosilicone-modified Polyimide Films

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Abstract

A series of novel polyimide-silica hybrid thin films were synthesized from pyromellitic dianhydride(PMDA), 4, 4'-oxydianiline(ODA) and hyperbranched organosilicon polymers containing polybasic amine via thermal imidiazation. And hyperbranched organosilicon polymers above were prepared using aqua pura, γ -aminopropyltriethoxysilan and tetraethoxysilane. The polyimide-silica hybrid thin films were analyzed and characterized by FTIR and TGA, and the physical properties of hybrid thin films were tested. Results revealed that the content of element Si increased and the color and transmittance of hybrid thin films changed from transparent light yellow to translucent dark yellow with the increasing mass fraction of hyperbranched organosilicon polymers. The TGA results showed that the temperature of hybrid materials increased with increasing mass fraction of hyperbranched organosilicon polymers the at 5% weight loss. Polyimide-silica hybrid thin films showed excellent heat resistance.

Keywords: polyimide films; hybrid; hyperbranched organosilicon

Polyimides (PIs) are utilized in a wide range of advanced technologies in the microelectronic, aerospace and automotive industries because of their excellent mechanical properties, high thermal stability, good electrical properties and good resistance to organic solvents [1]. Polyimides have been recognized as high-temperature polymers for optoelectronics due to their excellent thermal stability, chemical resistance, mechanical properties, and dielectric properties. Different polyimide-silica hybrids have been prepared [2], which show outstanding thermal stability and mechanical strength. The transparency of the polyimide-silica hybrids prepared without a coupling agent was limited to the silica content [3]. Above this value, silica particles larger than 1 μ m were observed and the hybrid materials became opaque. To enhance the interaction between the organic moiety and the inorganic network, a coupling agent [4] was added to connect the polyimide and silica.

The modification of PI structure is a major research interest. Some general approaches have an emphasis on reducing molecular regularity, rigidity and cohesive energy density. There are many approaches to modify PI properties, particularly, such as replacing aromatic groups with alicyclic groups, using meta-substituted phenyl monomers, and introducing fluorinated groups. Although PI synthesized from PMDA and ODA is well known, few papers deals with the chemical modification of this famous PI [5]. Most deal with PI/inorganic hybrid materials.

In this study, hyperbranched organosilicon polymers containing amine was synthesized, containing amines groups to copolymerize with ODA and PMDA in an attempt to modify polyimides and obtain special property polyimides, which could have high T_g, high functionality and excellent heat resistance properties. The effects of various contents of hyperbranched organosilicon polymers on the thermal, mechanical properties of PI copolymers were also studied.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA, 99%, analytical reagent grade) was sublimated and

4,4'-oxydianiline (ODA, 99%, analytical reagent grade) was dried under vacuum for 2 h at 120°C. N,N-dimethylacetamide (DMAc, analytical reagent grade, 99.5%, analytical reagent grade) was vacuum distilled from CaH₂. γ -aminopropyltriethoxysilan (KH-550, analytical grade), tetraethoxysilane (TEOS, analytical grade) were all used as received.

Preparation of hyperbranched silicone polymers [6-8]

Hyperbranched silicone polymers were prepared by hydrolysis reactions of deionized water, KH-550 and TEOS. A certain amount of KH-550 and TEOS were added into the reactor with stirring, thermometer and condenser at room temperature. Then a small amount of ammonia as catalyst was added and stirred, even deionized water was dropped within 20 min. The molar ratio of deionized water and silane monomer was 1.3. After 30 min, the mixture was heated to 50°C for 2h. Then the mixture was heated to 55°C under -0.075MPa pressure, and alcohol of reaction was removed, the liquid of a certain viscosity was obtained. That liquid was the hyperbranched silicone polymers. Amine content: 0.36mmol/g

The FTIR spectra of the hyperbranched silicone polymers are shown in Figure 1. IR (KBr): ~3390 cm⁻¹ (—NH₂ stretching); ~1128 cm⁻¹ (Si—O—Si). The TGA curve of hyperbranched silicone polymers is shown in Figure 2. Hyperbranched silicone polymers have a good heat resistance from the TGA curve.

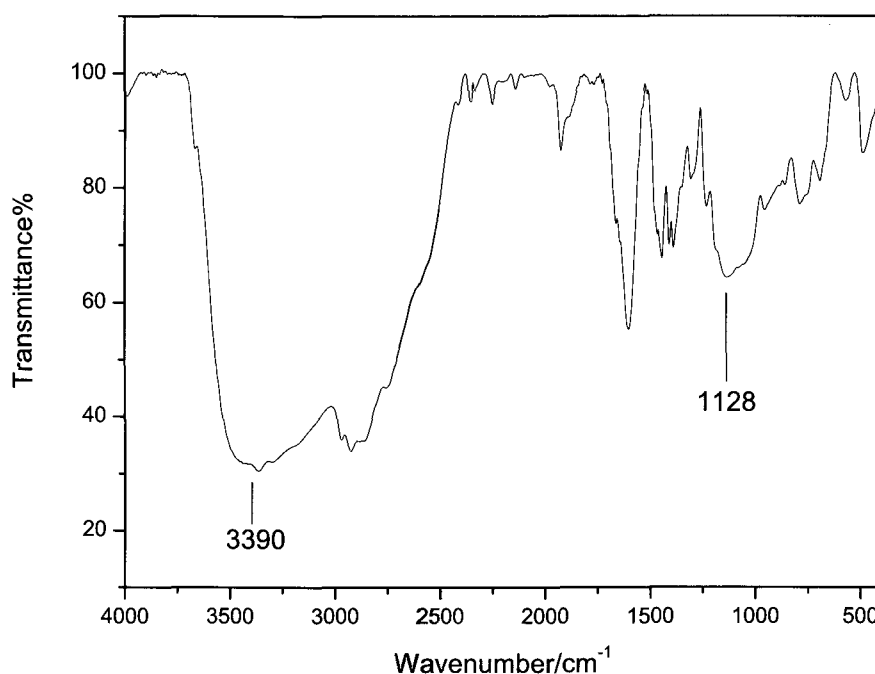


Figure 1 FTIR spectra of hyperbranched silicone polymers containing amine

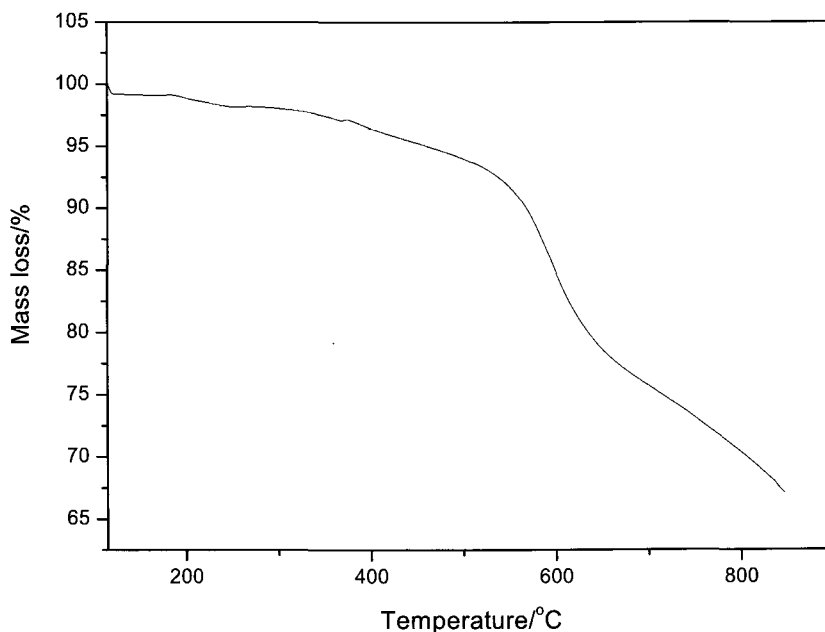


Figure 2 TGA curve of hyperbranched silicone polymers

Preparation of Polyimide-silica hybrid thin films

The copolyimides were synthesized by reacting hyperbranched silicone polymers and ODA with PMDA.

A 150ml three-necked flask fitted with a stirrer, argon inlet, drying tube and stopper, was purged with dry nitrogen for 30 min. Various molar ratios of organosilicon polymers and ODA were charged into the reactor through an addition funnel (the amounts used are listed in the **Table 1**). The vessel was then charged with DMAc (36 g, solid content 15%), PMDA (3.27 g, 0.015 mol) was added to the reactor in three portions, 40%, 30% and 30%, respectively, through another addition funnel over a period of 1 h until complete dissolution of the diamines was achieved. The reaction mixture was stirred at 20°C in a dry nitrogen atmosphere resulting in a viscous copolyamic acid solution after 24h. The precursor solutions may be stored in dry bottles at -5°C under nitrogen atmosphere [9].

The precursor solutions were cast onto a glass substrate using a hand-coater system. The poly (amic acid) films were heated at 80°C in a forced air for 1h to move most of the solvent. Then they were converted to the copolyimide with a heating program of 90°C for 30min, then 150°C for 40min, 220°C for 1h and 360°C for 1h. The films were then cooled to room temperature, soaked in water and stripped from the plates. After drying the films at 120°C for 8h in vacuum, the light-yellow PI₀ and copolyimide films denoted PI1-4 in Table 1 were obtained.

Table 1 Monomer compositions used for copolyimide synthesis

Polymer Code	PMDA (mol%)	ODA (mol%)	PSA (mol%)
PI0	1.00	1.00	0.00

PI1	1.00	0.99	0.01
PI2	1.00	0.95	0.05
PI3	1.00	0.90	0.10
PI4	1.00	0.85	0.15

RESULTS AND DISCUSSION

Table 2 summarized the tensile properties of polyimide film obtained from the stress-strain curves. The introduction of hyperbranched silicone polymers containing amine caused the tensile strength to decrease (from 145 MPa to 98 MPa). When the content of hyperbranched silicone polymers was lower, the changes of copolyimides films characteristics were not more significant. But the effects of characteristics became obvious with hyperbranched silicone polymers content increased.

Table 2 Heat resistance and mechanical properties and color of copolyimides

Polymer Code	Tensile properties			5% mass loss Temperature(°C)	Color
	Tensile strength(MPa)	Elongation at break(%)	Initial Modulus(GPa)		
PI0	145	40	2.32	480	Light yellow
PI1	140	38	2.38	485	Yellow
PI2	130	30	2.91	496	Orange
PI3	112	23	3.32	504	Reddish brown
PI4	98	16	3.62	512	Deep reddish brown

This resulted in greater separation between chains, reducing the strength of the interchain interactions, and decreasing the elongation at break (from 40% to 16%). The polymer became rigid because the strain was reduced considerably more than the tensile strength, while maintaining a higher initial modulus (from 2.32 GPa to 3.62 GPa). The polymer materials thus changed from strong and flexible to strong and rigid as the content of hyperbranched silicone polymers increased. Nonetheless, the values of modulus and tensile strength measured on these copolyimides corresponded to fairly good mechanical properties.

The temperatures of 5% mass loss increased with the increasing content of hyperbranched silicone polymers (480 °C~512°C) in **Table 2**. So polyimide-silica hybrid thin films showed an excellent heat resistance.

The color of polyimide/copolyimide films were presented in **Table 2**. The color of hybrid thin films changed from light yellow to deep reddish brown with the increasing mass fraction of hyperbranched silicone polymers, but the hybrid thin films were transparent. The color in copolyimides might have many origins, including presence of chromophoric units, colored impurities from starting materials (dianhydrides and diamines), and side reactions that form isoimides and charge-transfer complexes. (Next see p122)