Preparation and Characteristics of Nonflammable Polyimide Materials

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ABSTRACT: The thermal and flame-retardant properties of homo- and copolyimides were evaluated. Those containing sulfone linkages in the backbone were found to be more flame retardant. Both properties were dependent on the composition. A polyimide/silica nanocomposite was obtained through sol–gel processing. The effects of the addition of silica on the dispersion, interfacial adhesion, fire resistance, mechanical properties, and thermal stability of the composites were investigated. SEM analysis showed a good dispersion of silica with a diameter of 50–300 nm in the organic matrices. The addition of silica increased the fire retardancy and mechanical properties of the composites. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 384–389, 2000

Key words: nanocomposites; fire retardancy; mechanical properties; polyimide; silica

INTRODUCTION

Polyimides have aroused considerable interest in recent years because of their outstanding thermal stability and good mechanical properties. Currently, fire safety requirements are of particular interest, especially in the aircraft, aerospace, and electronics industries.[1,2] To produce a fire-safe polyimide, the most commonly used way is to add a fire-retardant agent to the polymer in a physical fashion. The additives include aluminum trihydrate, magnesium hydroxide, halogens, phosphorus, and antimony, but they offer disadvantages due to toxicity and loading.

The most desirable solution to the problem is to develop fire-resistant, low smoke emitting, low toxicity, cost-effective materials in a chemical fashion. Two ways of meeting these requirements are

1. The introduction of heterocyclic rings, sulfone, silicone, nitrogen, phosphorous, and boron into the backbone which may influence the flame resistance of the polymer. Earlier work with polycarbonate epoxy, polyamide, and phenol resins indicated these improvements.[3–10]

2. The sol–gel reaction, which has been applied to the reaction in the polymer matrix to prepare inorganic and organic hybrid materials. Polymer/silica nanocomposites have been obtained from tetraethyoxysilane and the polymers such as polyamide 6,[11] polyoxytetramethylene,[12] polyoxyethylene,[13] sodium poly(4-styrene sulfonate),[14] perfluorosufonic acid ionomer,[15] and poly-(ether ketone).[16] Most of the interest in this method is focused on the dispersion and the adhesion of the inorganic particles of the composites. McGrath et al. reported preferential migration of silica in composites to the polymer film surface,[5] so silica formed on the surface of a burning polymer may serve as a heat shield to retard further decomposition of the polymer, thus increasing the heat and flame resistance of polymeric materials.

For this article, we synthesized a copolyimide series by condensation of benzophenonetetracarboxylic acid dianhydride and the two diamine monomers (4,4′-oxydianiline and 4,4′-diaminodiphenyl sulfone). The ratios of two diamine monomers were varied systematically. The flammability, thermal stability, and mechanical properties were evaluated as a function of these ratios. In addition, a sol–gel process was employed to prepare copolyimide/silica nanocomposites. Their flammability, thermal behavior, and mechanical properties that change with the dispersion of silica are also discussed.

EXPERIMENTAL

Materials

Benzophenonetetracarboxylic acid dianhydride (BTDA) was vacuum-dried and 4,4′- diaminodiphenyl sulfone (4DDS) and 4,4′-oxydianiline (4-aminophenyl ether, 4ODA) were recrystallized twice from acetone before their 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.

Synthesis

BTDA–4DDS Polyimide

The synthesis essentially followed the technique reported by Summers.[17] To a 250-mL flask were added 6 g (24.16 mol) 4DDS and 7.7989 g (24.20 mol) BTDA. The system was purged, alternating nitrogen and a vacuum several times, before fresh DMAc was added. The 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. The film was prepared by casting the solution onto a glass plate. After the film had been dried at 100°C for 1 h, the film was heated at 200 and 300°C for 1 h each.

BTDA–ODA Polyimide

The preparation of the BTDA–ODA polyimide film was similar to that of the BTDA–4DDS polyimide film.

BTDA–4DDS/ODA Copolyimide

In a typical example, to a 250-mL flask were added 3 g (12.082 mmol) 4DDS, 2.4193 g (12.082 mmol) 4ODA, and 7.798 g (24.20 mol) BTDA. The system was then purged, alternating nitrogen and a vacuum several times, before fresh DMAc was added. The concentration was again held at about 20% solid. The reaction was allowed to continue for 8 h at room temperature under nitrogen. Poly(amic acid) copolymers with different mol ratios were synthesized in a similar way. The respective polyimide film was then obtained as the BTDA–4ODA polyimide film.

Preparation of Polyimide/Silica Nanocomposite

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

Measurements

Mechanical properties were examined by a Shimadzu AG-2000A mechanical tester with the tension rate at 5 mm/min. The glass transition temperature determination and thermogravimetry were performed with a Shimadzu thermal analyzer DT-30, using heating rates of 10°C/min. Scanning electron micrographs were obtained with a scanning electronic microscope.

RESULTS AND DISCUSSION

An attempt to produce fire-resistant polymers using monomers with bridge units such as sulfur, nitrogen, phosphorous, sulfone, and boron was successful. In this study, we utilized diamines containing sulfone linkages to potentially produce polyimides with improved thermal stability and nonflammability. The molecular structures of both BTDA–4ODA and BTDA–4DDS are shown in Scheme 1.

The molecular weights (as inferred from the viscosity) of the copolyimides generally increased with the contents of the 4ODA unit, and the viscosity of the poly(amic acid) of the BTDA–4ODA homopolymer was found to be highest in DMAc. Figure 1 shows the viscosity of the poly(amide acid) solution of homo- and copolyimides. Because the 4ODA is more reactive than is the diaminodiphenyl sulfone, the viscosity of the poly(amide

BDTA-4ODA

BDTA-4DDS
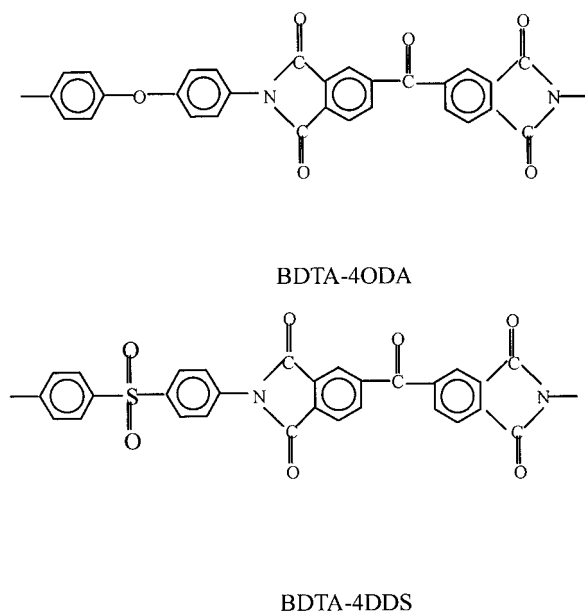
Scheme 1 Molecular structures of both BTDA–4ODA and BTDA–4DDS.

acid) solution of the BTDA–4DDS homopolymer was lower; the resultant film exhibited poor mechanical properties.

There appeared to be a correlation between the Limiting Oxygen Index (LOI) and the composition (mol %) of 4DDS/4ODA; the results for homo- and copolyimide are as in Figure 2. The LOI values
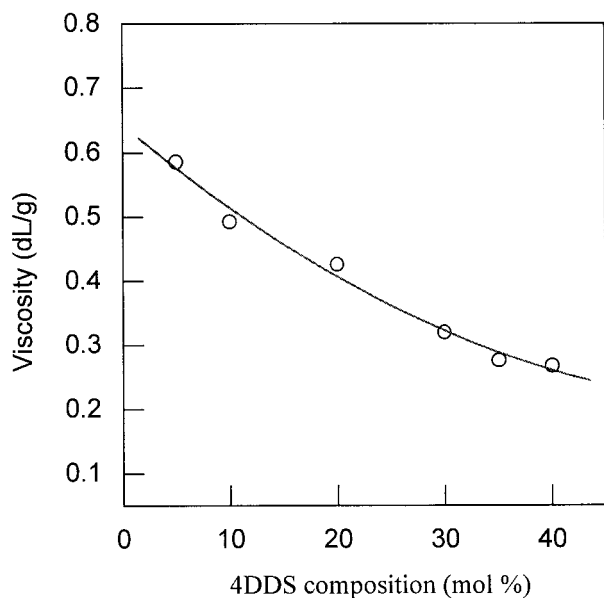

Figure 1 Viscosity of poly(amide acid) solution as a function of composition.
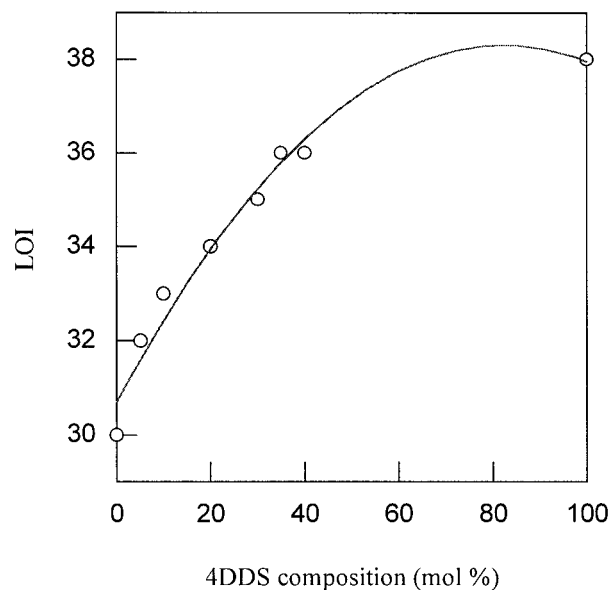

Figure 2 LOI of the copolyimides as a function of composition.

improved as the amount of the 4DDS unit increased. The LOI value of the BTDA–4ODA homopolymer is 30; a higher LOI value of 36 could be obtained when the 4DDS/4ODA ratio changed to 40/60 mol %, while the LOI value of the BTDA–4DDS homopolymer is only 38. The experimental results suggested that polyimide with sulfone linkage in the backbone should have higher flame retardancy.

For a better understanding of the flame retardancy, the thermal behavior of these composites was studied. Figure 3 shows the glass transition temperatures (T_g) of the polyimides. The glass transition temperature of the copolyimides varied only slightly with composition, indicating a similar flexibility of the polymer chains. Figure 4 shows the thermogravimetric analysis (TGA) of the polyimides. The temperature of 5% weight loss increased as a function of 4DDS content. It is noteworthy that the thermal stability is highly dependent upon the polymer structure, and the introduction of sulfone linkages into the main chain may increase the thermal stability of the polyimides.

Figures 5 and 6 show the mechanical properties of homo- and copolyimides. It can be seen that the tensile strength and elongation at break decreased gradually with increasing 4DDS content. To improve the mechanical properties of the copolyimides, we developed polyimide/silica nanocomposites by the sol–gel method.
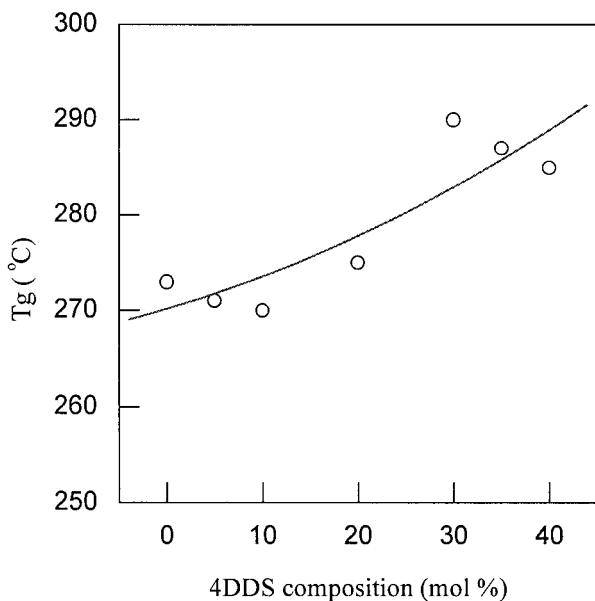
Figure 3 Glass transition temperatures of polyimides as a function of composition

Figure 5 Elongation as a function of composition.

To investigate the dispersion quality of silica particles, the morphology of the polyimide/silica nanocomposites were studied and the results are shown in Figure 7. The dispersed silica particles could be seen as white beads having a diameter of 100–300 nm. The particle size increased with increasing silica content.
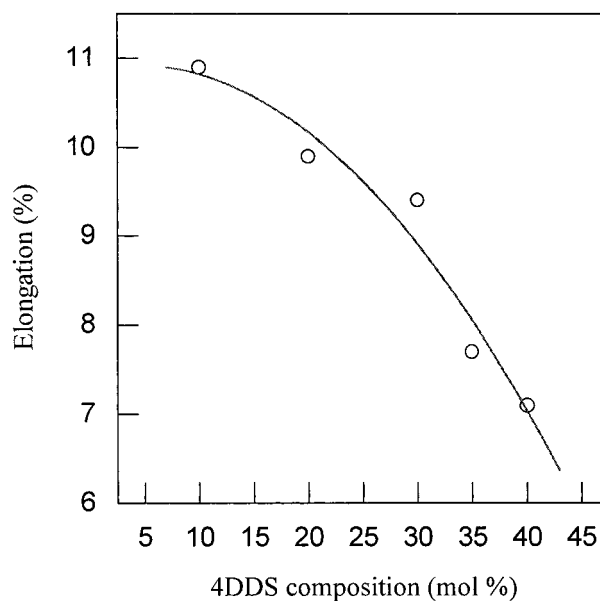
Table I shows the mechanical properties, flammability, and thermal resistance. Fire resistance increased remarkably with the content of silica, because silica in the composites produces an oxide network in organic matrices and forms a shield on the surface of a burning polymer to retard its further decomposition. The tensile strength decreased below 10 wt % silica content, whereas it increased significantly above 17 wt % silica content. The unique mechanical behavior of polyim-
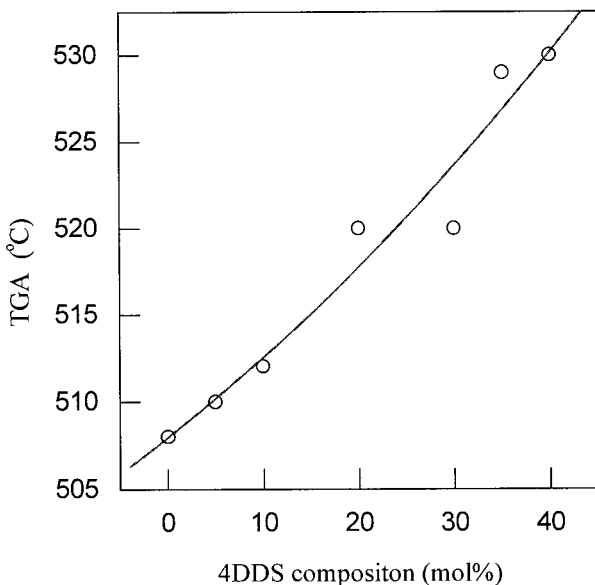

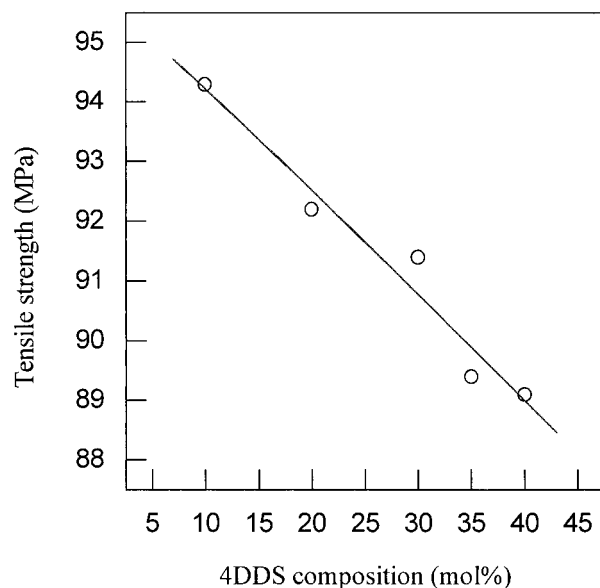**Figure 4** Correlation between thermal stability and content of 4DDS.

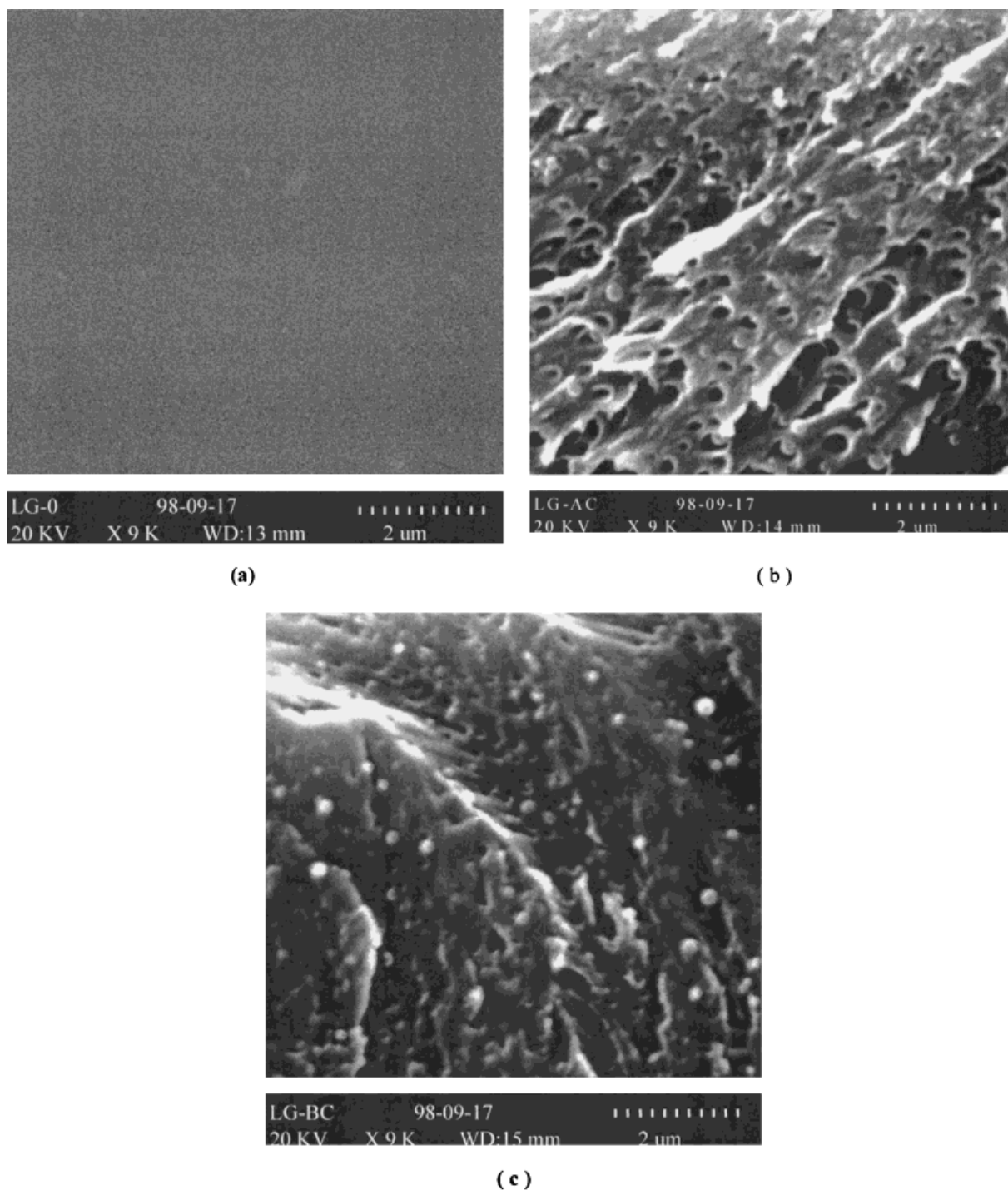**Figure 6** Tensile stress as a function of composition.

Figure 7 Photographs of scanning electron microscopy of copolyimides/silica hybrid film. Polyimide films containing (a) 0, (b) 10, and (c) 16 wt % of silica.

ide/silica nanocomposites resulted mainly from a good dispersion and interfacial adhesion of silica particles when the silica content was higher than 10 wt %. In addition, the thermal stability of the polyimide/silica nanocomposites was also found to be the same as that of the polyimides.

CONCLUSIONS

Homopolyimides and their copolyimides with high thermal stability were synthesized. There was an improvement in the LOI of the polyimides based on copolymerizing with a polyimide having

Table I Properties of Polyimide/Silica Nanocomposites

4DDS/4ODA Ration	Silica (wt %)	LOI	T_g (°C)	T_d (°C)	Tensile Strength (MPa)	Elongation (%)
35/65	0	36	287	529	89	7.7
35/65	10	41	282	505	75	6.3
35/65	17	43	288	520	112	5.6
35/65	28	44	292	530	115	5.2

fire-resistant segments, such as the BTDS–4DDS moiety. The thermal stability of the copolyimide was strongly dependent on the structure of both components and the copolymer composition.

Sol–gel processing was a good method for the preparation of polyimide/silica nanocomposites, which could avoid aggregation of the silica particles in the polymer matrices. SEM observation showed that silicas having a diameter of 50–300 nm disperse homogeneously in the organic matrix. The addition of silicas significantly increased the fire resistance and tensile strength of the copolyimide/silica nanocomposites and only slightly changed their thermal stability.

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