Polyimide–Silica Hybrid Materials Modified by Incorporation of an Organically Substituted Alkoxysilane

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Polyimide–silica hybrid materials were prepared by the *in situ* polymerization of tetramethoxysilane in a polyimide precursor (poly(amic acid)), which was subsequently cyclized at high temperatures. An organically substituted alkoxysilane, (aminophenyl)trimethoxysilane (APTMOS), was included to provide bonding sites between the polymer and the silica-like phase. The APTMOS was chosen for its high thermal stability (comparable to that of the polyimide) and its ability to undergo hydrolysis and polycondensation along with the tetramethoxysilane. These sol–gel reactions thus form ceramic-like domains having amino groups that can react with the carboxylic acid groups on the polyamic acid at elevated temperatures. Relatively small amounts of APTMOS were found to improve the modulus and strength of these hybrid materials, and their transparency was found to increase with increase in amount of APTMOS. The thermal decomposition temperatures they exhibited were approximately 570 °C, and their residual weights after exposure to 800 °C were directly proportional to their inorganic contents.

Introduction

There have now been numerous attempts to prepare novel organic–inorganic composites, the primary goal being to achieve a unique combination of properties from the organic and inorganic components. One successful approach has been the *in situ* polymerization of metal alkoxides in organic polymer matrices via the sol–gel process,[1–15] and many polymers have now been used in this type of study. Some examples are poly(dimethylsiloxane),[3–5] poly(tetramethylene oxide),[6–10] poly(methyl methacrylate),[11] epoxy resins,[12,13] and polyimides (PI).[14–17] Polyimides are of particular interest since they have gained commercial importance in the aerospace and electronic industries due to their reliable high-temperature stability, chemical resistance, and good mechanical strength. Unlike Kevlar or other aromatic, heterocyclic polymers, polyimides have a precursor molecule (poly(amic acid)) which is soluble in some organic solvents, such as *N,N*-dimethylacetamide (DMAC), 1-methyl-2-pyrrolidone, and *N,N*-dimethylformamide. There is thus the possibility of mixing this precursor molecule with metal alkoxides to generate homogeneously dispersed metal oxides in polyimide matrices through the usual hydrolysis and condensation reactions.

Several studies have in fact recently been carried out on the preparation of polyimide–silica hybrid materials.[14–17] Usually, the hybrid films were obtained by hydrolysis and polycondensation of TEOS, followed by drying, and then heating of the polyamic acid to high temperatures. The resulting films which contain less than 10 wt % silica were found to be transparent but were opaque at higher silica levels. Unfortunately, mechanical strengths had decreased, relative to those of the pure polyimides. Apparently, phase separation takes place during the drying and curing process, thus making the films opaque and giving them relatively poor mechanical properties. Constraining phase separation between the polymer and inorganic clusters to a smaller scale may therefore provide optically transparent materials with improved properties. To this end, Sen and co-workers have used the concept of "site isolation" to reduce the silica particle size.[17] In their work, TEOS was added to the monomer mixture of 1,2,4,5-benzenetetracarboxylic anhydride and 4-aminophenyl ether instead of to the polyamic acid solution. The transparency of the films was improved thereby. Kakimoto and co-workers introduced ethoxysilyl groups into the polymer backbone, which then acted as bonding sites for the silica.[18] The silica particle size was indeed found to decrease and the modulus to increase as the number of bonding sites increased.

In the present study, the silica clusters produced by the hydrolysis and polycondensation of tetramethoxysilane (TMOS) were bonded to polyimide chains by the introduction of (aminophenyl)trimethoxysilane (APTMOS) [$H_2N–C_6H_4–Si(OCH_3)_3$]. APTMOS can undergo hy-

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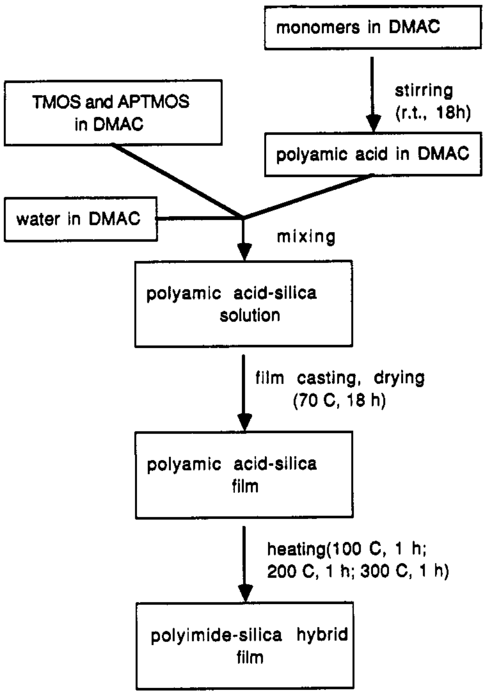
Scheme 1



drolysis and polycondensation along with TMOS, while its amino groups can react with the carboxylic acid groups in the poly(amic acid) precursor at high temperatures. APTMOS was chosen for its high thermal stability (up to 550 °C,[19] and thus comparable to that of the polyimides). The preparative details and the morphology, thermal stability, and mechanical properties of the composites thus prepared are described below.

Experimental Details

Preparation of the Polyimide–Silica Hybrid Films. The monomers used to synthesize the polyimide samples were 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) and 4-aminophenyl ether (ODA). They were obtained from Aldrich Chemicals and dried under vacuum for 24 h, at 90 and 70 °C, respectively. TMOS and APTMOS were obtained from Huls America, Inc., and used without further purification. Anhydrous DMAC was obtained from Aldrich Chemicals and stored under nitrogen.

The polymer precursor, poly(amic acid), was synthesized by the reaction of the dianhydride and diamine in DMAC in 15% solids concentration. In a typical synthesis, ODA was dissolved in DMAC, and a stoichiometric amount of PMDA was added to the solution and mixed into it with stirring. Stirring was continued at room temperature for 18 h, resulting in a viscous yellow solution. These preliminary steps and the subsequent conversion of the resulting materials to polyimide–silica hybrid films are shown in Scheme 1. In brief, different proportions of TMOS and APTMOS were first mixed in DMAC, and then various amounts of the mixture were stirred into the poly(amic acid) solution. Calculated quantities of water, diluted in DMAC, were then added to the mixtures. The resulting homogeneous mixtures were stirred for an additional 4 h at room temperature, placed into glass dishes, and then dried at 70 °C for 18 h to form the poly(amic acid)–silica hybrid films. The final polyimide–silica hybrid films were obtained by heating the precursor hybrid films consecutively at 100, 200, and 300 °C, each for an hour under vacuum.

Each sample was given the designation of PI-x-y-$(100 - y)$, where x is the total weight percent silica introduced, and y is the weight percent of this amount coming from the APTMOS bonding agent.

Table 1. Appearance of the Polyimide–Silica Hybrid Materials

hybrid material	silicate content[a]	APTMOS/TMOS[b]	remarks[c]	
PI-0-0-0	0		T	F
PI-5-0-100	5	0/100	T	F
PI-10-0-100	10	0/100	O	F
PI-20-0-100	20	0/100	O	F
PI-30-0-100	30	0/100	O	F
PI-5-20-80	5	20/80	T	F
PI-10-20-80	10	20/80	T	R
PI-20-20-80	20	20/80	T	R
PI-30-20-80	30	20/80	T	R
PI-20-3-97	20	3/97	O	F
PI-20-5-95	20	5/95	O	R
PI-20-8-92	20	8/92	O	R
PI-20-10-90	20	10/90	T	R

[a] Weight percent of total silica or polymeric silicate in the hybrid material, as calculated from the initial amounts of TMOS and APTMOS, assuming complete reaction. [b] Weight ratio of polymeric silicate obtained from APTMOS to that obtained from TMOS. [c] T, transparent; O, opaque; F, flexible; R, rigid.

Characterization of the Polyimide–Silica Hybrid Films. Thermogravimetric analyses (TGA) were performed using a Perkin-Elmer Model TAS-7 system at a heating rate of 20 °C/min, under a N_2 atmosphere.

Scanning electron micrographs (SEM) were taken on cross sections of the films using a scanning electron microscope (Cambridge instruments 600), with inclusion of energy-dispersion X-ray analysis (EDAX).

Tensile properties were measured using an Instron Universal Testing Instrument Model-1122 at room temperature (23 °C). The drawing rate was 0.2 in./min.

A Durometer (Shore Instrument & Manufacturing Co., Inc.) having D-2 type indenter was used to measure hardness according to ASTM Method D2440.

Results and Discussion

During the preparation of the films, all the poly(amic acid)–silica mixtures remained homogeneous and transparent. However, phase separation took place in some of the films during the drying and curing steps. All of the polyimide–silica films having silica contents greater than 10 wt % and prepared without the addition of APTMOS were opaque. By including APTMOS, some of the films remained transparent, as described in Table 1. As expected, increase in the amount of silica generally increased rigidity.

The SEM results gave important information on the morphology of these hybrid materials. The fracture surface of the pure polyimide and hybrid films containing 20% silica observed by SEM are shown in Figure 1. The particles evident in the micrographs b–d are silica (SiO_2) or polymeric silicate clusters. They could be pure silica or a mixture of silica and silsesquioxanes ($RSiO_{1.5}$, which are products of the hydrolysis and polycondensation of silicaon tetraalkoxide and organic-substituted silicon trialkoxide, TMOS and APTMOS, respectively). The EDAX spectrum and its silicon distribution map shown in Figures 2 and 3, respectively, identify the dispersed silicon existing on the surface of the fracture cross section. As can be seen from part b of Figure 1, the average particle size observed in sample PI-20-0-100 (obtained without adding APTMOS) is in the range 1–2 μm. Sample PI-20-3-97 has 3% of the 20% silica coming from the APTMOS and is described in part c. The particle size is seen to be reduced to approximately 1 μm, with a more homogeneous size distribution, and the particles have a rougher surface. Part d shows that the particles in sample

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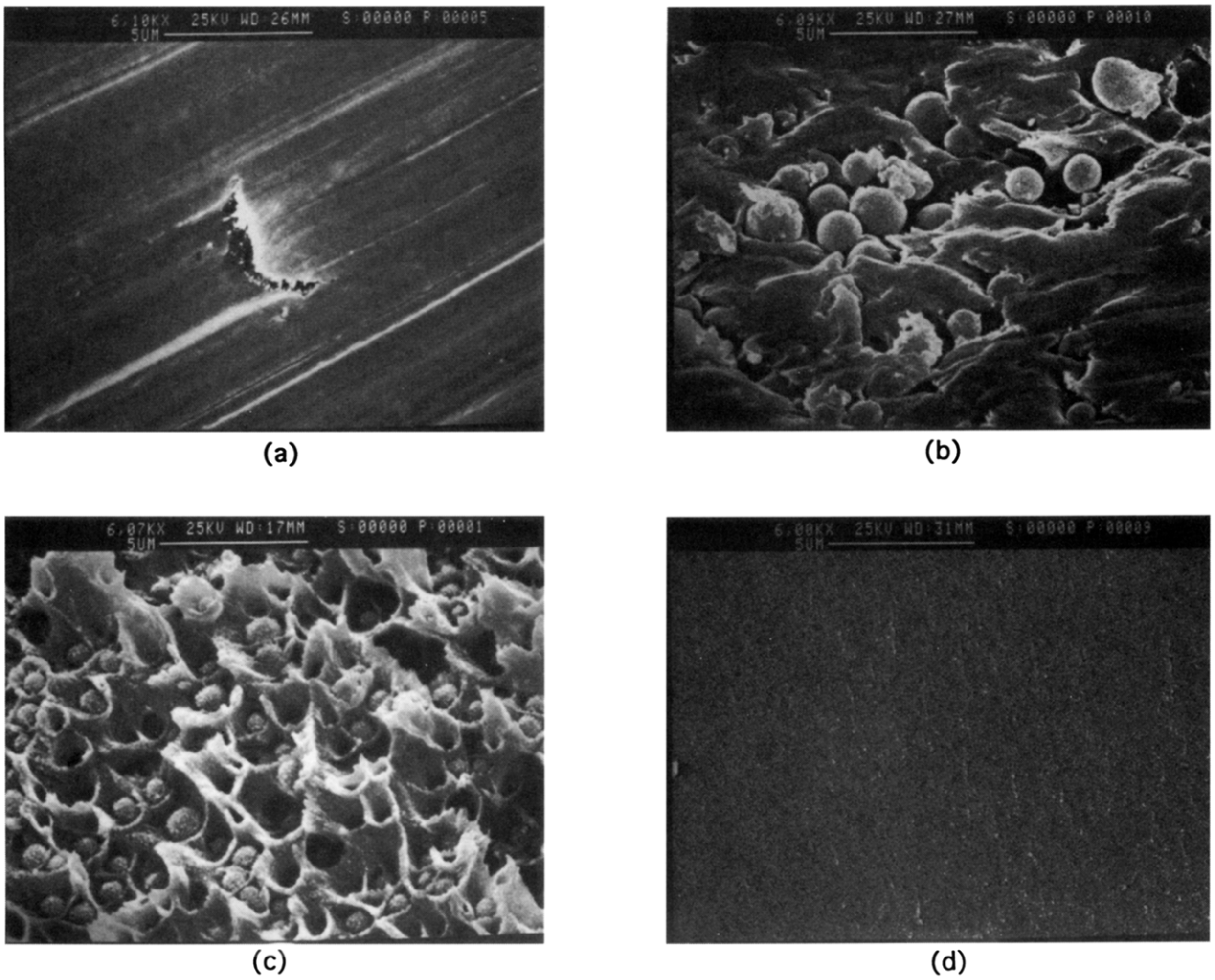

Figure 1. Scanning electron micrographs of hybrid materials PI-0-0-0 (a), PI-20-0-100 (b), PI-20-3-97 (c), and PI-20-10-90 (d). Designations are described in the text.

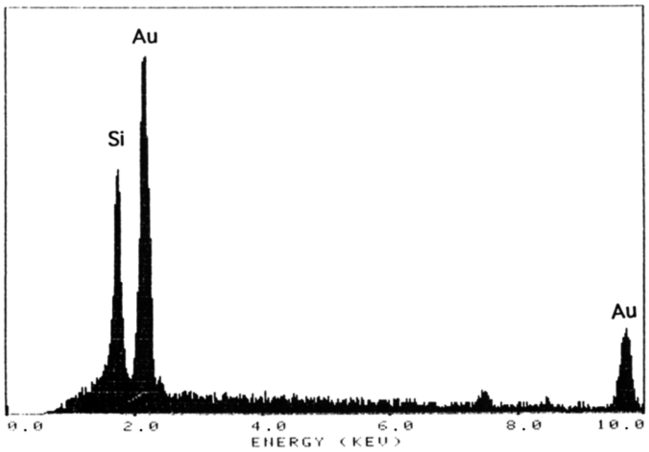

Figure 2. EDAX spectrum for sample PI-20-10-90.

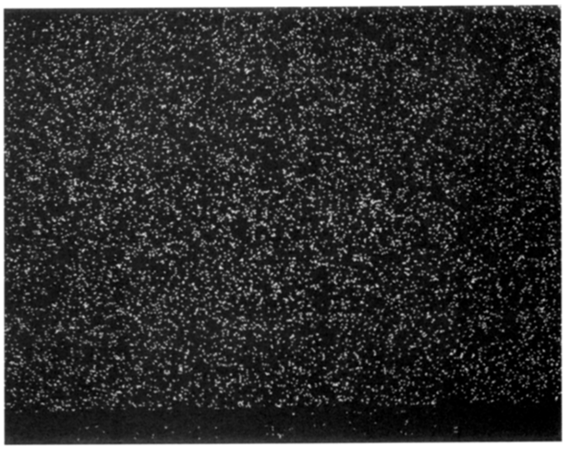

Figure 3. Silicon distribution map for sample PI-20-10-90.

PI-20-10-90 (of higher APTMOS content) are much smaller and more uniform, and the corresponding film was found to be transparent. The aminophenyl group on the substituted silicon trialkoxide probably reacts with the polymer chains, possibly improving the compatibility of the silica with the polymer. However, it apparently also has the tendency to prevent the formation of high molecular weight silicate, thus reducing the size of the clusters.

Because of the possible reaction between the amino groups in APTMOS and the carboxylic acid groups in the polyamic at high temperature, the cyclization of polyamic acid to form polyimide may not be complete, and this could have reduced the thermal stability of the polymer. However, the TGA curves in Figure 4 for these hybrid materials (having different proportions of APTMOS) show no apparent decrease in thermal decomposition temperature (as measured by the starting point of apparent weight loss). The materials have decomposition temperatures of approximately 570 °C. For the hybrid materials containing the same amount of APTMOS but varying amounts of silica or polymeric silicate, the weight residue remaining at 800 °C is proportional to the content of silica or

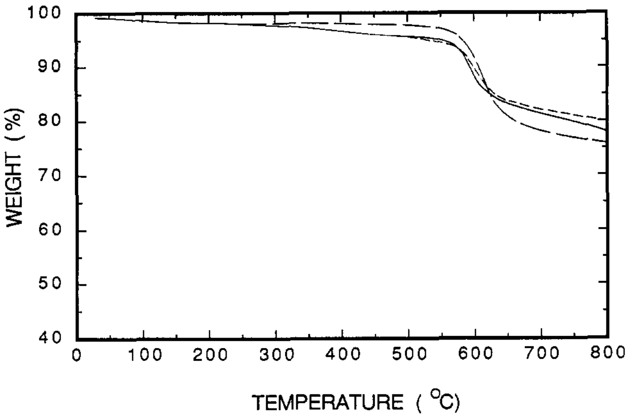

Figure 4. TGA curves of samples PI-0-0-0 (– – –), PI-20-0-100 (—), and PI-20-4-96 (- - -), at a heating rate of 20 °C/min under N_2.

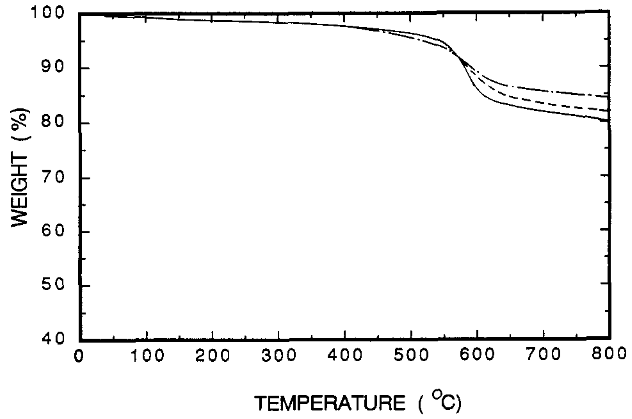

Figure 5. TGA curves of samples PI-10-20-80 (—), PI-20-20-80 (- - -), and PI-30–20–80 (– – –), at a heating rate of 20 °C/min under N_2.

polymeric silicate, as shown in Figure 5. The weight loss occurs at lower temperatures for the films containing silica, possibly because of the further condensation of silica.

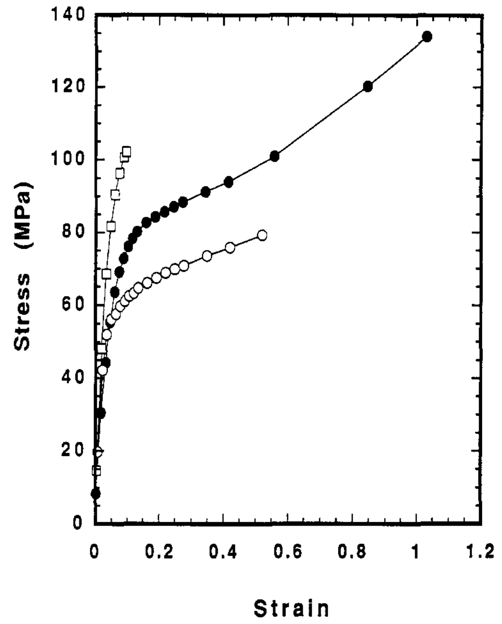

Figure 6. Stress–strain curves of samples PI-0-0-0 (●), PI-20-0-100 (○), and PI-20-3-97 (□).

Table 2. Mechanical Properties of the Polyimide–Silica Hybrid Materials

hybrid material	ultimate strength[a] (MPa)	ultimate elongation[b] (%)	modulus [c] (MPa)
PI-0-0-0	134	103	1400
PI-20-0-100	79	52	2000
PI-20-3-97	102	10	2593

[a] Stress at break. [b] Elongation at break. [c] Initial slope of the stress–strain curve.

Table 3. Durometer Hardness of the Polyimide–Silica Hybrid Materials

sample	PI-0-0-100	PI-20-0-100	PI-20-3-97	PI-20-8-92
hardness (D)[a]	80.5	71.5	84.5	87.5

[a] Hardness measured according to ASTM Method D2440, using a D-2 type indenter.

Another advantage of introducing APTMOS to bond the polymer and the silica is the possibility of achieving reinforcement of the hybrid material. As shown in this study, introducing silica into the polyimide by the sol–gel process gives well-dispersed particles in the polymer matrix. However, the strength is known to be reduced if there are no bonding sites between the organic polymer phase and the inorganic ceramic phase.[14] This is presumably due to the inert nature of the polyimides and the weak interactions between these polymers and the silica. In this case, the silica acts as an nonreactive, nonreinforcing filler. It is generally believed that external stress on a plastic composite is transferred from the continuous phase (polymer matrix) to the discontinuous phase (filler). Thus the ultimate properties of the composite are dependent on the extent of bonding between the two phases, the surface area of the filler, and the arrangements between the filler particles.[20] Typical stress–strain curves for the hybrid materials are presented in Figure 6. In comparison with the pure polyimide (sample PI-0-0-0), sample PI-20-0-100 (containing 20% of silica but no APTMOS) has lower strength but higher initial modulus. This is consistent with the results of the earlier study.[14] However, it can be seen that there is an apparent increase in modulus as well as strength for hybrid film PI-20-3-97. Comparing this film with PI-20-0-100 shows that the modulus and the strength are improved by addition of the small amount of APTMOS. Specific values of the ultimate properties and the modulus of these samples are listed in Table 2. The reinforcement thus obtained presumably results from both reductions in particle size (increases in interfacial area) and introduction of bonding between the polymer chains and the silica filler.

The results of durometer hardness measurements are presented in Table 3. As was the case for the strength, the hardness is seen to decrease upon introduction of silica without any APTMOS. However, the hardness increases with increasing amounts of this bonding agent.

Future work will involve small-angle X-ray and small-angle neutron-scattering studies, and possibly mass spectrometry.[21] Measurements will be carried out to characterize the morphologies of these composites, in particular the interfaces between the organic and inorganic phases.

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