Preparation and Properties of Rigid-Rod Polyimide/Silica Hybrid Materials by Sol–Gel Process

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ABSTRACT: Polyimide (PI) materials with a low coefficient of thermal expansion (CTE) while still retaining high strength and toughness are desirable in various applications. In this study a sol–gel process was used to incorporate silica into homopolyimides and copolyimides with highly rigid structures in an attempt to pursue this aim. A number of highly rigid monomers were used, including pyromellitic dianhydride (PMDA), *p*-phenylene diamine (PPA), *m*-phenylene diamine (MPA), benzidine, 2,4-diaminotoluene, and *o*-toluidine. No homopolyimide flexible films were obtained. However, it was possible to obtain flexible films from the copolyimides. Therefore, a copolyimide based on PPA, MPA, and PMDA (PPA/MPA = 2/1 mol) was then chosen as the matrix to prepare the PI/silica hybrids. Flexible films were obtained when the silica content was below 40 wt %. The hybrid films possessed low in-plane CTEs ranging from 14.9 to 31.1 ppm with the decrease of the silica content. The copolyimide film was strengthened and toughened with the introduction of an appropriate amount of silica. The thermal stability and the Young's modulus of the hybrid films increased with the increase of the silica content. The silica particle size was assessed by scanning electron microscopy and was about 100 nm for the hybrids containing 10 and 20 wt % silica and 200–500 nm for the hybrids containing 30 and 40 wt % silica. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 794–800, 2001

Key words: polyimide; silica; hybrids; sol–gel process; rigid rod

INTRODUCTION

Polyimide (PI) is a type of high performance polymeric material with outstanding mechanical properties, electrical properties, and radiation resistance, especially at elevated temperatures, and it has been widely used in the aerospace, electrical, and microelectronics industries.[1–4] With the rapid technological improvement of these industries, PI materials are required to possess higher thermal stability, higher mechanical properties, lower dielectric constants, and lower coefficients of thermal expansion (CTE). Among these properties, the lower CTE is extremely desirable because the incompatibility of the large CTE of the PI and the low CTE of inorganic substrates such as silicon chips, copper, and glass is one of the main causes of failure of electronic devices such as integrated circuits and flexible printed circuit boards. A lot of work has been carried out on the PIs with low CTE by using monomers with high rigidity such as pyromellitic dianhydride (PMDA), biphenyl-3,3′,4,4′-tetracarboxylic dianhydride, *p*-phenylene diamine (PPA), and so forth. The increase in the rigidity of the PI structure, however, leads to a decrease in the flexibility of the PI, which in turn results in PIs that are too brittle to be used in various applications. For example, use of the PI based on PMDA and PPA would not be practical because of its high brittleness.

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The incorporation of nanometer size inorganic particles such as silica is very effective in decreasing the CTE of the polymer matrix.[5–24] More remarkably, this decrease in CTE by the incorporation of silica particles may not lead to the loss of mechanical properties. The strength and the toughness can be improved simultaneously if the silica particle content is below a certain value. Furthermore, the introduction of silica can also lead to increased thermal stability and adhesion to inorganic substrates. The nanometer silica particle is usually introduced into the polymer matrix by the sol–gel method.[25,26] The sol–gel process is based on the homogeneous hydrolysis and condensation of metallic alkoxides to form a 3-dimensional inorganic network. Our intention in this work was to prepare PI/silica hybrids with very low CTE while retaining high mechanical properties. On the basis of the study of various kinds of highly rigid PIs and copolyimides, an appropriate PI was chosen to prepare the rigid-rod PI/silica hybrids. Their preparation, characterization, and properties are described.

EXPERIMENTAL

Materials

The PMDA (industrial product, purchased from Shanghai Tar Chemical Company, Shanghai) was recrystallized from acetic anhydride before use. The PPA, *m*-phenylene diamine (MPA), benzidine (BD), 2,4-diaminotoluene (DAT), and *o*-toluidine (OT; all chemical reagent grade, Shanghai Wulian Chemical Co., Shanghai) were used as received. Tetraethoxysilane (TEOS, chemical reagent grade, Beijing Chemicals Company, Beijing) was used as received. *N*-Methyl-2-pyrrolidone (NMP, analytical reagent grade, Shanghai Reagent Company, Shanghai) was dried over molecular sieves before use. Common reagents such as acetic acid and acetic anhydride were used without further purification.

Preparation of PI and PI/Silica Hybrids

An equimolar amount of PMDA was added to the diamine/NMP solution (10 wt % solid content). The polycondensation reaction at room temperature for 16 h gave a viscous poly(amic acid) (PAA) solution. A mixture of TEOS, distilled water (4/1 based on moles of TEOS), and acetic acid (to keep the pH value at 4) was added to this PAA solution. The mixture was stirred at room temperature for 6 h to give a transparent solution. The solution was cast on a glass substrate and thermally treated at 80°C for 12 h, 120°C for 4 h, 200°C for 2 h, and 270°C for 2 h. The thickness of the imidized films was about 50 μm. The films were peeled off the glass substrates with the aid of deionized water and dried for several hours at 100°C in a vacuum oven.

Characterization

The FTIR spectra of PI/silica hybrid films were recorded on a Perkin–Elmer Paragon 1000 IR spectrophotometer. The scanning electron microscopy (SEM) analysis of the cross section of the PI/silica hybrid films was carried out on a Hitachi S-2150 scanning electron microscope. The thermal gravimetric analysis (TGA) was conducted on a Perkin–Elmer TGA 7 thermal analyzer under a flow of N_2. The heating rate was 20°C/min. The in-plane CTEs of PI and PI/silica hybrid films were measured by dynamic mechanical analysis (DMA) with a Perkin–Elmer DMA7e in a thermomechanical analysis mode. To remove the residual stress, the film specimens were heated to 270°C with a heating rate of 10°C/min, kept there for 10 min, and then cooled to 30°C at a cooling rate of 10°C/min before each measurement. The load on the film was 30 mN, and the heating rate for the measurement was 5°C/min. A temperature range of 75–125°C was selected to determine the CTE. Dynamic thermal analysis curves were also recorded on a Perkin–Elmer DMA7e dynamic mechanical analyzer. The stress–strain curves of PI and PI/silica hybrid films were recorded on an Instron-4465 universal tester at room temperature at a drawing rate of 5 mm/min. The densities of the PI/silica hybrids were measured using a density gradient tube at 25°C. The intrinsic viscosities of the PAA were measured with an Ubbelohde viscometer using NMP as the solvent at 30°C. The standard concentration was 1 g/dL.

RESULTS AND DISCUSSION

Preparation of Highly Rigid Homopolyimides and Copolyimides

The formulations of the copolyimides and homopolyimides chosen for this study are listed in Table I. All monomers used in this study were "rigid" and did not contain any "flexible" linkages. However, the different diamine monomers pos-

Table I Preparation of Rigid Rod of Copolyimides and Homopolyimides

	2:1:3[a]	1:1:2	1:2:3	1:0:1	[η][b]
PPA:MPA:PMDA	+[c]	+−[c]	−[c]	−	1.05, 1.05, 1.02
PPA:OT:PMDA	−	−	+−[c]	−	1.09
PPA:DAT:PMDA	+[c]	+−	−	−	0.95
MPA:OT:PMDA	−	+−	+[c]	−	1.10
DAT:MPA:PMDA	+−[c]	+−	−	−	0.97
OT:DAT:PMDA	+[c]	+−	+−	−	1.13
BD:PPA:PMDA	−[c]	−	−	−	1.10
BD:MPA:PMDA	+[c]	+−	−	−	1.07

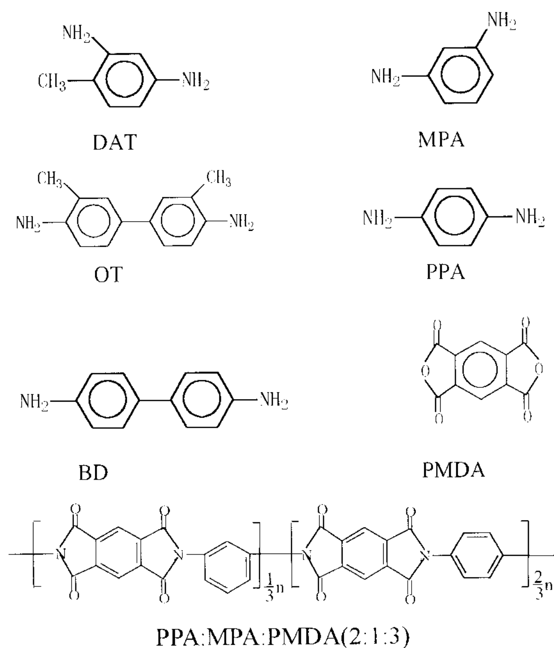
(+) Flexible, (−) very brittle, (+−) brittle.
[a] Molar ratio.
[b] The intrinsic viscosity of copoly(amic acid)s measured at 30°C using NMP as the solvent.
[c] The intrinsic viscosity of this copoly(amic acid) was tested.

sessed different rigidities and symmetries (linearities) and also led to different degrees of chain packing. PPA and BD had very high symmetry (linearity), and the PIs based on these two monomers tended to have "rodlike" extended conformations. PPA also had higher rigidity than BD. Although MPA may have a rigidity similar to PPA, its lower symmetry (linearity) leads to a more "twisted" conformation of its PI. DAT and OT were different from MPA and BD, respectively, in the existence of methyl side groups. The existence of the methyl side groups leads to a decrease in the chain packing density of their PIs. We observed that none of the homopolyimides prepared in this study gave flexible films upon casting from their PAA solutions and thermal treatments. This was because of the rigid nature and the high structural regularity of the homopolyimide molecules. Flexible films were obtained from copolyimides, however. The copolyimides had lower molecular regularity than the homopolyimides. Furthermore, the linearity of the PI molecular chain also had a large effect on the film formation and its flexibility: the copolyimide films were very brittle if both codiamine monomers were either "linear" or "nonlinear." For instance, the copolyimides based on PMDA and either of the two linear diamine monomers such as PPA/OT and BD/PPA or two nonlinear diamine monomers such as MPA/DAT were very brittle. The reason for the brittleness of the copolyimides based on two linear diamine monomers was that the copolyimide molecules still retain the rodlike conformation, although the structural regularity was somewhat reduced. By contrast, the copolyimide molecules containing only the nonlinear diamines had a twisted conformation and the chain segmental movement may have been very restricted by the steric hindrance during the film formation and thermal imidization process.[4] So the "ideal" conformation could not be achieved, and the final films were brittle and full of residual stress. The copolyimides containing both the linear and nonlinear diamine, such as MPA:PPA:PMDA (1:2:3), PPA:DAT:PMDA (2:1:3), OT:MPA:PMDA (2:1:3), DAT:OT:PMDA (1:2:3), and BD:MPA:PMDA (2:1:3), had low molecular regularity, reasonable molecule packing density, and chain linearity, and formed flexible films. In addition, we observed that the copolyimides containing a high proportion of linear diamine and a low proportion of nonlinear diamine were easier to form into flexible films. We also observed (Table I) that the incorporation of the methyl side groups had only a minor influence on the PI film formation. It should be pointed out that the copoly(amic acid)s in this study had high and similar intrinsic viscosities that minimized the influence of the molecular weight on the film formation. The intrinsic viscosity of the homopoly(amic acid) based on OT and PMDA was also tested: even if its intrinsic viscosity was higher than all the copoly(amic acid)s, it could not be made into film after imidization.

All of the studies on the preparation and properties of PI/silica hybrids described below were based on the copolyimide PPA:MPA:PMDA (2:1:3), which possessed the best film formation ability among the PIs studied and had high rigidity and chain packing density. The structure of this copolyimide is depicted in Scheme 1.

Preparation of Hybrids

The preparation of PI/silica hybrids was a typical three-step process.[10,20] The solution polyconden-



Scheme 1 The chemical structures of dianhydride, diamines, and copolyimide.

sation gave a PAA solution. TEOS was then introduced together with a certain amount of water and acid catalyst. After the hydrolysis process, the homogeneous PAA/TEOS solution was film cast. The thermal treatment led to the condensation of hydrolyzed TEOS to form a silica network and the imidization reaction to convert PAA to PI. Because the highly rigid PIs used in this study were not organosoluble, the films could only be cast at the processable PAA stage.

FTIR Spectra of Hybrids

Figure 1 is the FTIR spectrum of a PI/silica hybrid containing 20 wt % silica. The characteristic absorption bands of C═O stretching at 1777 and 1721 cm^{-1} and C—N stretching at 1375 cm^{-1} in the imide groups are clearly visible. The characteristic bands of network Si—O—Si at 1090 and 850 cm^{-1} can also be observed.[10,20] These results indicate that the PI/silica hybrids were successfully obtained.

SEM Analysis of Hybrids

Figure 2 shows the SEM photographs of the cross section of PI/silica hybrid films containing various amounts of silica. When the silica content was below 20 wt %, the silica particle size was 100 nm. However, when the silica content was increased to 30 and 40 wt %, the particle size was increased to 200 and 500 nm, respectively. The increase in the silica particle size clearly resulted from the increase in the aggregation tendency as the silica content and the silica particle number were increased.

In-Plane CTE of Hybrid Films

Figure 3 shows the relationship between the silica content and the in-plane CTE of the PI and PI/silica hybrid films. Because of the use of rigid monomers, the resultant PI had a relatively low CTE (31.1 ppm). When the silica was introduced, the CTE was further decreased. The CTE was decreased by 28.6% from 31.1 ppm for a pure PI to 22.2 ppm for a hybrid with 10 wt % silica. The CTE was further decreased to 19.2, 16.2, and 14.9 ppm for the hybrids with 20, 30, and 40 wt % silica, respectively. These data were close to the CTE of some inorganic substrates. Morikawa et al.[10] and Mascia and Kioul[21] also reported on the CTE of aromatic PI/silica hybrid films. The PI they used was based on PMDA and 4,4′-diaminodiphenyl ether (ODA), and the CTE of Morikawa et al.'s[10] PI/silica (10 wt %) and Masica and Kioul's[21] PI/silica (25 wt %) hybrid films were 48 and 55 ppm, respectively, which were much higher than the CTE of our rigid-rod PI and PI/silica hybrid films. This decrease in the CTE of the PI/silica hybrid films clearly resulted from the low CTE of the silica and the existence of the strong interaction between the silica and PI and the possible interpenetrated structure,[27] which makes the silica particles act as the "crosslink points." It was also observed that the rate of the decrease of

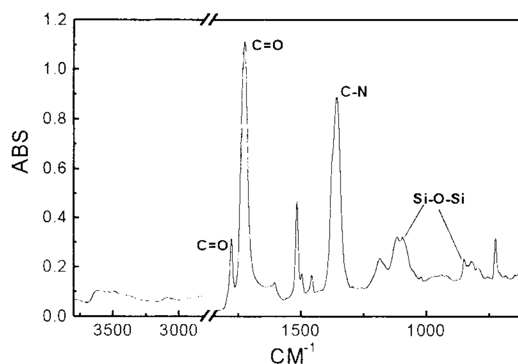


Figure 1 An FTIR spectrum of a copolyimide [PPA:MPA:PMDA (2:1:3)]/silica (20 wt %) hybrid film.

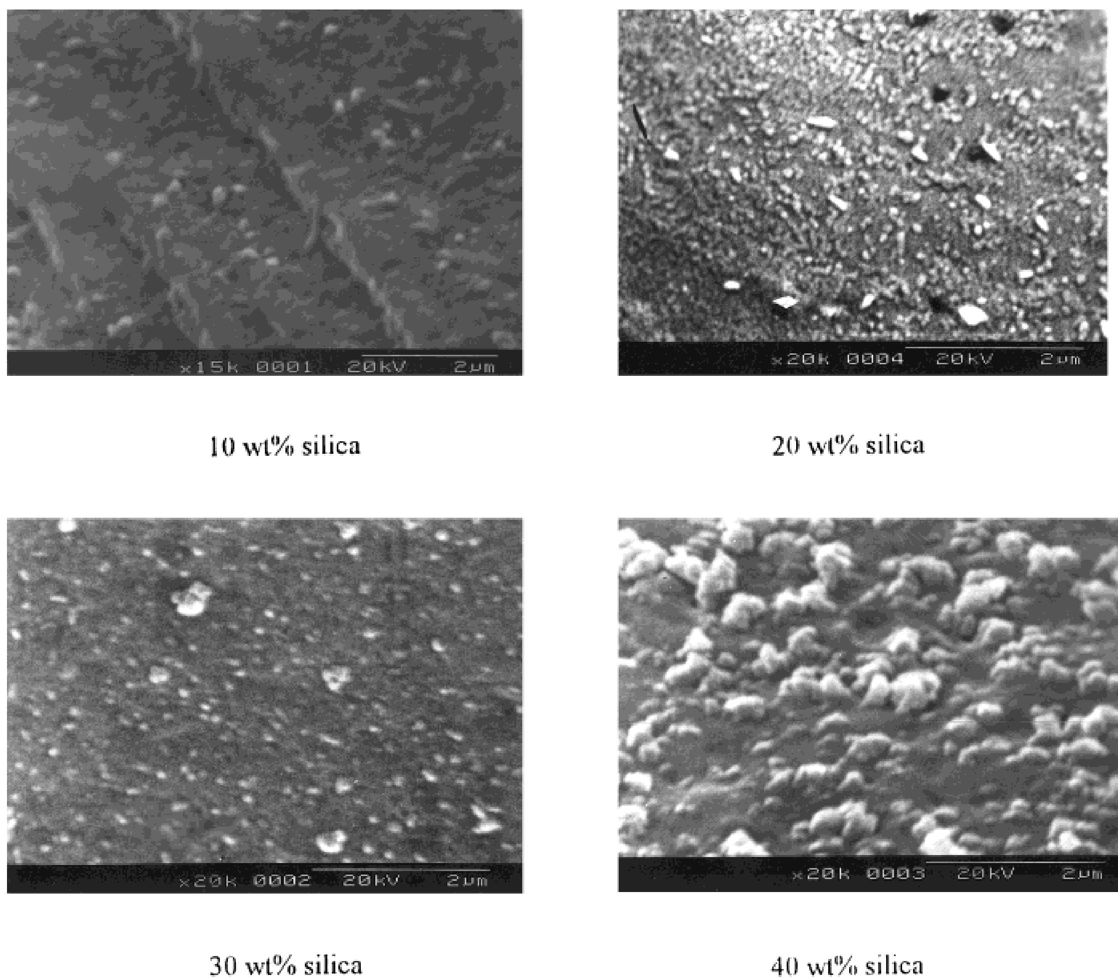


Figure 2 SEM photographs of the cross section of copolyimide [PPA:MPA:PMDA (2:1:3)]/silica hybrid films.

the CTE with the increase of the silica content decreased as the silica content was increased. This may be caused by aggregation of the silica particles as shown in the SEM micrograph, which led to a slowing down of the increase of the number of the silica particles and consequently the crosslink points.

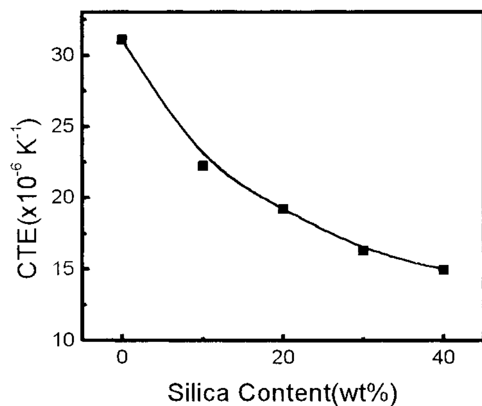


Figure 3 The coefficient of thermal expansion of copolyimide [PPA:MPA:PMDA (2:1:3)]/silica hybrids.

Thermal Stability of Hybrids

Figure 4 shows the TGA curves of the PI and PI/silica hybrids. Because of the rigid nature and the absence of side groups, the PI had a high decomposition temperature. The initial thermal decomposition temperature (T_d, on-set temperature) was 592.6°C. This thermal stability was further improved when silica was introduced. The hybrid containing 10 wt % silica had a T_d of 623.8°C. The increase in the thermal stability may have resulted from the high thermal stability of silica and the crosslink point nature of the silica particles.

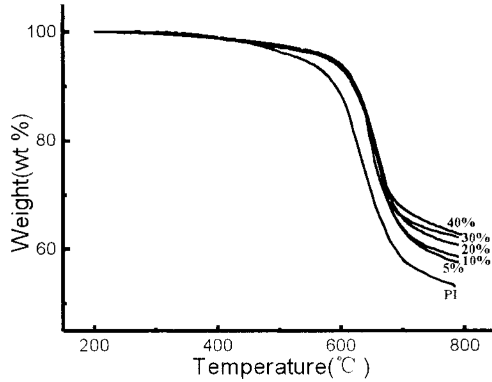


Figure 4 TGA curves of copolyimide [PPA:MPA:P-MDA (2:1:3)]/silica hybrids.

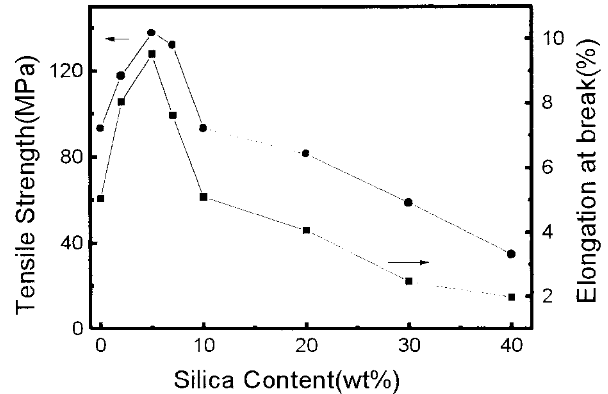


Figure 6 The tensile strength and elongation at break of copolyimide [PPA:MPA:PMDA (2:1:3)]/silica hybrid films.

Mechanical Properties of Hybrids

Figure 5 shows the influence of the silica content on the Young's modulus of the hybrids. Because of the rigid nature of the PI molecular chain, the in-plane Young's modulus of the pure PI was quite high. The Young's modulus increased linearly with the increase of the silica content. Figure 6 shows the effect of the silica content on the tensile strength (failure) and the elongation at break of the PI and PI/silica hybrid films. It was remarkable to observe that the tensile strength and the elongation at break both increased with the increase of the silica content up to a silica content of 5 wt %. The tensile strength was increased by about 47.7% while the elongation at break was increased by about 88.7% when 5 wt % silica was introduced. These strengthening and toughening effects may have resulted from the strong interaction and the interpenetrated nature between PI molecules and silica networks, which led to the formation of the "physical crosslinks." The strength and the toughness of the hybrid were, of course, dependent upon the density of the crosslinks. In an appropriate range of the crosslink density, the crosslinks could exhibit the strengthening and toughening effects. When the silica content was further increased, the tensile strength and the elongation at break were both decreased. No obvious glass transition was observed in the DMA curves (storage modulus and tan δ). Figure 7 shows that at temperatures above 300°C, the storage modulus of the PI/silica hybrids was higher and decreased more slowly than the pure PI. This may further indicate the existence of a strong interaction between the silica particles and the PI matrix, which limits the movement of the PI molecules.

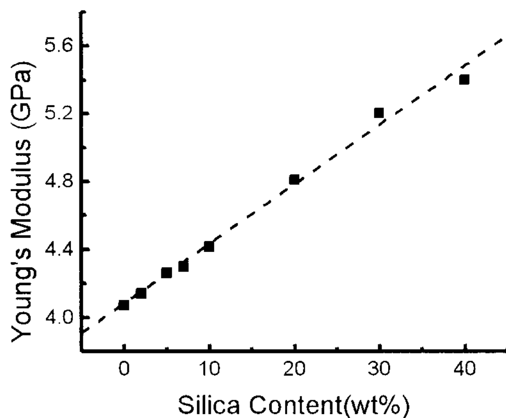


Figure 5 The Young's modulus of the copolyimide [PPA:MPA:PMDA (2:1:3)]/silica hybrid films.

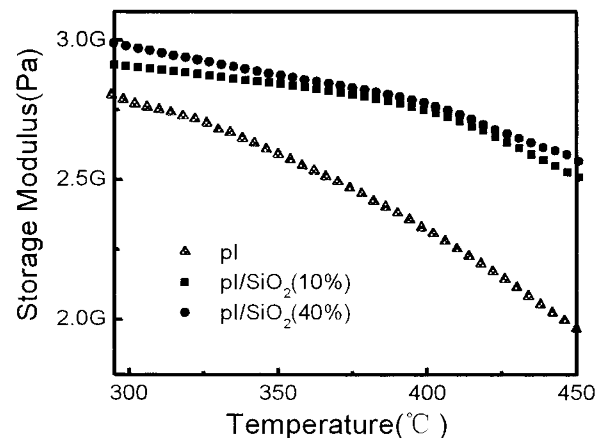


Figure 7 Storage modulus curves of copolyimide [PPA:MPA:PMDA (2:1:3)]/silica hybrid films.

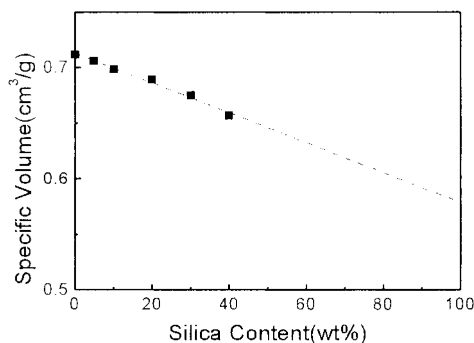


Figure 8 The specific volume of copolyimide [PPA:MPA:PMDA (2:1:3)]/silica hybrids.

Specific Volume of Hybrids

Figure 8 shows the relationship between the silica content and the specific volume of the hybrids. A basically linear relationship was observed. When the straight line was extrapolated to a silica content of 100 wt %, a specific volume of 0.58 mL/g was obtained. This value was clearly greater than the specific volume of SiO_2 glass (0.45 mL/g). This may have resulted from several factors. The network of the SiO_2 is a porous structure and the sol–gel process may generate more microvoids than were observed in previous work.[21] In addition, the conversion from TEOS to SiO_2 may not be complete and —OH groups may exist on the surface of the SiO_2 network.

CONCLUSIONS

Various rigid-rod copolyimides and homopolyimides were investigated and one copolyimide based on PPA, MPA, and PMDA (PPA/MPA = 2/1 mol) was then chosen as the matrix to prepare the rigid-rod PI/silica hybrids. When the silica content was below 40 wt %, flexible PI/silica hybrid films were obtained. The silica particle size was about 100 nm for the hybrids containing 10 wt % silica and it increased with the increase of the silica content. The in-plane CTE of the hybrid films was effectively reduced by the introduction of the silica. The strength and the toughness of PI/silica hybrids were improved simultaneously in a certain silica content range. The thermal stability and Young's modulus of the hybrid films were also increased with the increase of the silica content.

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