Silica/Polyimide Hybrids and Their Dielectric Properties. I. Preparation with an Improved Sol–Gel Process with Poly(amic acid) as the Precursor

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ABSTRACT: A series of hybrid polyimide–silica hybrids films were prepared by a sol–gel process via the blending of tetrathoxysilane and a coupling reagent in a pyromellitic anhydride/4,4'-oxydianiline (ODA) based poly(amic acid) solution in N,N-dimethylacetamide, the casting of the films, the evaporation of the solvent, and thermal imidization, in that order. Fourier transform infrared, transmission electron microscopy, atomic force microscopy, and thermogravimetric analysis were used to characterize the structure of the obtained hybrids. The dispersion of silica in the hybrids was suggested to be in two states: a dominant network structure and minor discrete aggregate particles. On the basis of the network structure, the mechanical behavior of the hybrids was interpreted. An investigation of the dielectric properties revealed that the dielectric constant of the hybrids increased slowly with the concentration of SiO_2. For hybrid films containing 30 wt % SiO_2, the constant increased to 4.2 from the value of 3.2 for pure polyimide. Moreover, the incomplete hydrolysis and decomposition of tetrathoxysilane and the coupling reagent were the main factors contributing to the thermal stability and the uncertainty of the dielectric constant of the hybrids. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 20–24, 2005

Key words: dielectric properties; polyimides; silicas; gels

INTRODUCTION

Organic–inorganic hybrids, or nanocomposites, have been proved as new advanced materials because they combine the advantages of organic components [e.g., flexibility, low dielectric constant (ε), and processability] and inorganic components (e.g., rigidity, strength, durability, and thermal stability).[1–11] The enhanced properties of these hybrids mainly arise for two reasons. First, the discrete inorganic phases, smaller than 100 nm, provide a very large interfacial area between the organic phase and inorganic phase and correspondingly cause the enhancement of the mechanical and thermal properties of hybrids. Second, hybrids obtained at a molecular level of dispersion can result in hybrid polymers with specific properties.[12]

Possessing versatile properties (especially dielectric and mechanothermal properties) and used in a wide range of applications, polyimides (PIs) have been extensively investigated as matrices for hybrids in the search for novel materials for microelectronics and engineering. On the other hand, silica has been considered an ideal separated domain component in hybrids for improving the thermal and mechanical properties of materials.[13] For achieving the best combined properties of PI/inorganic hybrids, improving the compatibility of two phases and reducing the phase separation are critical considerations. In fact, compatibility enhancement is usually generated by an improvement in the interaction between two phases and by a reduction in the size of separated domains. These expectations are usually realized by (1) the use of reactive polymers and their conversion into PI network matrices, (2) the conversion of an inorganic precursor into a network phase, and (3) the addition of a coupling agent to enhance the interaction between the inorganic and PI phases. Because of the difficulty of synthesizing functional PI or PI precursors, the last two routes can contribute to the effectiveness of the preparation of PI/silica hybrids. Usually, the mechanical properties of hybrids obtained with route 2 do not have good enough mechanical properties, and route 3 commonly generates larger discrete inorganic domains. In fact, route 2 is a sol–gel process, in which the silica domain, derived from the hydrolysis of tetraalkoxysilane, is added to PI or its precursor solution.[14] In the past decade, the investigated properties of silica/PI hybrids have mainly been their thermal and mechanical behaviors,[15] whereas their dielectric properties have been rarely studied. In this study, an

improved sol–gel process, in which tetraethoxysilane (TEOS)/poly(amic acid) (PAA) blends containing 3-aminopropyl triethoxysilane (APTEOS) as a coupling reagent were used as precursors, was adopted for the preparation of silica/PI hybrid films. The structure, thermal properties, and ε values of the obtained hybrid films were examined as well. We expected an efficient method for preparing PI composites with controllable ε values and better complex performance.

EXPERIMENTAL

Materials

Pyromellitic anhydride and 4,4′-oxydianiline were purchased from Aldrich (Boston, MA) and were sublimated before use. TEOS and APTEOS were obtained from Acros Organics (Morris Plains, NJ) and used as received. N,N-Dimethylacetamide (DMAc, Sanaisi reagent Co., Ltd., Shanghai, China) was distilled from calcium hydrate. All the other chemicals were analytical-grade and were used without further purification.

Preparation of the silica/pi hybrid films

PAA with a 15% solid concentration in DMAc was synthesized by the reaction of dianhydride and diamine for 18 h at room temperature. After specific proportions of TEOS and APTEOS (TEOS/APTEOS = 9:1 w/w) were stirred into the PAA solution, a calculated quantity of water diluted in DMAc (40 wt % H_2O) was added, and the mixture was stirred for an additional 4 h at room temperature. The precursor hybrid films were obtained by the casting of the aforementioned homogeneous mixture onto glass plates and drying at 60°C over 18 h to evaporate the solvent. Heating the precursor films at 100, 200, and 300°C consecutively (for 2 h at each temperature) in an N_2 stream resulted in the final silica/PI hybrid films. As a reference, blank SiO_2 was obtained by the same process of hybridization with the same proportions of TEOS and APTEOS, except for PAA.

Characterization

Attenuated total reflectance/Fourier transform infrared (FTIR) spectroscopy (Bruker Vector 22, Germany) was used to confirm the chemistry structure of silica/PI hybrids. Differential scanning calorimetry and thermogravimetric analysis (TGA) were conducted on a Pyris 1 differential scanning calorimeter instrument (Perkin Elmer, Boston, MA) with 6–7-mg samples under nitrogen at a heating rate at 20°C/min. The mechanical properties were recorded on a DCS-500 universal tester (Shimadzu Corp., Kyoto, Japan) at room temperature. The structures of the hybrid films were investigated with transmission electron microscopy
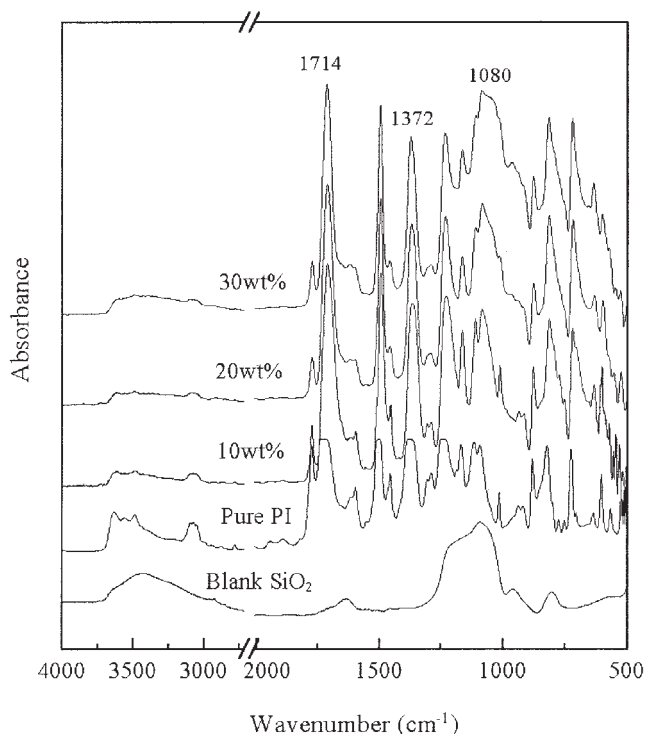

Figure 1 FTIR spectra of PI, the SiO_2 reference, and silica/PI hybrids containing different concentrations of SiO_2 by weight.

(TEM; JEM-200CX, Japan Electronics, Tokyo, Japan). The smoothness of the film surface was characterized with the atomic force microscopy (AFM) system of a Seiko SPA 400 (SII Nano Technology Inc., Chiba, Japan). The ε values were measured on a YD2810b LCR bridge meter (Yangzi Co., Ltd., Changzhou, China).

RESULTS AND DISCUSSION

FTIR spectroscopy characterization

FTIR spectra of the hybrids and pure PI films are shown in Figure 1. The characteristic absorption of PAA at 1650 cm^{-1} completely disappeared, and the characteristic absorptions of the imide unit at wave numbers of 1780, 1714, 1372, and 732 cm^{-1} were found for pure PI and the hybrids.[16] The addition of TEOS and APTEOS did not yield any negative effects on the imidization of PAA. On the other hand, the broad absorption around 1080 cm^{-1} was the asymmetric stretching of Si—O—Si units. The adsorption intensity of this peak increased with the TEOS concentration. In the FTIR spectra of the SiO_2 reference, the characteristic absorption at 1000–1100 and 3400 cm^{-1} was generated from Si—O—Si bonds and —OH/—NH$_2$ groups, respectively. The absorption similarity of Si—O—Si between the hybrids and reference specimen indicated that the silica sources in the form of TEOS and APTEOS were efficiently converted into
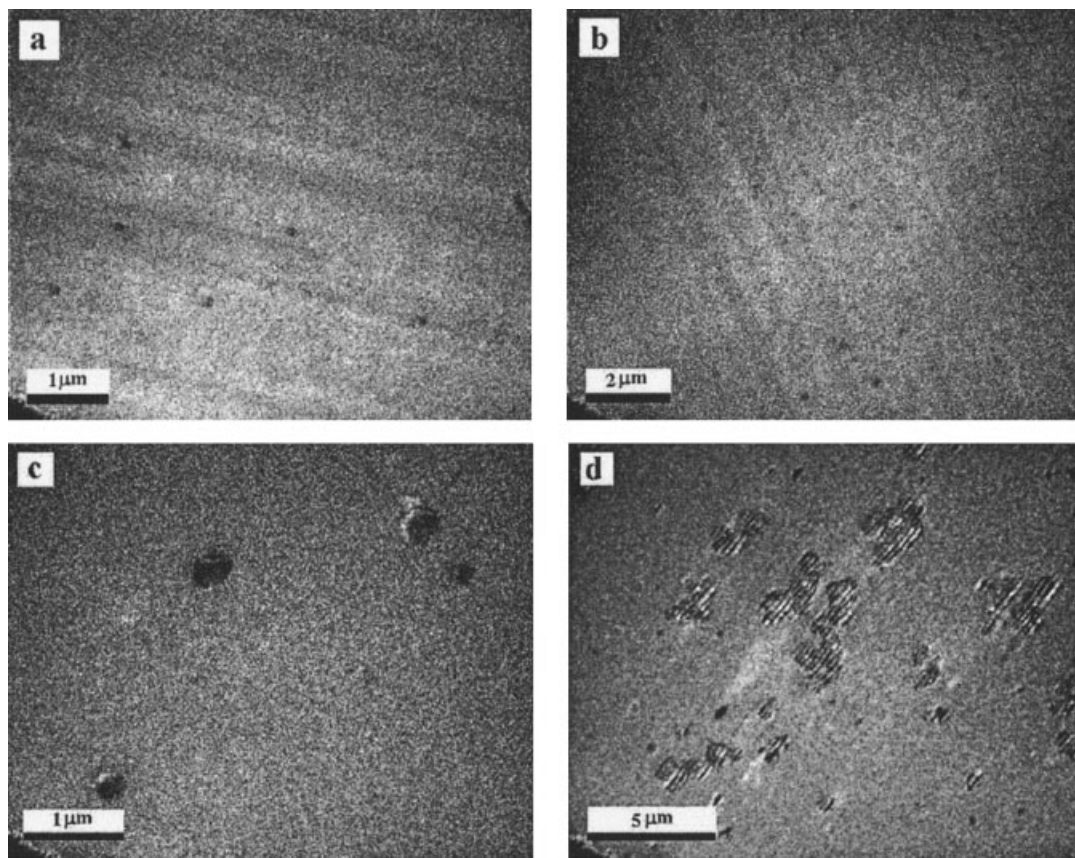
Figure 2 TEM patterns of fractured silica/PI hybrid films containing (a) 5, (b) 10, (c) 20, or (d) 30 wt % SiO$_2$.

Si—O—Si structures through the preparation of hybrids.

Structural morphologies

The TEM micrographs of the fractured hybrid films are shown in Figure 2. Some discrete SiO$_2$ domains, dispersed in PI matrices, obviously observed. The sizes of the obvious SiO$_2$ domains were 100, 200, 300–500, and 500–2000 nm for the hybrids containing 5, 10, 20, and 30 wt % SiO$_2$, respectively. These results revealed that the aggregation of SiO$_2$ increased as the concentration of TEOS increased. Such aggregation was probably caused by the interaction between the Si—OH groups. These Si—OH groups were formed through hydrolysis of TEOS and APTEOS. Because the hydrolysis occurred in the solution state and the viscosity of the solution was not very high, it was difficult to thoroughly prohibit the aggregation of the SiO$_2$ component. However, TEM images showed that the concentration of SiO$_2$ aggregates was much less than that calculated from the added TEOS and APTEOS. It was concluded that the size of most of the SiO$_2$ component was very small and beyond the observation of the adopted TEM measurements. Figure 3 shows AFM images of the surface of PI/SiO$_2$ hybrids (20% SiO$_2$). The

grain structures can be seen clearly in the planar image. The observed separated domain particles were 200 nm in size, in the same range found with TEM. The surface of the film was very smooth; the highest roughness was only 20 nm. These results were more proof that silica networks were restrained in the hybrids with much smaller aggregates.

Thermal properties

Figure 4 shows TGA for pure PI and hybrids with SiO$_2$ concentrations ranging from 10 to 30 wt %. The decomposition temperature of the hybrids was a little lower than that of pure PI. These phenomena might have been caused by the elimination of water from the Si—OH groups at SiO$_2$ at a higher temperature. This indicated that TEOS or APTEOS was not hydrolyzed completely during the preparation. With increasing temperature, the formation of the network proceeded continuously. As for the slow weight loss that also occurred in the TGA measurements of the reference SiO$_2$, it was reasoned that the decomposition of organic groups in TEOS or APTEOS was another source for the loss of the hybrids below 600°C. Because the temperatures of 5 wt % weight loss for the hybrids were still over 520°C, the thermal stability of these
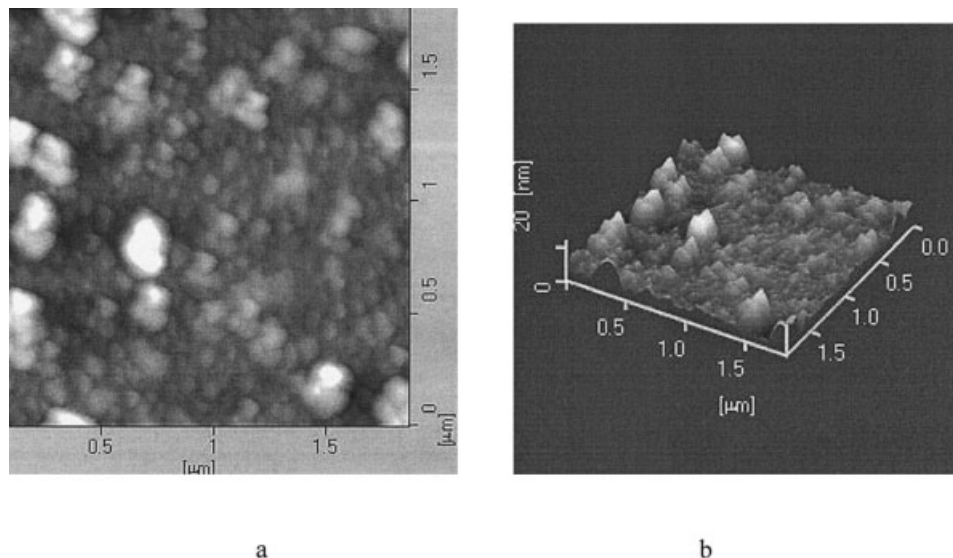
Figure 3 AFM images of hybrid films (20 wt % SiO_2): (a) a planar image and (b) a stereoimage.

hybrids would not limit possible applications, such as dielectric materials.

Mechanical properties

The tensile strength and elongation at break of the PI/SiO_2 hybrid films are shown in Figure 5. When the silica concentration was less than 10 wt %, both the tensile strength and the elongation at break increased in comparison with those of pure PI. When the silica concentration exceeded 10 wt %, both the tensile strength and the elongation at break decreased. Hybrids with less silica exhibited drastically improved

mechanical properties, and this could be explained in two ways: (1) nanometer-size silica dispersed relatively evenly throughout the PI matrix, and (2) PI chains strongly interacted with silica or silanol through hydrogen bonding and consequently became entrapped between silica particles.[17] The tensile strength and elongation decreasing with the concentration should be due to the formation of Si—O—Si networks in the hybrids. In comparison with the PI matrix, the fragile Si—O—Si networks possessed much weaker tensile strength and lower elongation properties. These properties imparted to the hybrids intrinsically decreasing mechanical performance, especially to the samples with higher SiO_2 concentrations. Although further work is being done to support this explanation practically, the results of the mechan-
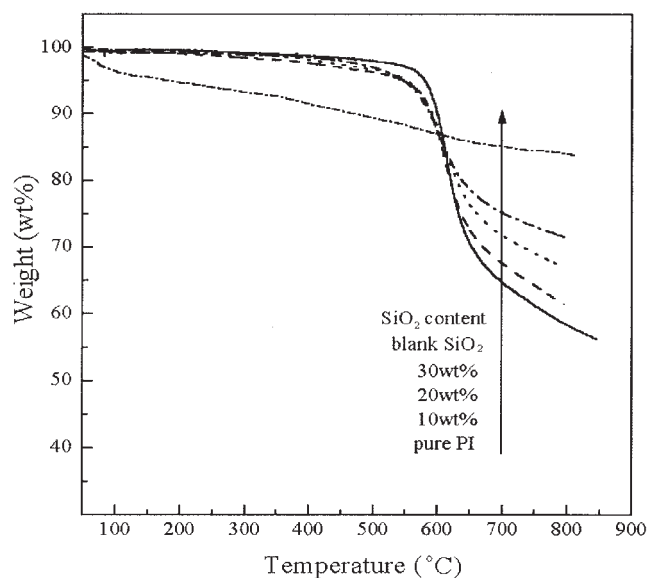

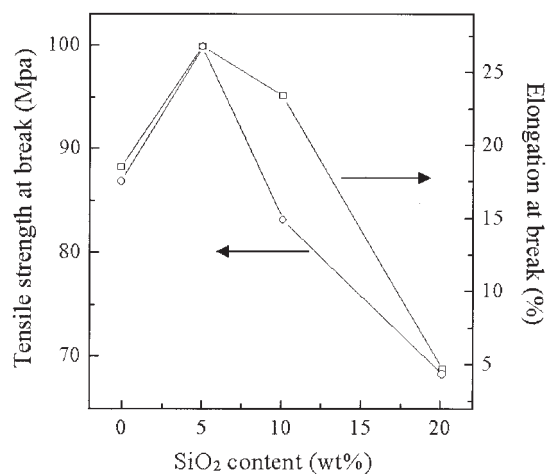**Figure 4** Effect of the SiO_2 concentration on the thermal stability of hybrid films.

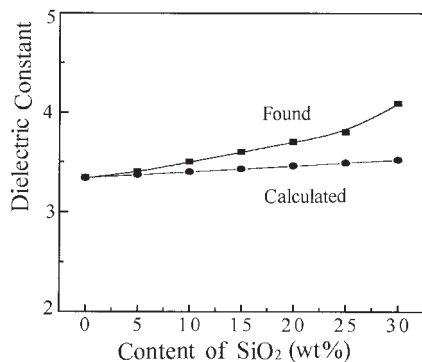**Figure 5** Influence of the SiO_2 concentration on the elongation and tensile strength of PI/SiO_2 films.

Figure 6 Influence of the SiO_2 concentration on ε of SiO_2/PI hybrids.

ical properties can be still regarded as more proof that Si—O—Si networks are formed more densely in hybrids containing more SiO_2.

ε

The ε values of pure PI and PI/SiO_2 hybrid films with different SiO_2 concentrations are shown in Figure 6. The ε values of the hybrids increased with the SiO_2 concentration. This phenomenon could be easily explained by the fact that the native ε value of SiO_2 (4.20)[18] was higher than that found for pure PI (3.34). When the Maxwell-Garnett equation for modeling ε of two-component systems[19] was used to calculate the ε values of these silica/PI hybrids, the observed values were larger than the calculated values. The reason was mainly the residues of —OH groups and organic units in TEOS or APTEOS, which had more influence on ε of the hybrids. Besides, the interphase between the SiO_2 phase and matrix also contributed to the increases of the hybrids.[20] The interphase and hydrolyzing residue acted as practical domains and influenced the hybrid properties. To predict the ε values of PI/SiO_2 hybrids in more detail, we will consider the role of the interphase and hydrolyzing residue in future work.

CONCLUSIONS

PI/SiO_2 hybrid films were prepared with an improved sol–gel process, in which TEOS and APTEOS were used as the main source of silica and as the coupling reagent, respectively. FTIR spectra confirmed the formation of Si—O—Si networks and the conversion from PAA into PI in the hybrids. The SiO_2 component in the hybrids was mainly dispersed in a fine network state. Moreover, relatively small amounts of SiO_2 could form into obviously separated domains in PI matrices. The size of these domains increased to a micrometer scale when the SiO_2 concentration was 30 wt %. However, the aggregation of SiO_2 did not influence the surface smoothness of the hybrid films greatly. The ε values rose slightly as the SiO_2 concentration increased. With further investigation on prohibiting the obvious aggregation of SiO_2, reducing the hydrolyzing residue, and calculating ε in detail, an efficient method should be found for designing and predicting high-performance PI materials for dielectric applications.

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