

Rapid Communication

Structure and infrared emissivity of silicon-containing polyimide/BaTiO₃ nanocomposite films

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Abstract

Silicon-containing polyimide/BaTiO₃ nanocomposite films were prepared by the direct mixing of silicon-containing polyamic acid and BaTiO₃ nanoparticles under ultrasonic wave irradiation, followed with thermal imidization. Structure and thermal properties were measured with FTIR, XPS, SEM, DSC and TGA. The results showed that the compatibility of BaTiO₃ and a polyimide might be improved by the introduction of dimethylsilylene groups into the backbone of a polyimide; and BaTiO₃ nanoparticles in the nanocomposites tended to form clusters. The clusters coalesced into a more uniform structure at a higher BaTiO₃ filling than at a lower one. The interfacial interaction between BaTiO₃ and the silicon-containing polyimide resulted in the increase of the glass transition and the thermal decomposition temperature. It was found that the nanocomposites exhibited lower infrared emissivity value than the pure polyimide and the magnitude of infrared emissivity value was related to the content of BaTiO₃ in the nanocomposites.

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Organic/inorganic composite films with low infrared emissivity present an attractive attention whether in civil or in military applications such as camouflaging military equipments or vehicles from infrared detection and the like. In recent years, several kinds of materials with low infrared emissivity, such as composite ceramics of Fe₂O₃–MnO₂–Co₂O₃–CuO, sol–gel indium tin oxide films of various composition, nanoscale indium oxide, or collagen-g-PMMA/In₂O₃ nanocomposites have been studied [1–4]. Especially, the collagen-g-PMMA/In₂O₃ nanocomposites exhibit lower infrared emissivity than other materials, but the collagen-g-PMMA/In₂O₃ nanocomposites can be used only at lower temperature owing to the low decomposition temperature of collagen [4]. Hybrid composites prepared by mixing micrometer- or

nanometer-scale BaTiO₃ particles with conventional polymers possess high decomposition temperature, however, those have been focused on the investigation of the dielectric, piezoelectric and pyroelectric properties, but little is known about infrared emissivity of polymer/BaTiO₃ nanocomposite [5–9].

In this communication, we prepared silicon-containing polyimide/BaTiO₃ nanocomposite films by the direct mixing of silicon-containing polyamic acid and BaTiO₃ nanoparticles under ultrasonic wave irradiation, followed with thermal imidization. The structure and infrared emissivity of silicon-containing polyimide/BaTiO₃ nanocomposite films were investigated.

The silicon-containing polyamic acid was synthesized by mixing an equivalence of relevant bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (SIDA) and 3,4-oxydianiline (3,4-ODA) at room temperature in *N,N*-dimethylacetamide (DMAc) solutions, reacting for 24 h. Quantitative amounts of BaTiO₃ nanoparticles in

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diametric range of 30–70 nm were added to the solution of silicon-containing polyamic acid in DMAc with vigorous stirring and ultrasonic wave irradiation. After the mixing process was completed, the mixture was cast on a clear glass plate. When the coat on the glass plate was gently baked at 50 °C in vacuo for 6 h, with most of solvent being withdrawn, the gel film was formed. To evacuate the DMAc remaining in the film, polyamic acid/BaTiO₃ gel film was continuously treated at 150 °C in vacuo for 10 h. Finally, the imidization of polyamic acid/BaTiO₃ thin film was performed in steps for 2 h at 200 °C and 1 h at 280 °C. The preparing process is described in Fig. 1.

The content of barium titanate in nanocomposite films was measured by inductively coupled plasma (ICP), using an IRIS intrepid spectrometer. The results are listed in Table 1. ATR-FTIR spectra of the polyimide and nanocomposite films were obtained with a Nicolet NEXUS 670 spectrometer. The characteristic absorption at 1719 and 1776 cm⁻¹ of C=O stretching in imide groups was observed. The absorption of C–N stretching at 1371 cm⁻¹ and C–N bending at 737 cm⁻¹, respectively, in imide groups was also observed. The characteristic Si–Ph absorption appeared at 1412 and 1066 cm⁻¹. The absorption at 1243 cm⁻¹ was based on the aromatic ether –O– in polyimide. The observation of these absorption bands clearly indicated the existence of imide groups and silicon groups, and confirmed the completely imidization of polyamic acid whether in pure polyimide or in polyimide/BaTiO₃ nanocomposite.

Scanning electron microscopy (SEM) was performed on a JSM-5900. The results of SEM studies of cross-section of free-standing nanocomposite films are shown in Fig. 2. Composite layer with low BaTiO₃ filling

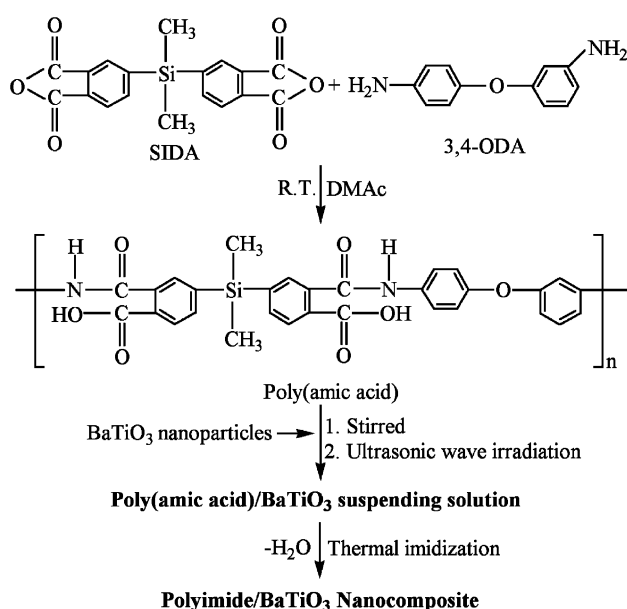


Fig. 1. Preparing process of polyimide/BaTiO₃ nanocomposites.

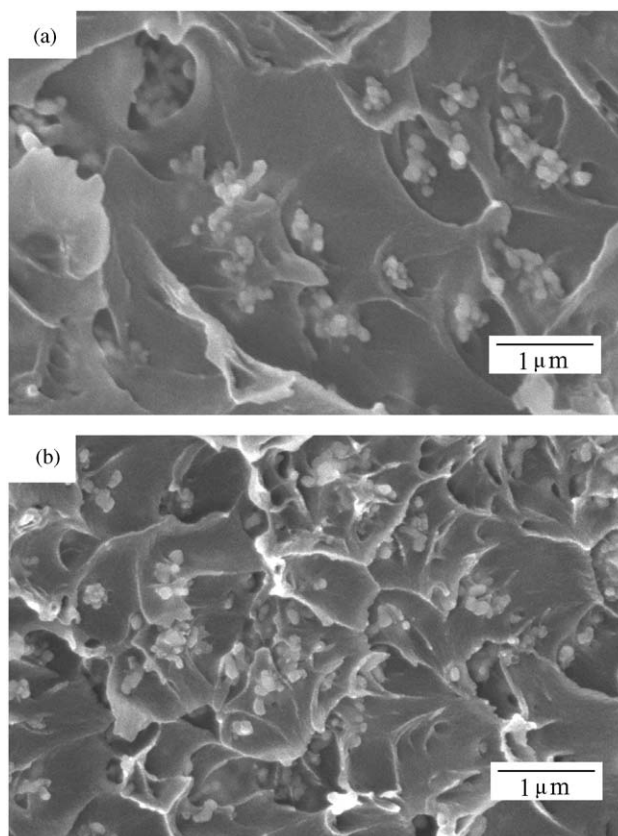


Fig. 2. Cross-section scanning electron micrographs of polyimide/BaTiO₃ nanocomposite films: (a) 14.7% BaTiO₃; (b) 28.7% BaTiO₃.

(14.7% BaTiO₃, Fig. 2a) revealed non-uniform dispersion of BaTiO₃ nanoparticles in polyimide matrix, and had tendency to form clusters. For higher filling (28.7% BaTiO₃, Fig. 2b), the clusters coalesced into more uniform structures. Consequently, BaTiO₃ nanoparticles in the nanocomposites tended to form clusters, and these coalesced into a more uniform structure at higher filling than at lower ones.

X-ray photoelectric spectra (XPS) of films were obtained with a VG ESCALAB-MK II photoelectron spectrometer system. A monochromatic X-ray source with a magnesium anode (MgK α) was used under vacuum of 5×10^{-6} Pa. The take-off angles used were 90°. All binding energies were referenced to the aromatic C(1s) photopeak at 284.6 eV. X-ray photoelectric spectra of the pure polyimide and the polyimide/BaTiO₃ nanocomposite film (28.7% BaTiO₃) exhibited well-defined Si(2p) photopeaks as can be seen from Fig. 3. The binding energy of Si(2p) photopeak for the pure polyimide was at 102.1 eV. When BaTiO₃ nanoparticles were incorporated to silicon-containing polyimide matrix, the binding energy of Si(2p) photopeak decreased to 101.6 eV, and the relative intensity became weaker markedly. However, the binding energy of O(1s) photopeak for the pure polyimide was compared with that for the polyimide/BaTiO₃ nanocomposite, the

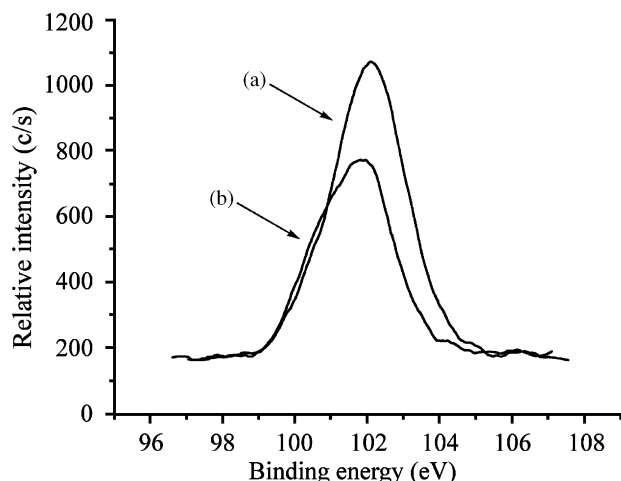


Fig. 3. XPS spectra of polyimide/BaTiO₃ nanocomposite films: (a) pure polyimide; (b) 28.7% BaTiO₃.

difference of both binding energy had only 0.2 eV. These results showed that the effect of BaTiO₃ nanoparticles on silicon atom in a silicon-containing polyimide was conspicuous. It also implied that the compatibility of barium titanate and a polyimide might be improved by the introduction of dimethylsilylene groups into the backbone of a polyimide.

The glass transition temperatures (T_g 's) of silicon-containing polyimide/BaTiO₃ nanocomposite films were determined with a TA instrument Q10, under a nitrogen purge, at a heating rate of 10 °C/min. The results are tabulated in Table 1. The T_g of the nanocomposites was affected by the incorporation of BaTiO₃ nanoparticles into the silicon-containing polyimide matrix. The T_g of the nanocomposites increased with the increase of the BaTiO₃ content in the nanocomposites. The increase of T_g with BaTiO₃ content was due to the restriction of BaTiO₃ nanoparticles to polyimide chain motion. This result was consistent with the fact that the T_g of a simple-filled system rises with increasing particle content [10]. In addition, no melting endothermal peak was observed from DSC traces. This verified the amorphous nature of the nanocomposites.

The thermal stabilities of the polyimide/BaTiO₃ nanocomposite films were characterized by thermogravimetric analysis (TGA). The TGA spectra were recorded on a TA instrument SDT Q600, under a nitrogen purge or an air purge. The scanning rate was 20 °C/min. The temperatures at 5% weight loss (T_{d5} 's) of the polyimide/BaTiO₃ nanocomposite films are summarized in Table 1. In general, the incorporation of BaTiO₃ or TiO₂ into conventional polyimides would make the decomposition temperature of hybrid composites decrease in air owing to catalytic oxidation of BaTiO₃ or TiO₂ [7,11]. However, a silicon-containing polyimide was used instead of the conventional polyimides to prepare polyimide/BaTiO₃ nanocomposites,

Table 1
Components and properties of the composite films

Content of BaTiO ₃ ^a (wt%)	T_g ^b (°C)	T_{d5} ^c		Infrared emissivity (ϵ_{TE} at 8–14 μm)
		In air (°C)	In N ₂ (°C)	
0	228	481	510	0.703
14.7	229	520	542	0.574
28.7	231	529	546	0.605

^aContent of BaTiO₃ in the nanocomposites was determined by ICP.

^b T_g 's were determined by DSC measurement conducted in nitrogen at a heating rate of 10 °C min⁻¹.

^c T_{d5} 's were determined by TGA in nitrogen or in air at a heating rate of 20 °C min⁻¹.

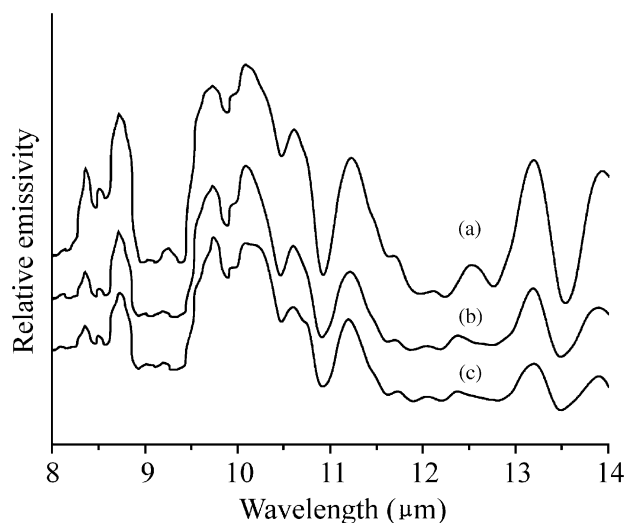


Fig. 4. Infrared emissivity spectra of polyimide/BaTiO₃ nanocomposite films: (a) pure polyimide; (b) 14.7% BaTiO₃; (c) 28.7% BaTiO₃.

their oxidation-resistant property was improved, and the T_{d5} of the nanocomposites also increased with the increase of the content of BaTiO₃ within the nanocomposites, whether in nitrogen or in air. The T_{d5} of the nanocomposites at lower BaTiO₃ concentration was smaller than that at higher BaTiO₃ concentration. These phenomena were ascribed to the presence of silicon atom in polyimide chain and the interfacial interaction between silicon-containing polyimide and BaTiO₃ nanoparticles.

Infrared emissivity values and spectra of polyimide/BaTiO₃ nanocomposite films were recorded on a Nicolet Magna-IR 750 spectrometer equipped with an FTIR emission accessory at 60 °C. The infrared emissivity spectra of pure polyimide and nanocomposite films are shown in Fig. 4. It was clearly seen that the pure polyimide had higher emissivity value than the nanocomposites, and the maximum emissive peaks occurred in the range of 9–11 μm for pure polyimide and nanocomposites. Referring to ATR-FTIR spectra, these

maximum emissive peaks were attributed to the vibration of Ph–Si and the imide ring.

The integrating values (ϵ_{TE}) of infrared emissivity in the range of 8–14 μm are summarized in Table 1. The ϵ_{TE} of the nanocomposites varied with the content of BaTiO_3 in the nanocomposites, and presented a smallest ϵ_{TE} value. Decreasing of the ϵ_{TE} value of the nanocomposites showed that polyimide and BaTiO_3 components exchanged interfacial interactions such as electrostatic forces. The presence of interfacial interactions between the polyimide and BaTiO_3 components had been certified by XPS mentioned above. These interfacial interactions altered vibration mode of molecules, atoms or pendant groups on the interface between the polyimide and BaTiO_3 components, which had direct influence on emissivity. Namely, there existed a special interface layer that had a different ϵ_{TE} value from that of the body of the polyimide and BaTiO_3 components. Therefore, the decrease in the ϵ_{TE} values of the nanocomposites was most likely to be a direct consequence of the interfacial interactions [4]. Increasing of the ϵ_{TE} value of the nanocomposites at the high BaTiO_3 concentration might be to coarsen the surface of the nanocomposite film.

In summary, the silicon-containing polyimide/ BaTiO_3 nanocomposite films had been produced based on mixing of silicon-containing polyamic acid and barium titanate nanoparticles under ultrasonic wave irradiation, followed with thermal imidization. BaTiO_3 nanoparticles in the nanocomposites tended to form clusters, and the clusters coalesced into more uniform structures at a

higher filling than at a lower one. The nanocomposite films obtained by this approach exhibited high thermal stability whether in air or in nitrogen. The decrease of infrared emissivity of nanocomposite films might have resulted from the interfacial interaction between silicon-containing polyimide and BaTiO_3 nanoparticles.

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