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Characteristics of polyimide/barium titanate composite films

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Abstract

In this study, the characteristics of the polyimide/$BaTiO_3$ composite films with various amounts of $BaTiO_3$ were evaluated. Modifier 1-methoxy-2-propyl acetate was added during composite preparation to disperse the $BaTiO_3$ particles in polyimide matrix. Conversion of polyamic acid (PAA) to polyimide was not completed for the composite film with a high $BaTiO_3$ loading (90 wt%). Dielectric constant of the film increases from 3.53 to 46.50, at the sweep frequency of 10 kHz, as the $BaTiO_3$ content increases from 0 to 90 wt% (0–67.5 vol.%), which is mainly due to the relatively high dielectric constant of $BaTiO_3$ particles in the polyimide matrix. The dielectric losses at 10 kHz is ranging from 0.005 to 0.015, which is due to the switching of the domain wall. Water absorption decreases considerably with increasing $BaTiO_3$ content. With 10 wt% (2.5 vol.%) $BaTiO_3$ addition, the water absorption of the composite film reduces 45% from that of pure polyimide. Also, high loading of $BaTiO_3$ is not beneficial to reduce the water absorption of the composite film.

Keywords: C. Dielectric properties; Polyimide; Barium titanate; Composite

1. Introduction

The construction of organic–inorganic composites has attracted considerable attention in many applications, such as packaging material, circuit board, interlayer dielectrics, antenna, and passivative protection. Composite materials are typically formed when at least two distinctly dissimilar materials are mixed to form a monolith [1]. Polymers possess limitations for much higher performance applications in which inorganic materials are used, because their intrinsic nature as organic materials. Inorganic materials exhibit excellent thermal stability and functional properties such as dielectric and magnetic properties, but high brittleness and bad film forming characteristics. Thus, the composite formation of polymers with inorganic material has been suggested to meet the demands of balanced properties for both organic and inorganic materials [2,3]. The overall properties of a composite material are determined not only by the properties of the parent components but also by the morphology, volume fractions, and connectivity of the phases as well as their interfacial properties [4,5].

Among the polymers, polyimides (PI) possess reliable high temperature stability, good mechanical strength and excellent chemical resistance. In recent year, the preparations of polyimide composite materials have been extensive studied due to the dramatic improvements over their pure state in the thermal stability, mechanical properties and other functional features by introducing only small fraction of inorganic fillers, such as SiO_2, Al_2O_3, AlN, TiO_2, and magadiite [2,5–10]. The polyimide based composite materials can be prepared via intercalation approach [4,5], sol–gel route [6,11], or blending process [8]. A wide range of organic–inorganic composites could be prepared by the appropriate selection of the raw materials and preparative approaches, in order to make finely dispersed particles in polymer matrix while minimizing agglomeration, and to obtain properties to meet the requirements of different applications [7,12].

In this study, barium titanate ($BaTiO_3$) was chosen as ceramic filler due to the fact that it possesses ferroelectric properties, a high dielectric constant at room temperature ($\varepsilon_r \approx 1000$–$2000$), a low dielectric loss, and a high dielectric breakdown strength. The polyimide/$BaTiO_3$ composite films

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were prepared by incorporation different amounts of $BaTiO_3$ to a diamine/dianhydride/solvent system and in situ polymerizing. Modifier 1-methoxy-2-propyl acetate was added during composite preparation to enhance the dispersity of $BaTiO_3$ particles in polyimide matrix. The chemical and electrical characteristics of the composite films with different $BaTiO_3$ contents were discussed through the results from Fourier transform infrared spectroscopy (FTIR), and RLC meter. Water absorptions by the composite films were also evaluated and discussed.

2. Experimental procedure

2.1. Materials

Analytical grade pyromellitic dianhydride (PMDA, Acros Co., Japan) and 4,4′-oxydianiline (ODA, Acros Co., Japan), the solvent *N*,*N*-dimethylacetamide (DMAc, 99%; Acros Co., Japan), and the modifier 1-methoxy-2-propyl acetate (BYK-140; Acros Co., Japan) were used in this study throughout. PMDA was recrystallized from acetic anhydride, ODA was purified by vacuum sublimation, and DMAc was dried over molecular sieves, prior to use. Commercial barium titanate ($BaTiO_3$) powder was purchased from Cabot Co., U.S.A., and dried in oven at 80 °C before use. The particle size of the $BaTiO_3$ is about ≈0.2 μm, measured by light scattering (HORIBA LA-920).

2.2. Preparation of polyimide/$BaTiO_3$ composite films

A schematic representative for preparation of polyimide/$BaTiO_3$ composite films is shown in Fig. 1. A proper amount of $BaTiO_3$ powder was added into DMAc solvent and mixed violently for several hours. A modifier 1-methoxy-2-propyl acetate was added to get a highly dispersed $BaTiO_3$ suspension and to increase the subsequent interaction between $BaTiO_3$ powder and polyimide. The extent of the $BaTiO_3$ in the composite ranges from 0 to 90 wt% (0–67.5 vol.%). For preparing a poly(amic acid) solution, the aromatic diamine ODA was added and dissolved in DMAc. Then, an equimolar amount of dianhydride aromatic PMDA particles was added stepwise into ODA/DMAc solution. The mixture was kept at room temperature for 24 h to obtain a viscous poly(amic acid) (PAA) solution. The above $BaTiO_3$ suspension and PAA solutions were then poured into a reactor together and stirring for 24 h, to produce a homogeneous and transparent $BaTiO_3$/PAA solution. The $BaTiO_3$ particles were well dispersed in the PAA solution, and no particle clustering or aggregation was observed. This PAA/$BaTiO_3$ suspension was then cast on a clean dust free glass plate and followed by successively heating at 80, 120, 150, 200, and 300 °C each for 1 h to remove the solvent and thermal imidization under vacuum oven. The polyimide/$BaTiO_3$ composite films with different $BaTiO_3$ contents were obtained.

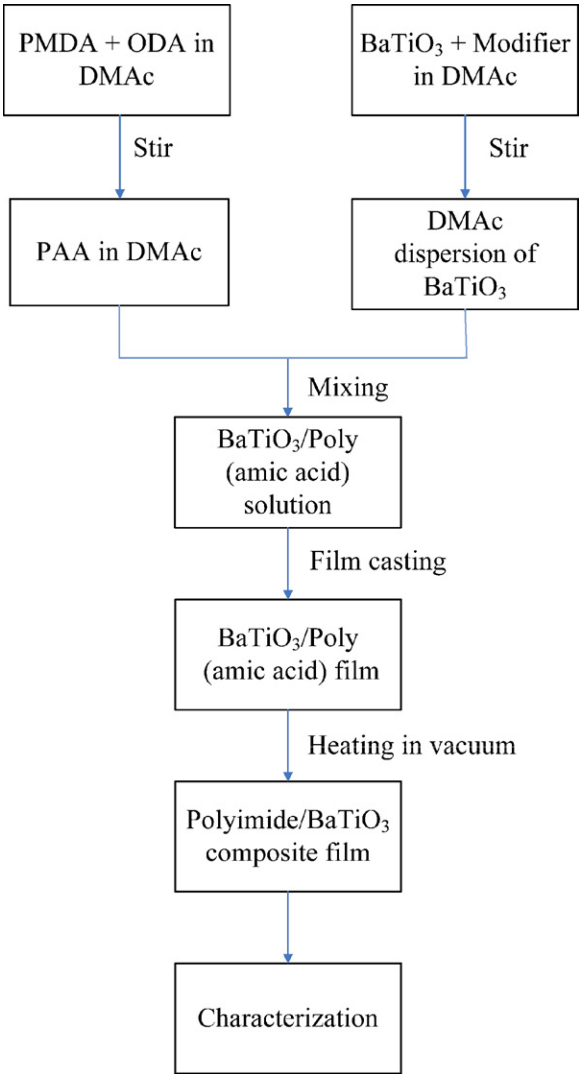

Fig. 1. A schematic representative for preparation of PI/$BaTiO_3$ composite films.

2.3. Chemical and electrical characterizations

Fourier transform infrared (FTIR) spectra of the composite films were measured on a Perkin-Elmer Model 2000 spectrophotometer, at the resolution of 4 cm^{-1}, to understand the chemical bonding among various species. The dielectric properties of the films were characterized using Agilent 4284A LCR meter at the frequencies ranging from 10 kHz to 1 MHz. Samples for the measurement were fabricated by sputtering a thin film gold pattern on the both sides of the polyimide/$BaTiO_3$ films. The moisture permeations of the composite films were evaluated using water absorption test. Samples of 15 cm × 15 cm with the thickness of 40–43 μm were dried in an oven at 80 °C overnight to eliminate any water absorbed prior the test. The dried composite films were then subjected to immersion in water for 24 h to ensure saturation. Water absorption was calculated according to the percentage of weight gained after the immersion.

3. Results and discussion

Fig. 2 shows the FTIR spectra of the pure $BaTiO_3$, pure PI, PI/50 wt%$BaTiO_3$ film, and PI/90 wt%$BaTiO_3$ film. Pure

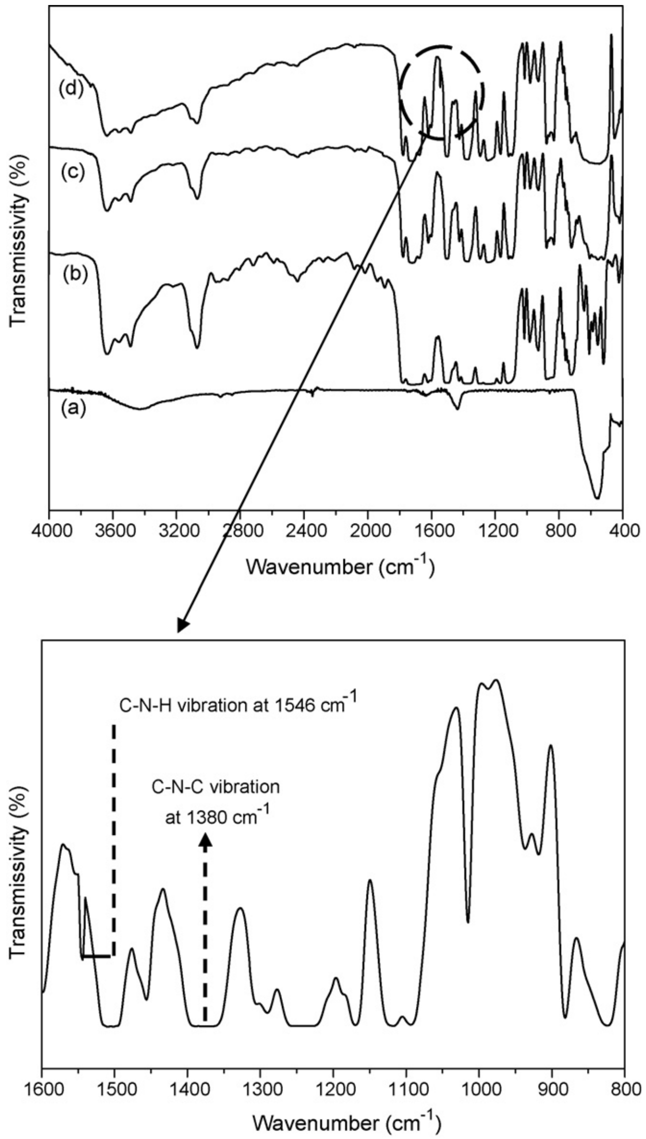

Fig. 2. FTIR spectra of the (a) pure $BaTiO_3$, (b) pure PI, (c) PI/50 wt% $BaTiO_3$, and (d) PI/90 wt% $BaTiO_3$ composite films.

$BaTiO_3$ exhibits a strong absorption at 500–700 cm^{-1}. After the thermal treatment, PAA was converted to polyimide. This is confirmed by the observation of the characteristic absorption bands of asymmetric and symmetric C=O stretching in imide groups at 1776 and 1725 cm^{-1} and the characteristic absorption band of C–N–C stretching in imide groups at 1380 cm^{-1} [11]. Comparing the PI with 50 and 90 wt% $BaTiO_3$ composite films (Fig. 2(c) and (d)), the FTIR spectra are a combination of PI and $BaTiO_3$ spectra, which indicates that the introduction of the $BaTiO_3$ by the blending process into the PI leads to the formation of PI/$BaTiO_3$ composite film. However, the presence of the absorption band, characteristic of C–N–H stretching vibration (1546 cm^{-1}) in Fig. 2(d), indicates that the conversion of PAA to polyimide was not completed for the composite film with a high $BaTiO_3$ loading. The C–N–H stretching in PAA would change to C–N–C stretching after imidization of polyimide.

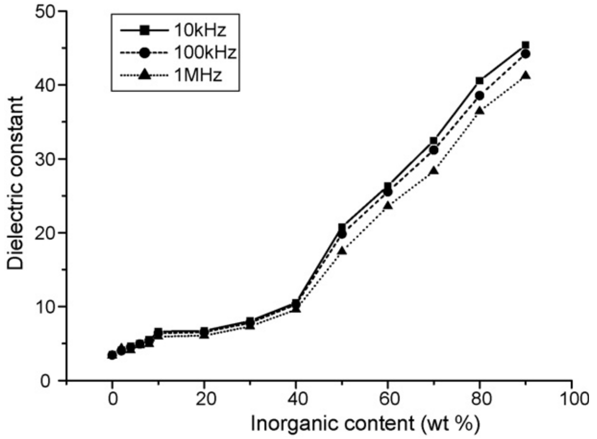

Fig. 3. The effects of $BaTiO_3$ content on the dielectric constants and dielectric losses of PI/$BaTiO_3$ composites, at the sweep frequencies of 10 kHz, 100 kHz, and 1 MHz.

Figs. 3 and 4 show the effects of $BaTiO_3$ content on the dielectric constants and dielectric losses of PI/$BaTiO_3$ composite films at the sweep frequencies of 10 kHz, 100 kHz, and 1 MHz. The dielectric constant varies with the sweeping frequency and $BaTiO_3$ content. Generally, it decreases with sweeping frequency, due to the fact that less dipoles could follow the switching field as frequency increases. The dielectric constant increases significantly with increasing $BaTiO_3$ content (Fig. 3). For instance, at the sweep frequency of 10 kHz, the dielectric constant increases from 3.53 to 46.50 as the $BaTiO_3$ content increases from 0 to 90 wt% (0–67.5 vol.%). The increment of the dielectric constant is mainly due to the relatively high dielectric constant of $BaTiO_3$ particles in the polyimide matrix. It seems that the increment of the dielectric constant with $BaTiO_3$ content has two regions, including one has a lower increment from 0 to 40 wt% (0–13.3 vol.%) and the other has a higher increment from 40 to 90 wt% (13.3–67.5 vol.%). Although the poly(amic acid) precursor for the PI/90 wt%$BaTiO_3$ composite film cannot be completely imidized during thermal treatment, it does not change the increasing-

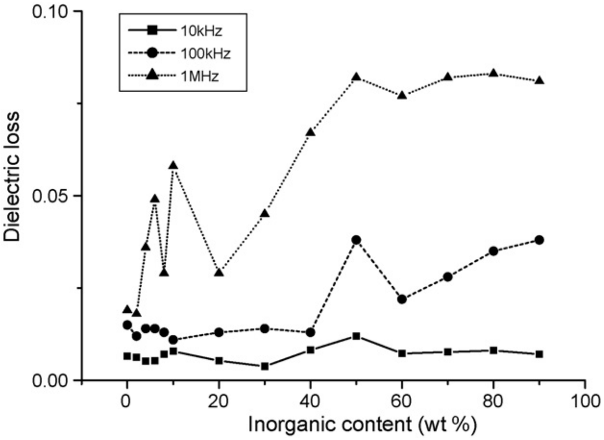

Fig. 4. The effects of $BaTiO_3$ content on the dielectric constants and dielectric losses of PI/$BaTiO_3$ composites, at the sweep frequencies of 10 kHz, 100 kHz, and 1 MHz.

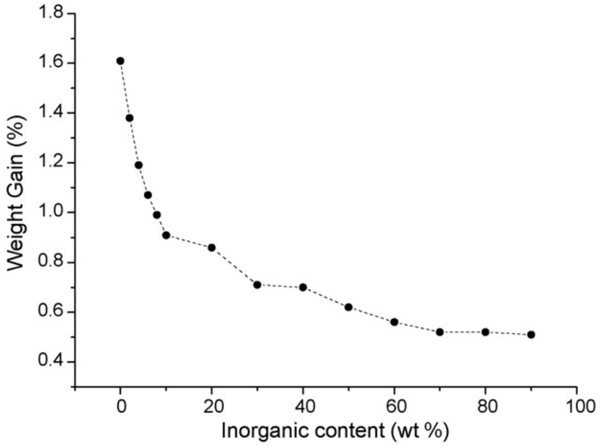

Fig. 5. The effect of $BaTiO_3$ contents on the weight gain of PI/$BaTiO_3$ composites due to water absorption.

trend of the dielectric properties. The high increment of the dielectric constant with increasing $BaTiO_3$ implies that the $BaTiO_3$ particles uniformly disperse in the PI matrix. Otherwise, the porosities associated with the agglomerated $BaTiO_3$ particles would significantly degrade the dielectric constant. It is evident that the addition of the modifier in the blending process provides an alternative route to prepare a deagglomerated and homogeneous distributed inorganic particles in the PI matrix, in additional to use sol–gel route which usually requires an expensive material cost.

The dielectric losses generally increase with sweeping frequency. It does not have a significant difference among composites with various amounts of $BaTiO_3$ at the sweep frequency of 10 kHz, ranging from 0.005 to 0.015, but increases significantly with $BaTiO_3$ content at 100 kHz and 1 MHz, ranging from 0.02 to 0.04 and from 0.025 to 0.085, respectively, which is due to the motion of domain wall in the $BaTiO_3$ particles. The higher the $BaTiO_3$ content, the larger the change in the dielectric loss with frequency is. Apparently, the major loss mechanism is due to the switching of the domain wall, but not the dc conduction.

Fig. 5 shows the effect of $BaTiO_3$ contents on the weight gain of PI/$BaTiO_3$ composites due to water absorption. The water absorption decreases considerably with increasing $BaTiO_3$ content. For the initial 10 wt% (2.5 vol.%) $BaTiO_3$ addition, the water absorption significantly reduces from 1.63 to 0.90%, which is 45% reduction from the original value. Water absorption proceeds through the initial fast filling at the preexisting microcavities and subsequent slow penetration into the defect-free continuous matrix [13]. The diffusion path of the water molecules increases with the extent of $BaTiO_3$ particles [14]. Particularly, when the $BaTiO_3$ particles are well dispersed in the PI matrix, it effectively increases the diffusion path and, in turn, reduces the water absorption. As the $BaTiO_3$ continuously increase from 10 to 90 wt%, the water absorption decreases from 0.9 to 0.52%. The decrease in the water absorption is mainly associated with the reduction in the volume fraction of polyimide in the composite film. For PI/90 wt%$BaTiO_3$ composite film, the volume fraction of the polyimide is 32.5 vol.% and the water absorption is 0.52%, which is 32% for that of the pure polyimide. High loading of $BaTiO_3$ particles is not beneficial to reduce the water absorption in the composite film.

4. Summary

In this study, characterizations of the polyimide/$BaTiO_3$ composite films with various $BaTiO_3$ contents were performed. Dielectric constant of 46.5 and dielectric loss of 0.015 were obtained for the composite film with 90 wt% (67.5 vol.%) $BaTiO_3$, at the sweep frequency of 10 kHz. Water absorption of the composite significant drops to a level of 0.52% as the $BaTiO_3$ content reaches 10 wt%. Continuously increase in the $BaTiO_3$ loading is not beneficial to reduce the water absorption of the composite film.

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