

Preparation of Polyimide/BaTiO₃/Ag Nanocomposite Films *via in situ* Technique and Study of Their Dielectric Behavior*

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Abstract Triphase polyimide nanocomposite films were fabricated using barium titanate (BaTiO₃) with high dielectric constant and silver (Ag) with high conductivity as fillers. *In situ* method was utilized to obtain the homogeneous dispersion of nanoparticles. The *in situ* polymerization of polyimide precursor-poly(amic acid) was performed in the presence of BaTiO₃ particles. Silver compound 1,1,1-trifluoro-2,4-pentadionato silver(I) was added into the BaTiO₃ containing poly(amic acid) solution to achieve silver nanoparticles *via in situ* self metallization technique. The thermally induced reduction converted silver (I) to metallic silver with concomitant imidization of poly(amic acid) to polyimide. Both BaTiO₃ and silver nanoparticles were uniformly dispersed in the polyimide substrate. The dependence of dielectric behavior on the BaTiO₃ and Ag contents was studied. The incorporation of small amount of silver nanoparticles greatly increased dielectric constant of composite films.

Keywords: Polyimide; Silver; Barium titanate; Nanocomposites; Dielectrics.

INTRODUCTION

Further demand for the thin film capacitors with high capacitance density, miniature dimensions and multifunction has stimulated the progress in developing polymer/ceramic composite materials which combines the high dielectric constant of ceramics and the easy processing and excellent mechanical properties of polymers^[1–4]. For this polymer/ceramic two-phase system, the dielectric properties have strong relationship with the loading concentration and dispersion of ceramic fillers. Generally, high dielectric constant values can be achieved at a high ceramic loading^[5–7]. However, there must be a great challenge for the flexibility of composite films under this condition. Because of the limitations of the above system, many research groups have introduced conductive fillers into the biphasic polymer/ceramic composites to realize a high dielectric constant at a low content of ceramic filler^[8–10]. The conductive fillers possessing high electrical conductivity act as microcapacitors in the insulating polymer substrate. When the conductive filler loading is close to the percolation threshold, an elevated dielectric constant can be obtained. In this triphase system, the dispersion of conductive filler is a critical factor to ensure uniform and stable dielectric properties of the desired composite films. Traditionally, these polymer based composites were prepared by directly mixing metal particles with polymer solution^[11]. It is difficult to obtain a homogeneous dispersion for the nanosized conductive fillers as their high surface area drives them to agglomerate into clusters. Therefore, there is a growing need for

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developing an effective route to obtain uniform dispersion of metal nanoparticles in the biphasic polymer/ceramic substrates.

In the present work, we concentrated our efforts on a simple method to prepare triphase polyimide (PI) system, in which the uniform dispersion of both BaTiO₃ and silver nanoparticles can be assured *via in situ* technology. Polyimide, as a well-known high-performance polymer, has been one of the most promising candidates for preparing polymer/inorganic composite materials due to its excellent mechanical strength, high thermal stability, preferable chemical resistance and easy film casting^[12, 13]. Our previous study has utilized the *in situ* technology to obtain reflective and electrically conductive silver layer on polyimide surface^[14–16]. That is silver ions were not only reduced to silver atoms but also followed by the migration and agglomeration of silver particles to form a well-established silver layer on the film surface. Little silver particles with smaller size dispersed in the inner polyimide substrates. However, homogeneous dispersion of silver particles can be observed at the early stage of thermal treatment. Therefore, this phenomenon stimulated us to perform homogeneously dispersed silver nanoparticles in PI/BaTiO₃/Ag composite films by reducing the thermal treatment time and temperature. Furthermore, the control of concentration, particle size and interparticle space can be realized by adjusting the silver compound loading and thermal treatment process. The dielectric behavior of the final composite films associated with the BaTiO₃ and silver contents is discussed in detail. The structural and morphological characteristics of the resulting films were analyzed by X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy and scanning electron microscopy.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (4,4'-ODA) were provided by Shanghai Research Institute of Synthetic Resins. PMDA was dried under vacuum at 160 °C for 5 h and 4,4'-ODA was recrystallized in ethyl acetate prior to use. *N,N*-dimethylacetamide (DMAc) (analytical pure, water content ≤ 0.1%) was purchased from Tianjin Fu Chen Chemicals Reagent Company and used without further purification. Barium titanate (BaTiO₃) was obtained from Shan Dong Guoteng Functional Ceramic Material Co., Ltd. with an average particle size of 100 nm. Silver acetate (AgAC) (analytic pure, ≥ 99.0%) and 1,1,1-trifluoro-2,4-pentanedione (TFAH) (≥ 98%) were purchased from Shanghai Shiyi Chemicals Reagent Co. Ltd. and Acros Organics, respectively, and were used as received.

Preparation of Composite Films

The following procedure was used to prepare (PMDA/4,4'-ODA)-based poly(amic acid) (PAA)/BaTiO₃ solutions. A precalculated amount of BaTiO₃ particles were dispersed in the DMAc solvent with ultrasonic agitation at room temperature. PAA synthesis was performed by dissolving 4,4'-ODA in BaTiO₃ suspended DMAc solution, followed by the addition of PMDA into the above mixed solution by portions. The content of BaTiO₃ in the PAA solution ranged from 0 wt% to 70 wt%. For the preparation of silver nanoparticles in the composite films, the (1,1,1-trifluoro-2,4-pentadionato) silver(I) (AgTFA) complex was freshly produced by dissolving AgAC in a small volume of DMAc containing TFAH with three times mole equivalent to the AgAC. AgTFA complex was then added to PAA/BaTiO₃ solution. Films were cast onto a clean glass plate. Large portions of solvent were removed by holding the films in the ambient environment for 12 h, and then thermal imidization was performed in a forced air oven to obtain PI/BaTiO₃/silver triphase composite films.

Characterization

X-ray diffraction (XRD) patterns were performed on an X-ray diffractometer (D/Max2500VB2+/PC, Rigaku, Japan) at a scanning rate of 0.18° per second, in the 10°–90° region. The X-ray beam was generated by a CuK α radiation source ($k = 0.154056$ nm), using a tube voltage of 40 kV and a current of 200 mA.

Fourier transform infrared (FTIR) spectra of the PI composite films were recorded using a Nicolet Nexus670 IR spectrometer.

The surface morphology was observed on a Hitachi S-4700 field emission scanning electron microscope (SEM) operating at an accelerating voltage of 20 kV. Samples were coated with a *ca.* 5 nm platinum layer prior to measurement.

Cross-sectional transmission electron micrograph (TEM) was taken with a Hitachi H-800 transmission electron microscope at an accelerating voltage at 200 kV. The samples were embedded in epoxy resin, and then sectioned into slices using an ultramicrotome with a diamond knife. These thin sections were mounted onto the carbon-coated TEM copper grids for observation.

The dielectric properties of the composite samples were measured using an impedance analyzer (Agilent 4294A) in the frequency range of 10^2 Hz to 10^7 Hz at room temperature. A thin layer of Ag paste was coated on both sides of the sample prior to measurement.

RESULTS AND DISCUSSION

Polyimide/BaTiO₃ Biphase Composite Films

The loading of ceramic particles into the PAA solution was performed *via in situ* polymerization and was effectively assisted by ultrasonic technique. That is, BaTiO₃ particles got a uniform dispersion in DMAc solvent by ultrasonic treatment followed by the *in situ* polymerization of PAA in the BaTiO₃ suspension. As known, the viscosity of PAA solution gradually increased with the stepwise addition of PMDA. The low viscosity produced initially is favorable to the migration of PAA macromolecular chain between the gaps of BaTiO₃ particles. Therefore, the uniform dispersion of BaTiO₃ particles caused by applying ultrasonic can be maintained under this condition. Further increase of viscosity provides less opportunity for the already separated BaTiO₃ particles to reunite together because of the difficult movement of BaTiO₃ particles in high viscosity solution.

The cross-sectional TEM images of Figs. 1(a) and 1(b) and SEM image of Fig. 1(c) show the morphology of PI/BaTiO₃ composite films with BaTiO₃ content of 30%. BaTiO₃ with an average particle size of 100 nm well dispersed in the PI substrates, which indicated that both the assist of ultrasonic and *in situ* polymerization made great contribution to this dispersion of BaTiO₃ particles as proposed previously.

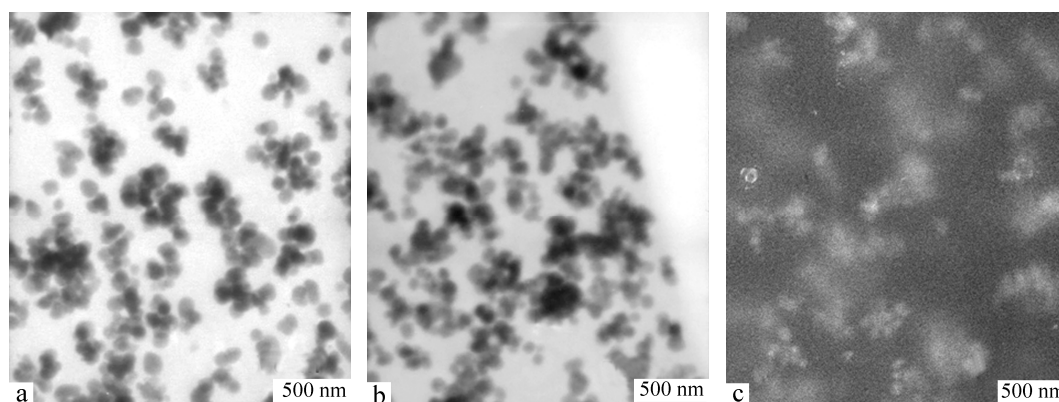


Fig. 1 (a) and (b) cross-sectional TEM and (c) SEM images of PI/BaTiO₃ composite films

Figures 2(a) and 2(b) show the development of dielectric properties of the composite films as functions of the BaTiO₃ content and frequency at room temperature. The dielectric constant performed a significant enhancement with the increase of BaTiO₃ content. For the sample tested at the frequency of 10^4 Hz, the dielectric constant increased from 3.51 to 17.81 as the BaTiO₃ content increased from 0 to 70 wt%. This improvement in dielectric constant is due to the high dielectric constant of ceramic particles. A significant drop in dielectric constant occurs when the frequency reaches to 10^7 Hz. This is attributed to the difficulty for dipoles to follow the switching field as frequency increases. Correspondingly, in high frequency region, the dielectric loss caused by polarization loss plays a predominant role resulting in the fast increase of loss tangent.

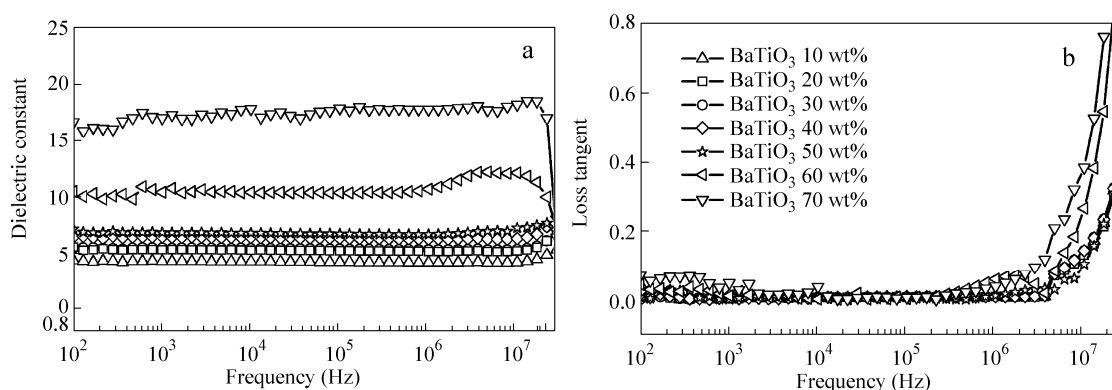


Fig. 2 Frequency dependence of the (a) dielectric constant and (b) loss tangent of PI/BaTiO₃ composite films

Polyimide/BaTiO₃/Ag Triphase Composite Films

The flexibility of PI composite films must be challenged if high concentration of inorganic phase is incorporated. In this respect, metal nanoparticles with high conductivity were incorporated into the biphasic polyimide/BaTiO₃ composites as the third component to realize a high dielectric constant at low inorganic loading levels. The size, dispersion and interparticle distance of metal nanoparticles strongly influence the dielectric behavior of the final composite films. The dispersion of nanoparticles has always been changeable because of their high surface area. In the present study, silver nanoparticles are incorporated into PI/BaTiO₃ composites by *in situ* self metallization technique as illustrated in Fig. 3. Silver compound with bridging β -diketonate ligands AgTFA, which possesses good compatibility with PAA solution, was employed as the silver precursor. Silver(I) has a favorable standard electrode potential ($E_0 = 0.8$ V) which allows silver(I) to be easily reduced upon simple thermal treatment.

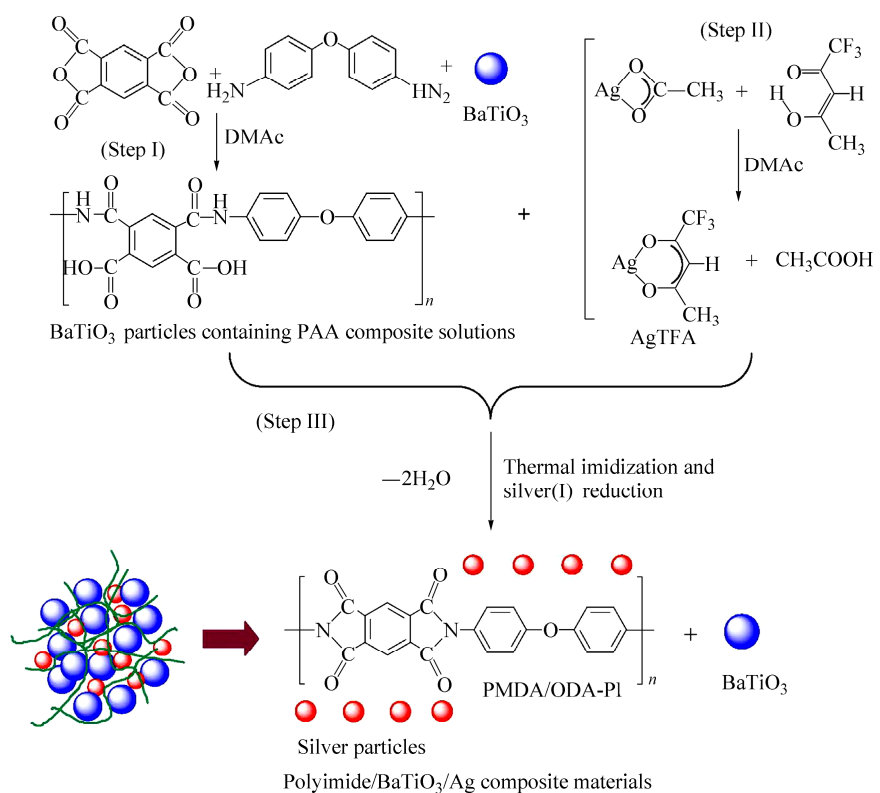


Fig. 3 Schematic illustration of the present process for the silver nanoparticles formation and the preparation of PI/BaTiO₃/Ag triphase composite films

This characteristic feature allows for the generation of silver nanoparticles in PI substrate in the process of thermal imidization of PAA. The formation of silver nanoparticles contains the reduction of silver (I) ions to silver atoms which continuously aggregate to form crystal silver particles. Thermal curing time and temperature are important factors to influence the dispersion of silver particles. As demonstrated in our previous publication^[14–16], well-defined silver layer will be formed on the film surface and the film surface presents the gray color of silver layer by prolonging thermal curing time and increasing temperature, which will seriously affect the dielectric property of triphase composite films. In order to guarantee silver particles to be reserved in the polyimide substrates, thermal curing conditions were adjusted in this work. The color of final film appearance exhibits a grass green, which presents the formation of small silver particles in the polymer bulk other than with metallic luster on the polymer surface.

The X-ray diffraction pattern in Fig. 4(b) for the PI/BaTiO₃ composite films containing 20 wt% BaTiO₃ exhibits the distinct diffraction peaks corresponding to the cubic BaTiO₃ crystallite. If silver of 5 wt% content was incorporated into PI and reduced in ambient circumstance at 200 °C for 3 h, the main XRD peaks in the silver (111) and (200) region appeared in Fig. 4(c) with rather week intensity as marked by asterisk, suggesting the formation of silver nanoparticles. A relatively small amount of silver compared with BaTiO₃ in the same sample resulted in this faint diffraction peak of silver. For clarity, the XRD pattern of only silver-contained PI composite films prepared by this *in situ* technique was illustrated in Fig. 4(a). The five diffraction peaks can be indexed as (111), (200), (220), (311) and (222) Bragg reflection of face-centered cubic silver crystallite^[15]. This result demonstrated that the reduction of silver(I) to silver(0) and the crystallization of silver nanoparticles can be totally realized through the simple thermal treatment.

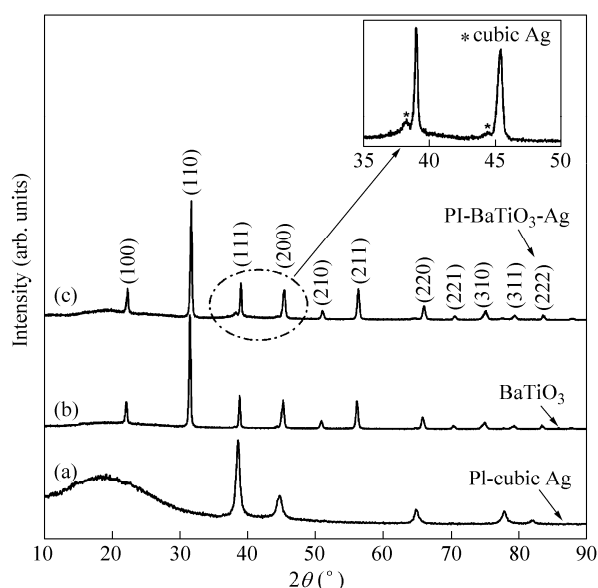


Fig. 4 XRD patterns of (a) PI/Ag composite films, (b) PI/BaTiO₃ composite films and (c) PI/BaTiO₃/Ag composite films (the asterisk indicates Ag)

The thermal treatment temperature was reduced to control the migration of silver nanoparticles. FTIR spectra of the composite films thermally treated at 200 °C for 3 h was collected to determine the degree of imidization reaction as shown in Fig. 5. The typical absorbance bands of PAA are visible at 1660 cm⁻¹ (amide I; carbonyl stretching) and 1543 cm⁻¹ (amide II; coupling of C—N stretch and N—H deformation) (Fig. 5a). Upon applying the thermal treatment, the absorbance peaks arising from imide ring bands appeared at 1720, 1770, 1502, and 1380 cm⁻¹, corresponding to symmetric carbonyl stretching, asymmetric carbonyl stretching, benzene ring C=C stretching and imide ring C—N—C stretching, respectively. This indicates that the imidization

reaction of the composite film proceeds at 200 °C for 3 h. The unchangeable peak of benzene ring C=C stretching at 1502 cm⁻¹ is generally used as the internal standard for determining the degree of imidization. The calculation is performed by comparing the ratio of the intensity of the absorbance at 1720 cm⁻¹ to that at 1502 cm⁻¹ (A_{1720}/A_{1502}). For the pure polyimide film thermally treated at 300 °C for 1 h, the peak height of imide rings at 1720 cm⁻¹ divided by the peak height of the peak at 1502 cm⁻¹ was regarded as the standard for a degree of imidization of 100%. After the composite films thermally treated at 200 °C for 3 h, the relative degree of imidization reached to 77.2% indicating that the imidization reaction can not proceed completely under this experimental condition. However, the composite films can provide enough strength and flexibility for the applications.

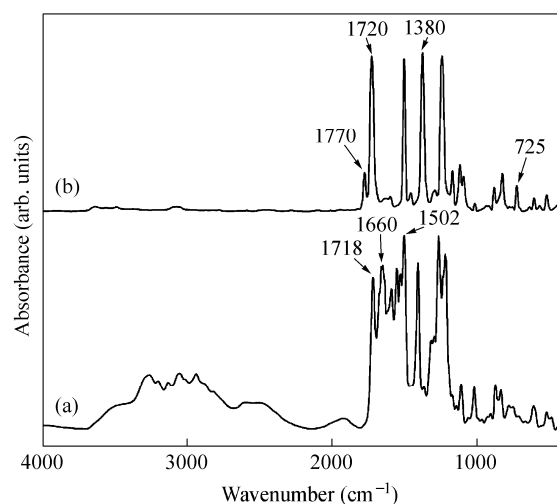


Fig. 5 FTIR absorption spectra of (a) PAA and (b) polyimide film thermal treated at 200 °C for 3 h

For the sample containing 5 wt% silver cured at 200 °C for 3 h, silver nanoparticles can be clearly observed among the BaTiO₃ particles. There is no obvious concentration gradient of silver nanoparticles from the inside to the surface comparing Fig. 6(a) with Fig. 6(b). The SEM image of Fig. 6(c) also indicated that many silver nanoparticles with diameters on the order of 10 nm or less were uniformly dispersed on the film surface. These small silver aggregates were all island-like and separated from each other. This favorable result suggested that the decrease of thermal curing time and temperature made it possible for the silver particles remaining in the inner polyimide bulk with small sizes.

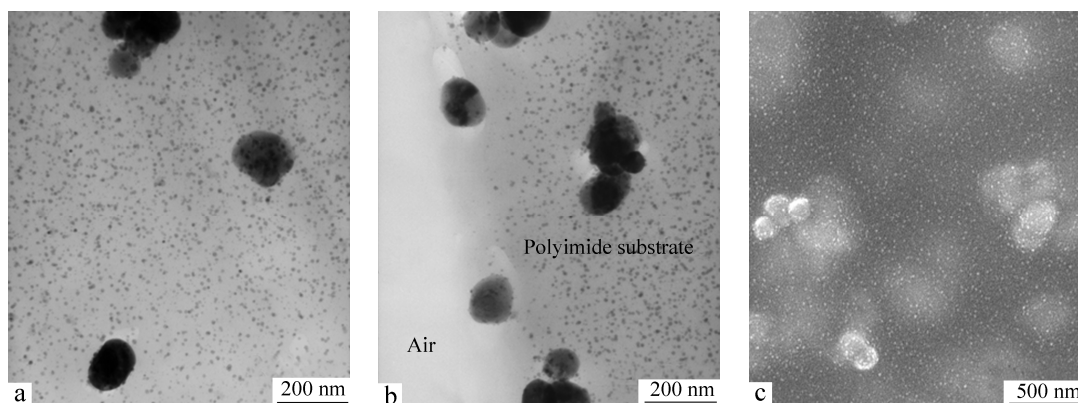


Fig. 6 (a) and (b) cross-sectional TEM and (c) SEM images of PI/BaTiO₃/Ag composite films

The incorporation of high electrical conductivity metal has a significant influence on the dielectric properties of the PI/BaTiO₃ composite films. Figs. 7(a) and Fig. 7(b) display the variation of dielectric constant and loss tangent with frequency for various contents of silver. For the samples measured at 10⁴ Hz, the dielectric constant was 5.25, 10.02 and 13.72 for the BaTiO₃ content of 30 wt% and the silver content of 0 wt%, 1 wt% and 2 wt%, respectively. The dielectric constant of the composite films apparently increases as the silver loading increases. It is worthy to notice that the dielectric constant of the PI/BaTiO₃/silver composite film with 30 wt% BaTiO₃ and 2 wt% silver (13.72) was nearly the same as that of PI/BaTiO₃ film with BaTiO₃ content up to 60 wt% (13.89) at the frequency of 10⁴ Hz. The use of well dispersed silver nanoparticles which can act as microcapacitors contributes to this significant enhancement in dielectric constant. Simultaneously, the addition of silver greatly decreased the amount of ceramic phase for the same dielectric constant value, which is favorable for the flexibility of composite films. Both the dielectric constant and the dielectric loss present stable values in the frequency range of 10³–10⁶ Hz, which is very important in a number of applications. The decrease of dielectric constant and the increase of loss tangent caused by the dipole relaxation lags behind the fast change of applied field can be observed in the high frequency region.

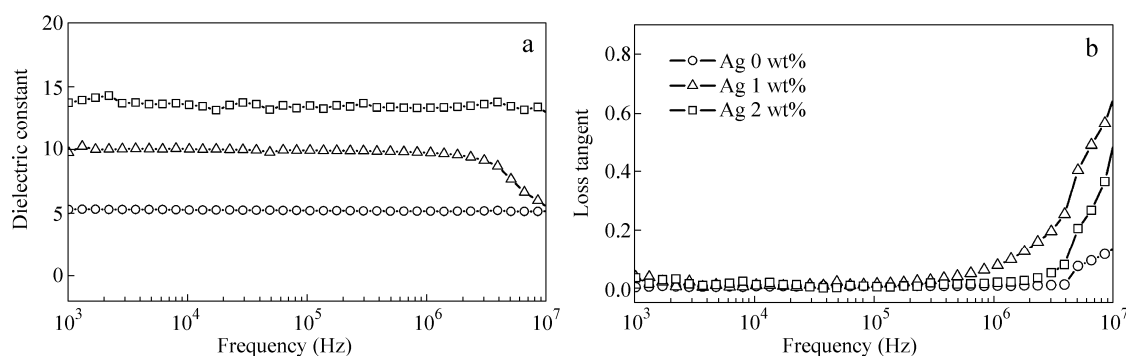


Fig. 7 Frequency dependence of the (a) dielectric constant and (b) loss tangent of PI/ BaTiO₃/Ag composite films

CONCLUSIONS

The present work demonstrates the preparation of triphase PI/BaTiO₃/Ag composite films. BaTiO₃ particles with the diameter of 100 nm can be uniformly dispersed in the polyimide matrix using *in situ* polymerization assisted by the ultrasonic technique. Silver nanoparticles of 10 nm have been readily formed and homogeneously dispersed in the polyimide/BaTiO₃/Ag composite films using AgTFA as the silver precursor *via in situ* technique. It was found that the dielectric constant of two-phase PI/BaTiO₃ systems increased with the increasing content of BaTiO₃. The incorporation of silver nanoparticles greatly enhanced the dielectric constant value of triphase systems. Thus this *in situ* technique provides an effective way to develop uniformly dispersed inorganic nanoparticles in PI/ceramic/metal triphase system which could be used in a variety of energy storage applications.

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