

PREPARATION OF POLYIMIDE-BaTiO₃ HYBRID FILMS BY A DISPERSION PROCESS AND THEIR MICROSTRUCTURE*

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Abstract Barium titanate (BaTiO₃) powders with particle sizes of 30~50 nm were prepared from barium stearate, titanium alkoxides and stearic acid by stearic acid-gel method. Dispersing the agglomerate of BaTiO₃ nanoparticles into poly(amic acid) solution followed by curing led to the formation of polyimide hybrid films. The hybrid films were transparent and well distributed with BaTiO₃ nanoparticles when the BaTiO₃ content was less than 1 wt%. Highly loaded hybrid film containing 30 wt % BaTiO₃ was tough, had a smooth surface and possessed much higher dielectric and piezoelectric constants than the parent polyimide.

Keywords Polyimide, Barium titanate, Nanocomposite, Hybrid film

INTRODUCTION

Barium titanate (BaTiO₃) is a scientifically and technologically important dielectric material and has been extensively used in microelectronics and integrated optics technology^[1]. Much interest has been focused on the fabrication of crystalline thin films of BaTiO₃ for the purpose of exploiting its high dielectric constant and piezoelectric activity in a variety of applications. In order to increase the dielectric constant per unit volume for capacitor and to miniaturize electronic components, many research projects were carried out to reduce the film thickness. However, there are several restrictions to using these approaches^[2, 3]. For example, it is difficult to produce a capacitor with a thickness of less than 200 μm using conventional processing methods. Composite systems of polymers and BaTiO₃ are expected to offer an alternative route for the fabrication of crystalline thin films of BaTiO₃ since they may show superior mechanical and fabrication properties as well as excellent dielectric properties^[4]. Polyimides are promising candidates for the matrix of the hybrid due to their high glass transition temperature and the flexibility of synthesis routes. It is desired to investigate the possibility of preparing polyimide-BaTiO₃ nanocomposite film by a convenient process. Polyimide hybrid can be prepared by three approaches: (i) sol-gel process, (ii) doping process and (iii) dispersion process. It is generally accepted that inorganic particles, especially nanoparticles are not stable systems. So the dispersion approach is more challenging than the others. The mechanical stirring and physical chemical interaction of surfaces may contribute to the de-agglomeration and stabilization of nanostructural system. In this study, the nanoparticles of BaTiO₃ were prepared and dispersed into poly(amic acid) solution followed by thermal transformation leading to the hybrid. Their structure and properties have also been investigated.

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EXPERIMENTAL

Barium stearate, titanium *n*-butoxide $\text{Ti}(\text{OBU})_4$ and stearic acid were purchased from Aldrich Chemical Co. and used without further purification. 3,3',4,4'-Thiodipthalic dianhydride (TDPA) was prepared from 4-chlorophthalic anhydride according to the procedure described in a previous paper^[5]. 4,4'-Oxydianiline (ODA) was available commercially. TDPA and ODAD were purified by sublimation or recrystallization before use. Anhydrous grade *N,N*-dimethylacetamide (DMAc) was distilled under a reduced pressure over P_2O_5 and stored under a nitrogen atmosphere.

Preparation of Polyimide/ BaTiO_3 Films

BaTiO_3 nanocrystals were synthesized by stearic acid-gel method according to the procedure in the literature^[6]. The polyamic acid precursors were prepared by solution condensation of TDPA with a stoichiometric amount of ODA. The agglomerated BaTiO_3 nanoparticles were mixed with DMAc to form a 2% *W/V* suspension. At room temperature and a stirring speed of 1000 rpm, the suspension was stirred followed by supersonic agitation for several days. Ten days later, a white milky suspension was formed in which the agglomeration had been reduced to such an extent that no sedimentation was observed. By adding this BaTiO_3 suspension to a poly(amic acid) solution, a milky solution with a ratio of BaTiO_3 /poly(amic acid) of 1 wt% was formed after stirring for 10 h at room temperature. A portion of the solution was cast on a clean glass slide. The film sample was first dried in an oven at 40°C and then thermally cured at 100°C for 1 h, at 200°C for 2 h and at 300°C for 1 h.

For the high loaded hybrid system, the dispersion of BaTiO_3 in poly(amic acid) solution was obtained by adding the poly(amic acid) solution to a BaTiO_3 suspension prepared by the method as described above, and the suspension was agitated supersonically for 24 h at room temperature. The milky suspension was then treated by a procedure similar to the low loaded system to obtain the hybrid films.

Measurement

Intrinsic viscosities of poly(amic acid)s were measured at 0.5 g/dL in DMAc with an Ostward viscometer at $30 \pm 0.1^\circ\text{C}$. Ba and Ti contents were determined by inductively coupled plasma (ICP) spectrometry according to the procedure described by Farinas and Barba^[7], using a TJA POEMS spectrometer. FTIR spectra were obtained with a Bio-Rad Digilab Division FTS-80 spectrometer. Thermogravimetric analysis (TGA) was performed on 10 ± 2 mg sample with a Perkin-Elmer TGA-2 thermogravimetric analyzer in nitrogen and air and at a heating rate of 10 K/min. Wide angle X-ray diffraction (WAXD) measurements were conducted on a Rigaku D/May-ITB X-ray diffractometer with $\text{CuK}\alpha_1$ radiation ($\lambda = 1540.5$ nm, 40 kV, 30 mA). X-ray photoelectric spectra (XPS) were obtained with a VG ESCALAB-MKII photoelectron spectrometer system. The morphologies of the polyimide/ BaTiO_3 hybrid films were examined using transmission electron microscopy (TEM) and atomic force microscopy (AFM).

RESULTS AND DISCUSSION

Among the various approaches, the stearic acid-gel process has been proved to be a particularly effective approach for preparing BaTiO_3 nanopowders^[7]. Hence the stearic acid-gel process was utilized in this work. The structure of as-prepared BaTiO_3 powders was evaluated using FTIR spectra and WAXD measurement and was in very good agreement with the results reported in the literature^[8, 9]. The morphology of as-prepared BaTiO_3 powders were examined using TEM. The average particle size of the as-prepared BaTiO_3 powder was below 50 nm. The elemental composition and the ratio of Ba to Ti for the as-prepared BaTiO_3 powder were evaluated by ICP and they agreed well with the theoretical value. Table 1 lists some properties of the as-prepared BaTiO_3 powders, suggesting that the nanoparticles with high dielectric constant were good candidates for the synthesis of polyimide nanocomposite.

It has been reported that inorganic ultrafine particles can be directly dispersed into polyimide or polyimide precursor matrix^[10-12]. In some cases, hybrid films with inorganic nanoparticles homogeneously dispersed in polyimide were obtained. To our best knowledge, however, BaTiO_3 nanoparticles have not yet been used for

preparing polyimide composite film. Therefore, in this work, we prepared polyimide-BaTiO₃ hybrid films by dispersion and studied their microstructure. The polyimide chosen for our study was TDPA/ODA. BaTiO₃ nanoparticles were dispersed into poly(amic acid) solution by high speed and long-term stirring associated with supersonic agitation. When the low BaTiO₃ loaded systems (BaTiO₃ content no more than 1 wt%) were adopted, a white milky suspension of poly(amic acid) and then a transparent film of polyimide hybrid was obtained. For the high concentration system, agglomerated BaTiO₃ nanoparticles were observed and sedimentation took place after stirring has been stopped. However, the flexible composite films with smooth surface and well-distributed inorganic particles can be obtained by a controlled dispersion procedure.

Table 1. The properties of as-prepared BaTiO₃ powder

Compound (powder)	Ba/Ti ^a (mol)	Size ^b (nm)	Dielectric properties		Binding energy (eV)	
			ϵ	$\tan\delta$	Ba (3d _{5/2})	Ti (2p _{3/2})
BaTiO ₃	1.02	30–50	800	0.03	778.8	457.7

^aDetermined by ICP

^bDetermined by TEM

The incorporation of BaTiO₃ into polyimide can be confirmed by ICP. The content of BaTiO₃ assuming there was no loss in the hybridization was in fairly good agreement with that determined by ICP and was verified again by TGA. Further characterization of barium and titanium species present in polyimide matrices was achieved by X-ray Photoelectron Spectroscopy. XPS of the hybrid film obtained at a takeoff angle of 90° for maximum sampling depth showed well-defined Ba (3d_{5/2}) and Ti (2p) photopeaks on both sides of the film. Figure 1 shows that the values of binding energies of Ba and Ti in the hybrid are closer to those of free BaTiO₃ powder (refer to Table 1), indicating no obvious change of BaTiO₃ in hybridization.

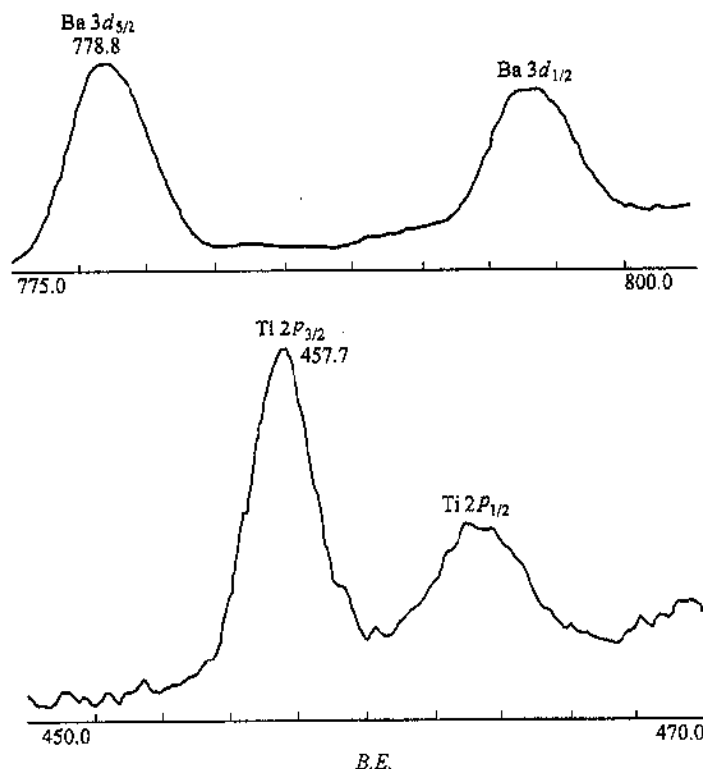


Fig. 1 XPS of polyimide and polyimide/BaTiO₃ (0.91 wt%) hybrid film

Hybrid films containing no more than 1 wt% BaTiO₃ were transparent. This indicated that BaTiO₃ nanoparticles are homogeneously dispersed in polyimide matrix. The morphology of hybrid film was further examined using TEM and AFM. The transmission electron microphotograph shown in Fig. 2 revealed a uniform distribution of spherically shaped particles, no more than 50 nm in size, throughout the bulk of the film. The AFM microphotograph shows that the morphology of the hybrid film surface is reasonably similar to that of the parent polyimide films. The surface roughness of hybrid film was below 10 nm.

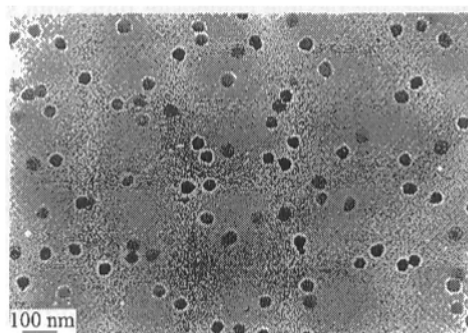


Fig. 2 TEM micrograph of polyimide/BaTiO₃ (0.91 wt%) hybrid film

It is generally accepted that nanoparticles are a thermodynamically unstable system and the agglomeration interaction in the dispersion may be preliminary rationalized as follows. (1) The long stirring time and the strong stirring force may cause a loosening of the structure in the agglomerates and improve the dispersion of nanoparticles. (2) In polar solvent, the particles adsorb solvent molecules onto the particle-solution interface, forming an electrical double layer and (3) mechanical attrition of the agglomerated particles creates a porous structure, resulting in the interpenetration of poly(amic acid) chains into these porous structures and the introduction of electrostatic repulsive forces. These factors would eventually prevent the gathering of nanoparticles into heavily agglomerated particles and result in the dispersion of nanoparticles in the polyimide matrix.

When the content of BaTiO₃ increases, the appearance of hybrid films changes from transparent to opaque due to the agglomeration of BaTiO₃ nanoparticles. However, the highly loaded hybrid films are flexible films with a smooth surface. Figure 3 shows the morphology of polyimide/BaTiO₃ (30 wt%) hybrid film surface. In the 2-D image, bright domains referring to the inorganic particles together with their relatively less bright surroundings were observed. To investigate more precisely the film surface, the 2-D image was reconstructed as a 3-D image, which shows a rather regular topology of pillow-like islands separated by polyimide matrix. Even if

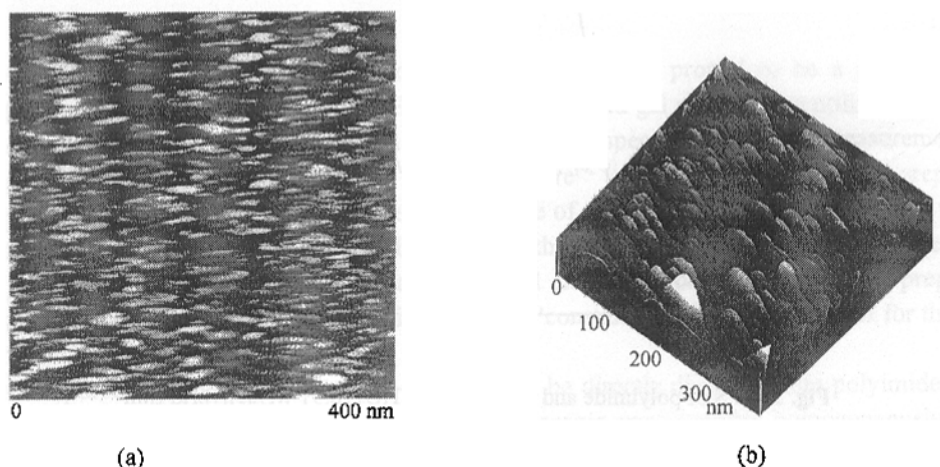


Fig. 3 AFM micrograph of polyimide/BaTiO₃ (30 wt%) hybrid film

the BaTiO₃ content is higher than 60% a self-standing film still can be obtained. This is in sharp contrast to the inorganic system, in which a film with a thickness of less than 200 μm is difficult to produce and handle. As shown in Table 2, the tensile modulus of hybrid films is higher than that of pristine films, while the tensile strength and elongation at break are lower than that of polyimide films, which is a common observation in polyimide hybrid. The hybrid film is thermally stable with only 5% weight loss at a temperature higher than 500 °C, in spite of a decrease in thermal stability as compared with the polyimide film.

Table 2. The properties of polyimide and polyimide/BaTiO₃ hybrid films

Film	Polyimide film	hybrid film
BaTiO ₃ (wt%) ^a	0	29.8
$T(^{\circ}\text{C})^b$, in air	594	519
$T(^{\circ}\text{C})^b$, in N ₂	613	565
Tensile strength (MPa)	98.3	38.2
Elongation at break (%)	13.5	1.89
Tensile modulus (GPa)	1.95	2.17
ϵ	3.3	6.2
$\tan\delta$	1.2	5.9
$d_{33} (\times 10^{-12} \text{ C/N})$	3.8	5.4

^a Determined by ICP

^b 5% Weight loss temperature

The incorporation of BaTiO₃ into polyimide actually increases the dielectric constant of polyimide. Addition of 30% BaTiO₃ to the polyimide causes a rise of dielectric constant from 3.3 to 6.2. However, with regard to the high dielectric constant of pure BaTiO₃ at room temperature (see Table 2), this increase in dielectric constant seems too low. Main reason might be that the polarization response to the dielectric properties decreases as the particle size gets smaller^[13, 14]. Effect of the particle size of BaTiO₃ on the preparation of hybrid films and their properties especial the dielectric properties are in study.

CONCLUSION

Nanostructured barium titanate (BaTiO₃), prepared by a stearic-gel process, has been successfully dispersed and stabilized in a polyimide matrix. Hydrodynamic and surface physicochemical interaction forces may be responsible for the de-agglomeration and stabilization. The hybrid film containing less than 1% BaTiO₃ is transparent and homogeneous in appearance. The composite films with 30 wt % BaTiO₃ are still flexible and thermally stable with enhanced dielectric properties.

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