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## Calcium copper titanate/polyurethane composite films with high dielectric constant, low dielectric loss and super flexibility

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### ABSTRACT

Calcium copper titanate(CCTO)/polyurethane composite films with high dielectric constant, low dielectric loss and super flexibility were fabricated by incorporating CCTO ceramic powders into millable polyurethane elastomer (MPU) matrix using a rubber milling combined with hot compression molding method. The composite films show uniform microstructures and the dielectric constant is as high as 35.2 while the dielectric loss is only 0.041 when CCTO content reaches 40 vol% at 100 Hz and room temperature (RT). Moreover, it is important to note that this film has stable dielectric constant and dielectric loss in a relatively wide temperature range (from 0 °C to 70 °C), which is significantly important to the practice use of electronic devices based on CCTO composites. In addition, the flexibility of the film could be retained even when the CCTO content is up to 40 vol% and the elongation at break of this composite film is as high as 159.1%. Theoretical analysis indicates that the experimental data are in good conformity to the effective medium theory (EMT) model with a derived  $n = 0.21$ , suggesting more close association of the dielectric constant with the CCTO filler size and shape.

### 1. Introduction

Materials with high dielectric constant, low dielectric loss and good flexibility are crucial for many electronic devices, such as energy-storage capacitors, memory devices and power systems [1,2]. High dielectric constant materials enable higher capacitance in a smaller size, thus providing the probability to reduce the size of devices. Although many ceramic materials with excellent dielectric properties are presently used in electronic industry, they are usually prepared in a complicated process and sintered at high temperature and suffer from brittleness. Polymers are almost flexible, but unfortunately, most of them have low dielectric constant. To fabricate materials with good dielectric properties and outstanding flexibility, ceramic/polymer binary composites are better alternatives, and show more excellent properties, such as simple and low-temperature fabrication process, adjustable dielectric properties and good machinability [3–5].

Many dielectric ceramics, especially relaxor ferroelectrics such as BaTiO<sub>3</sub> [6–8], Ba<sub>0.95</sub>Ca<sub>0.05</sub>Zr<sub>0.15</sub>Ti<sub>0.85</sub>O<sub>3</sub> [9], Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> [10], BaSrTiO<sub>3</sub> [11] and Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> [12] are commonly used as fillers due to their relatively high dielectric constant ( $\sim 10^2$ – $10^4$ ). However, ferroelectric ceramics always have a strong piezoelectric effect and their dielectric properties strongly depend on temperature, which limits the reliability of electronic devices [13]. In addition, many ferroelectric fillers are lead-based ceramics, which might have bad effects on human health and environment.

Recently, a pseudo-perovskite structure material, CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO) has drawn substantial interests among researchers as it provides a new opportunity to create ceramic/polymer dielectric composites owing to the fact that CCTO is lead-free and has no piezoelectric property, and exhibits a colossal and stable dielectric constant ( $\sim 10^4$ ) in a wide temperature range (100–600 K) [14,15].

Although CCTO ceramic was successfully fabricated as early as in

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1967, the mechanisms of the abnormally high dielectric constant are still not very clear despite that several theoretical models have been proposed to clarify the extraordinary dielectric behaviors in literatures [16]. Among these models, the Maxwell-Wagner (M-W) polarization mechanism is generally accepted as the primary origins leading to the colossal dielectric constant [17].

Much effort has been devoted to explore the possibility of obtaining CCTO-based composites with high dielectric constant. As reported by Thomas et al. [18], CCTO/poly(vinylidene fluoride) (PVDF) composites with 55 vol% CCTO filler had a dielectric constant of 95 and a dielectric loss of  $\sim 0.2$  at 100 Hz and RT. According to Yang et al. [19], the dielectric constant of CCTO/PVDF composites using the surface-modified CCTO particles reached up to 84 (with a dielectric loss of  $\sim 0.17$ ) at 1 kHz and RT. Arbatti et al. [20] found that CCTO/poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE) composites exhibit a dielectric constant of  $\sim 610$  and a dielectric loss of  $\sim 0.6$  at 100 Hz and RT when the ceramic filler is 50 vol%. Zhang et al. [21] reported that the dielectric constant of CCTO/P(VDF-TrFE) composites can be improved to about 10 times by using proper layer-by-layer preparation process, and the dielectric constant of the composites can exceed 1000 with a dielectric loss of  $\sim 0.1$ . Mohd et al. [22] found that the surface-modified CCTO/epoxy composite film had a maximum dielectric constant of 27.8 with a dielectric loss of  $\sim 0.1$  at 100 Hz and RT. Dang et al. [23] fabricated a polyimide(PI)/CCTO film which shown a dielectric constant of 49 and a dielectric loss of  $\sim 0.2$  at 100 Hz and RT with 40 vol% CCTO content. Yang et al. [24] found that PI/nanosized CCTO film had a dielectric constant of 171 and a dielectric loss of 0.45 at 100 Hz and RT. But these polymers have limitations, such as ferroelectricity of PVDF and P(VDF-TrFE), and relatively poor flexibility of PVDF, epoxy and PI based composites. It was reported that the CCTO/PVDF composites exhibited an elongation at break of only 16% with 50 wt% CCTO content [25]. According to Xu et al. [26], PI filled with 14 vol% carbon nanotubes shown an elongation at break of only 12.8%. Moreover, almost all CCTO/organics composites based on these polymers had relatively high dielectric loss (higher than 0.1).

In the present work, an advanced ceramic/polymer composite film was successfully fabricated by using colossal dielectric constant CCTO ceramic powders as the functional filler and millable polyurethane elastomer (MPU) with super mechanical properties as the polymer matrix. CCTO powders employed here were prepared by a simple and reliable molten-salt method. CCTO/polyurethane composite films were fabricated by incorporating CCTO powders into MPU using a rubber milling combined with hot compression molding method. It is found that the as-prepared CCTO/polyurethane composite films show excellent dielectric and mechanical properties. For example, at RT and measurement frequency of 100 Hz, the dielectric constant of the composite film with 40 vol% CCTO content reaches 35.2 while the dielectric loss is only 0.041. Moreover, this film still has super flexibility and shows an elongation at break of more than 159%, which is much higher than that of the CCTO/polymer composite films reported previously.

## 2. Experimental

### 2.1. Synthesis of CCTO powders

CCTO powders were synthesized using a simple molten-salt method reported previously [27]. In short, firstly, a stoichiometric mixture of  $\text{TiO}_2$  ( $\geq 99.0\%$ ),  $\text{CuO}$  ( $\geq 99.0\%$ ) and  $\text{CaCO}_3$  ( $\geq 99.0\%$ ) was ball-milled in ethanol medium for 2 h. Then  $\text{NaCl}$  ( $\geq 99.5\%$ ) (three times of the oxides mass) was added into the mixture and continued further ball-milling for 2 h. After ball-milling, the mixture was oven-dried and then heated at  $800^\circ\text{C}$  in an electric furnace for 2 h. After furnace cooling to RT, the reaction product was then washed in  $80^\circ\text{C}$  deionized water to remove  $\text{NaCl}$ . Finally, the obtained powders were oven-dried at  $100^\circ\text{C}$ .

### 2.2. Preparation of CCTO/polyurethane composite films

Firstly, CCTO powders and silane coupling agent, 3-aminopropyltriethoxysilane (dosage: 2 wt% of CCTO powders, purity:  $\geq 97\%$ , GBXF Silicones Co., Ltd., China) were added into a stirrer and mixed for 5 min. The MPU (UR101, Guangzhou SCUT Bestry Technology Co., Ltd., China) was then dumped onto a rubber mixing mill. CCTO powders and sulfurizing agent, 2, 5-Dimethyl-2, 5-Di (Tertbutyl peroxide) hexane (dosage: 3 wt% of MPU, purity:  $\geq 93\%$ , Nantong Quanyi Rubber Co., Ltd., China) were subsequently mixed into the MPU to form a homogenous mixture in the rubber mixing mill. At last, the mixture was vulcanized by compression molding at  $160^\circ\text{C}$  and 4 MPa for 10 min using a film mold of  $60 \times 60 \times 0.1$  mm.

### 2.3. Measurements and characterization

An X-ray diffractometer (XRD, RIGAKU,  $\text{CuK}\alpha$ , Japan) were employed to identify the phases of specimens. Microstructures were observed under a field emission scanning electron microscope (FE-SEM, Zeiss Sigma HD, Germany). For dielectric measurements, both sides of CCTO/polyurethane composite films (thickness: 80–100  $\mu\text{m}$ , diameter: 9.5 mm) were coated with platinum conductive thin film electrode using an ion sputtering coating equipment. Dielectric properties were measured using an Agilent 4294A impedance analyzer over a frequency range from 100 Hz to 1 MHz and a temperature range from  $-40^\circ\text{C}$  to  $120^\circ\text{C}$ . Tensile stress-strain tests were performed on dumbbell-shaped specimens (total length: 35 mm; gauge length: 10 mm; width: 6 mm; inner width: 2 mm; thickness: 80–100  $\mu\text{m}$ ) using an electronical universal testing machine (WT-6002, Shenzhen Reger instrument Co. Ltd., China) with a crosshead speed of 60 mm/min.

## 3. Results and discussion

Fig. 1a shows the XRD pattern of CCTO powders synthesized by the molten-salt method employed in this experiment. Almost all diffraction peaks belong to CCTO centrosymmetric bcc crystal structure except very weak peaks of  $\text{CaTiO}_3$ . Compared with the tedious traditional solid-state reaction method that needs relatively long reaction time and high synthesis temperature (typically at  $1000^\circ\text{C}$  for 10–20 h), and might still produce unwanted phases because of the limited atomic diffusion, the molten-salt method is a low-temperature, simple and reliable synthesis technique for synthesizing of CCTO powders. Fig. 1b illustrates XRD patterns of pure polyurethane and CCTO/polyurethane composite films. The broad diffraction peak at about  $2\theta = 20^\circ$  in pure polyurethane could be ascribed to the orderliness of the polyurethane polymer chain. However, with the increasing of CCTO filler content the peak moves to lower scale and diminishes, indicating the increasing of the averaged interplanar distance of the polyurethane polymer matrix or even the destruction of the ordered structure owing to the incorporation of CCTO powders. Fig. 1c-d show FE-SEM micrographs of the as-synthesized CCTO powders and CCTO/polyurethane composite films. Almost all CCTO particles are smaller than 1  $\mu\text{m}$  and agglomerate together. But the composite films have uniform structure and CCTO particles distribute well in the polyurethane matrix due to the mechanical mixing process in a rubber mill for the preparation of the composite films.

The dependence of the dielectric properties of the CCTO/polyurethane composite films on CCTO filler content at 100 Hz and RT is shown in Fig. 2a. The dielectric constant ( $\epsilon'$ ) is close to a monotonous increasing and reaches up to 35.2 when the CCTO filler is 40 vol%. Dielectric loss ( $\tan\delta$ ) also increases with CCTO volume concentration, which can be attributed to that CCTO is a semiconductor and has higher conductivity than the polyurethane matrix. However, the dielectric loss is still very low and is only 0.041 even when the CCTO filler is 40 vol%. The low dielectric loss could be primarily ascribed to the low dielectric loss of polyurethane matrix, the uniform microstructure of the

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