Advanced Powder Technology 27 (2016) 1162–1172

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

# Effect of silicone coupling agent on dielectric properties of barium titanate/silicone elastomer composites

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ARTICLE INFO

*Article history:*
Received 9 October 2015
Received in revised form 19 February 2016
Accepted 31 March 2016
Available online 7 April 2016

*Keywords:*
Barium titanate
Silicone coupling agent
Silicone elastomer
Dielectric
Piezoelectric

ABSTRACT

$BaTiO_3$ is a type of ceramic with a high dielectric constant, while silicone is a type of elastomer with low elastic modules. Composites made by blending these two materials together can obtain both of their advantages, which has many possible applications in the area of actuators or mechanical sensors. In this study, to improve the dispersity of the $BaTiO_3$ particles, a novel silicone coupling agent was used to modify the surface of the particles. TG and FTIR results showed that the coupling agent was successfully coated on the surface. Raw $BaTiO_3$ and $BaTiO_3$ modified by the silicone coupling agent were incorporated into the silicone elastomer to fabricate the $BaTiO_3$/silicone membranes. Particle size distribution measurements and SEM observations showed that the BT particles can obtain a higher compatibility with the silicone, and both the dispersity of the $BaTiO_3$ particles and the dielectric properties of the $BaTiO_3$/silicone membranes were improved after the surface modification, even without a poling process during the fabrication or measurement. The measuring circuit containing the $BaTiO_3$/silicone membrane is expected to have several applications such as mechanical sensors.

## 1. Introduction

$BaTiO_3$ is a type of significant dielectric material with ferroelectric properties under its curie point, which is widely used in ceramic capacitors [1]. The dielectric constant of $BaTiO_3$ significantly depends on the grain size; coarse-grained ceramics of 20–50 nm $BaTiO_3$ had a dielectric constant of about 1500–2000 at room temperature, while the room-temperature dielectric constant has a maximum of about 3500–4000 when the fine-grained $BaTiO_3$ was about a 1 μm size [2]. Although having such a high dielectric constant, $BaTiO_3$ still suffers from some problems such as a low breakdown strength, brittleness and processing difficulties. On the other hands, despite of the low dielectric constant, polymeric materials have several advantages that are suitable for new types of electric applications such as low dielectric loss, high electric breakdown strength, low elastic modules and good processability [3,4]. Silicone is a type of polymeric material with an excellent flexibility and insulation; all types of silicones are known to be good dielectrics [5]. The silicone elastomer has always been considered as a type of inorganic polymer, comprised of a backbone of silicone–oxygen–silicone that is able to withstand a higher temperature than other elastomers [6,7]. Composites made by blending $BaTiO_3$ and silicone together could obtain both a high dielectric constant and low elastic modules, which has many novel applications. For instance, a dielectric elastomer actuator can be made by sandwiching a membrane of dielectric composites between two compliant electrodes, and when loading a voltage difference between the compliant electrodes, compression in the thickness direction and stretching in the area direction of the elastomer membrane could occur due to the Coulombic force [8–13].

Because of the relatively poor compatibility between inorganic dielectric particles and the organic silicone elastomer, agglomeration of the particles is difficult to avoid, leading to a higher dielectric loss and producing much pores that reduce the dielectric constant of the composites [4]. Obviously, it is of great significance to improve the compatibility between the inorganic dielectric particles and elastomers. Shu-Hui Xie, Bao-Ku Zhu and their coworkers [14] synthesized polyimide/barium titanate composites by a colloidal process, finding that the $BaTiO_3$ particles with the size of 100 nm were homogeneously dispersed in the polyimide matrix without aggregation. Dang Zhi-Min and his coworkers [15] increased the dielectric constant in the PVDF matrix composites with $BaTiO_3$ treated by the 1.0 wt% silane coupling agent, KH550. Their group also found that [16] an appropriate silane coupling agent can be used to improve the interaction between the $BaTiO_3$

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http://dx.doi.org/10.1016/j.apt.2016.03.028
0921-8831/

and epoxy resin, producing high dielectric permittivity barium titanate/epoxy resin composites. Ramajo et al. [17] studied the influence of silane coupling agents on the microstructure and dielectric behavior of epoxy/$BaTiO_3$ composites, finding that their composites presented good dielectric properties and a strong dependence on the silane concentration. In this study, in order to improve the dispersity of the $BaTiO_3$ particles and avoid agglomeration, a new type of silicone coupling agent was used to modify the surface of the particles by a novel super-critical method. Raw $BaTiO_3$ particles and $BaTiO_3$ particles modified by the silicone coupling agent were incorporated into the silicone elastomer to fabricate the $BaTiO_3$/silicone membranes. Although poling of the $BaTiO_3$/silicone membrane may enhance the dielectric property in a specific direction, it has not been carried out during the fabrication and measurement in order to simplify the experimental procedure. The dispersity of the $BaTiO_3$ particles, dielectric properties and piezoelectric properties of the $BaTiO_3$/silicone membranes were evaluated.

## 2. Experimental

### 2.1. Material

$BaTiO_3$ with particle sizes of 300 nm and 500 nm (with average crystallite sizes of 35.1 nm and 31.4 nm, respectively) were provided by the KCM Corporation, Japan; a two-component RTV silicone elastomer KE-103 (containing main component and crosslinker); silicone coupling agent, triethoxysilylethyl polydimethylsiloxyethyl dimethicone; silicone oil, KF-96-6CS (a type of low viscosity dimethylsiloxane silicone oil) were supplied by Shin-Etsu Chemical Co., Ltd., Japan; aqueous hydrogen peroxide (30%) was provided by Tokyo Chemical Industry Co., Ltd., Japan; and ethanol, acetone and other reagents were obtained from Wako Pure Chemical Industries, Ltd., Japan.

### 2.2. Surface modifications of $BaTiO_3$ using silicone coupling agent

In this paper, BT is the abbreviation for $BaTiO_3$, while BT300 and BT500 are abbreviations of the $BaTiO_3$ particles with sizes of 300 nm and 500 nm, respectively. Before modification, the surfaces of the BT particles were activated by introducing hydroxyl groups using aqueous hydrogen peroxide, according to the report of Chang et al. [18]. Forty g of BT300 (or BT500) particles and 200 mL of aqueous hydrogen peroxide (30%) were added to a round bottom flask and the mixture was stirred at its boiling point (106 °C) for 5 h with refluxing, then the particles was washed several times by centrifugation using deionized water. The surface activated BT particles were then obtained after drying under vacuum at 60 °C for 12 h.

After the surface activation, the BT particles were modified by the silicone coupling agent at the super-critical state. Thirty-Five g of activated BT300 (BT500) particles, a predetermined amount of the silicone coupling agent, triethoxysilylethyl polydimethylsiloxyethyl dimethicone, and 80 mL hexane were added to a tubular bottle and mixed together. The coupling agent was added according to the amount listed in Table 1. The mixture was then placed in an autoclave and heated to the supercritical state (234.5 °C, 3.01 MPa), maintaining the condition for 1 h. The coupling agent modified particles were obtained after cooling to room temperature, being washed several times by acetone and dried under vacuum at 60 °C for 12 h.

**Table 1**
Addition amounts of coupling agent.

| Modified BT300 (BT500) | BT300-0 (BT500-0) | BT300-1 (BT500-1) | BT300-3 (BT500-3) | BT300-5 (BT500-5) |
|---|---|---|---|---|
| Activated BT300 (BT500) | 35 g | 35 g | 35 g | 35 g |
| Coupling agent | 0 | 1 g | 3 g | 5 g |
| $m$ (coupling agent)/ $m$ (BT particles) | 0 | 2.86% | 8.57% | 14.29% |

### 2.3. Preparation of $BaTiO_3$/silicone composites

The required quantity of the raw and modified BT300 or BT500 particles were mixed together with the main component of the silicone elastomer according to Tables 2 and 3 using a high shearing blender that can load a high mechanical force. The crosslinker was next added to the mixture and totally dispersed, in which the ratio of $m$ (main component): $m$ (crosslinker) was controlled to 100:5. The BT/silicone membrane was finally obtained by pouring the mixture into a PTFE mold and allowing it to cure at room temperature for 72 h.

### 2.4. Characterization

Trace chemical groups on the surface of the BT particles were detected by Fourier-transform infrared spectrometry (FTIR) using a JASCO FT/IR-6200 Fourier Transform infrared spectrometer. The thermogravimetric analysis (TG) was done at the heating rate of 10 °C/min in air using a Rigaku Thermo plus TG 8120. Scanning electron microscopy (SEM) images were obtained at the accelerating voltage of 15 kV using a JEOL JSM-7600F field emission scanning electron microscope. The particle size distribution was measured by a MALVERN nanoseries particle size measuring instrument. The dielectric constant and dielectric loss ($\tan\delta$) were measured by a NF ZM 2371 LCR meter. The mechanical properties were measured by a SHIMADZU AGS-G Autograph. The instantaneous current was measured by a KEITHLEY 2000 multimeter.

## 3. Results and discussion

### 3.1. Surface modifications of $BaTiO_3$

On the surface of the BT particles, the amount of active groups, such as amino groups or hydroxyl groups is too low to be modified. To solve this problem, hydroxyl groups were introduced on the surface using hydrogen peroxide to activate the surface of the BT particles according to the method of Chang et al. [18]. When using boiling hydrogen peroxide to treat the BT particles, $H_2O_2$ will decompose and hydroperoxyl radicals ($^{\cdot}OH$) will generated on the surface. The $^{\cdot}OH$ will then react with $H_2O_2$ to form the hydroperoxyl radical ($^{\cdot}O_2H$) or further react with the produced $^{\cdot}O_2H$ to form water and oxygen. Due to the highly acidic property of $^{\cdot}O_2H$, hydroxyl groups can be easily produced by the reaction between $^{\cdot}O_2H$ and the oxygen ions on the surface of the BT particles. In addition, the $O_2^{-\cdot}$ radical can continue to react with water to produce hydroxyl anions in the water and reduce the pH. The reaction procedures are shown in Fig. 1 and the last equation shows the overall reaction.

Fig. 1 shows the structure of the silicone coupling agent. It is a type of oligomer silicone that has a structure similar to the silicone elastomer and contains silicon-ethoxyl groups which can easily hydrolysis when in contact with moisture in the air. A predetermined ratio of BT particles and the silicone coupling agent were both dispersed into hexane and heated in an autoclave until reaching 234.5 °C and 3.01 MPa, at which the hexane will convert to the supercritical state. During this procedure, the –OH groups on the surface of the BT particles and Si–OH groups from the silicone coupling agent can easily make contact and obtain a high reaction