

# Study on microstructure and dielectric property of the BaTiO<sub>3</sub>/epoxy resin composites

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## Abstract

High dielectric permittivity barium titanate/epoxy resin (BaTiO<sub>3</sub>/EPR) composites with different size BaTiO<sub>3</sub> particles were prepared and their dielectric properties were studied via a wide range of temperature and frequency. The results show that an appropriate silane coupling agent can be used in order to improve the interaction between BaTiO<sub>3</sub> and EPR, and subsequently induces a high dielectric permittivity and a low loss tangent. The size and concentration of BaTiO<sub>3</sub> particles also have an effect on the microstructure and dielectric property of composites. Additionally, the dielectric properties of the composites with different size of BaTiO<sub>3</sub> particles give different temperature dependence because of the existence of phase transition of large size BaTiO<sub>3</sub> particles at its Curie temperature.

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**Keywords:** Dielectric properties; B. Microstructure; BaTiO<sub>3</sub>; Silane coupling agent

## 1. Introduction

Electronic systems are composed of active and passive components. Passive components include resistor, capacitor, and inductor [1]. In recent years, there is an increasing interest in passive components because the number of (occupying more than 70% real estate of substrate) passive components is steadily growing as a rapid progress of the electronic technology. Among passive components, special interest is focused on capacitors because they are used for various functions, such as decoupling, by-passing, filtering, and timing capacitors. Materials with relative dielectric permittivity in the range of 25–170 are required because of the development of advanced decoupling capacitor in order to reduce the power distribution noise [2]. Ferroelectric ceramic/polymer composite materials have been considered for this type of capacitor, since the combination of polymer and ceramic may give the composites some

advantages from both sides by a careful design and preparation [3–9].

Although the composites employing conductive filler have made a promising progress in the dielectric property, ceramic/polymer composites are still attractive to researchers because of simple and convenient process, cheap cost, excellent property and outstanding compatibility with printed wiring board (PWB), such as lower dielectric loss, lower conductivity and leakage current. In these studies [6–11], different systems have been demonstrated in order to obtain the desirable dielectric properties. The agglomeration and size of the BaTiO<sub>3</sub> particles in the composites are considered to play an important effect on deciding the final dielectric property. To eliminate the agglomeration of ceramic particles with high dielectric permittivity, a few kinds of surface treatment agents (coupling agents and dispersants) are often used to disperse the ceramic particles into polymer matrix, which have been confirmed as an effective method to improve the dispersion of ceramic powders and the packing density of composites since the use of treatment agents can strengthen the interaction between cera-

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mic phase and polymer one [3–5]. In addition, to reach well balanced properties between high dielectric permittivity and low loss tangent, the particle size ranging from 0.5  $\mu\text{m}$  to 0.7  $\mu\text{m}$  in diameter is often chose for embedded capacitors. Very recently, nanosized ceramic powders have also been utilized in order to increase the packing density, which will further result in an increase in dielectric permittivity and a decrease in film thickness of ceramic/polymer composites used in the embedded capacitor [6–8]. Dielectric permittivity of 90 of composites with epoxy as matrix was obtained using 100 nm  $\text{BaTiO}_3$  and another 916 nm  $\text{BaTiO}_3$  power mixture. To address this issue, ceramic/polymer has been evaluated as candidate dielectric materials for new-type capacitor.

In this study, effect of  $\text{BaTiO}_3$  size and use of coupling treatment agents on microstructures and dielectric properties of the  $\text{BaTiO}_3$ /EPR composites was investigated via a wide range of frequency and temperature. The results will be helpful to realize the use of this kind of EPR matrix composites with high dielectric permittivity in the embedded capacitor fields.

## 2. Experimental procedures

### 2.1. Raw materials

Barium titanate ( $\text{BaTiO}_3$ ) was chosen as ceramic filler because it was widely used as ferroelectric material with high dielectric permittivity. In this study, two kinds of  $\text{BaTiO}_3$  powers (0.1  $\mu\text{m}$  and 0.7  $\mu\text{m}$ , which are denoted as BT-01 and BT-07 respectively) were from Guoteng electronic ceramic company. Their particle sizes and other physical parameters that were acquired at room temperature were summarized in Table 1. The epoxy resin (EPR), bisphenol-A epoxy resin (DER661 from Dow chemical) with a dielectric permittivity of 3.7, was chosen as polymer matrix. It is in a solid state at room temperature and can be dissolved in acetone. To achieve a good dispersion of the ceramic in the EPR matrix composites, silane coupling agent (KH550) and phosphated ester (BYK-9010) dispersant were used as surface treatment agents in order to improve the dielectric permittivity of the composites and the miscibility between polymer and ceramic particles. The amount of KH550 and BYK-9010 was 1.0 wt% in comparison with the  $\text{BaTiO}_3$  powders used. Meth-

yltetrahydrophthalic anhydride (MeTHPA, from Aldrich) that was often used during the preparation of EPR-type electronic materials was chosen as a harder in 10/4 (EPR/MeTHPA) weight ratio. The catalyst was 2-ethyl-4-methyl-imidazole (2,4-EMI), its concentration is about 1.0 wt% in comparison to the content of EPR for all composites.

### 2.2. Preparation of the $\text{BaTiO}_3$ /EPR composites

First, suspensions containing  $\text{BaTiO}_3$  powder, KH550 and solvent were prepared in a polytetrafluoroethylene (PTFE) bottle. Ultrasonic was applied to the suspensions in order to prohibit from the agglomeration of  $\text{BaTiO}_3$  powders, and then EPR, curing agent and catalyst were added into the suspensions. The mixture solutions were grinded by using a planetary ball-milling machine for 24 h. Afterwards, the solution was heated to 75  $^\circ\text{C}$  for 1 h to evaporate the most solvent, then dried at 75  $^\circ\text{C}$  for 30 min to remove solvent residue. Finally, the dry mixtures were molded by hot-pressing at a temperature range of 150–160  $^\circ\text{C}$  in order to satisfy the curing process of the  $\text{BaTiO}_3$ /EPR composites.

Table 1  
Physical property of  $\text{BaTiO}_3$  (BT) particles measured at room temperature in this study

Physical property	No.	
	BT-01	BT-07
Particle size ( $\mu\text{m}$ )	0.1	0.7
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	9.0–1.3	1.6–1.4
Moisture (wt%)	<0.4	<0.1
Ignition loss (wt%)	<2	<0.25
Crystal phase	Cubic	Tetragonal

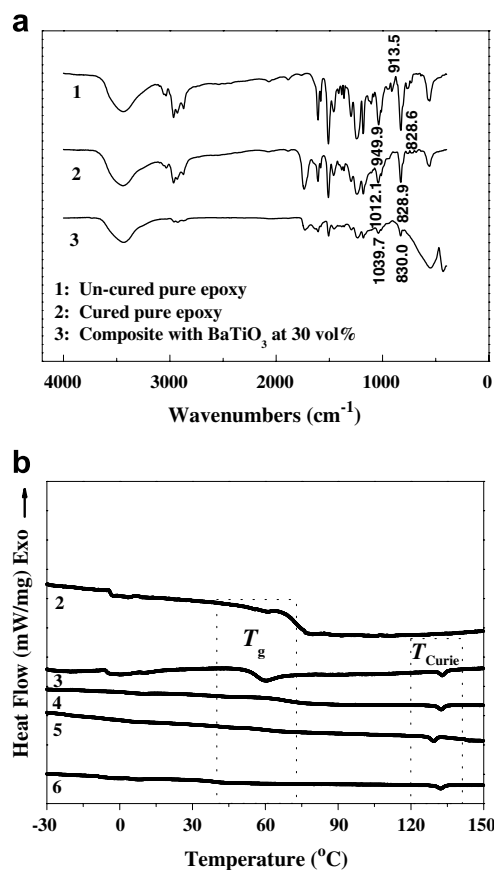


Fig. 1. (a) FTIR spectrum of (1) un-cured pure EPR, (2) cured pure EPR and (3) the cured composite with 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  at 30 vol%, (b) differential scanning calorimeter analysis (DSC) of (2) cured pure EPR and the cured composite with 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  (3, 4, 5, 6) at 30, 40, 60, 70 vol%, respectively.

### 2.3. Characterization of the BaTiO<sub>3</sub>/EPR composites

Curing characteristics of composites were investigated by Fourier transform infrared spectra (FTIR: Nexus 670) and differential scanning calorimetry (DSC: Dupont TA 2010) measurements. The fractured surface morphologies of the BaTiO<sub>3</sub>/EPR composites were investigated by scanning electron microscope (SEM, Hitachi S-4700).

### 2.4. Dielectric measurement of the BaTiO<sub>3</sub>/EPR composites

The alternating current (ac) dielectric properties of the composite samples were measured using an impedance analyzer (Agilent 4294A) both in the frequency ranges of 10<sup>2</sup>–10<sup>6</sup> Hz and in temperature ranges from –60 °C to 150 °C. Prior to measurement, electrodes were deposited with gold on the two sides of all samples.

Table 2  
Data obtained from the DSC curves

Sample no.	BaTiO <sub>3</sub> (vol%)	$T_c$ (°C)	$T_g$ (°C)	$\Delta H_g$ (J/g)	$T_{Curie}$ (°C)
2	0	64.3	69.4	65.43	–
3	30	50	53	52.51	129.8
4	40	57.4	65.4	39.61	129.7
5	60	55.3	57.4	14.54	129.4
6	70	35.1	35.3	13.57	129.5

## 3. Results and discussion

### 3.1. Curing characteristics of the BaTiO<sub>3</sub>/EPR composites

To understand of the curing behavior, the FTIR results of non-cured pure EPR, cured pure EPR and the BaTiO<sub>3</sub>/EPR composite with 0.7  $\mu\text{m}$  BaTiO<sub>3</sub> at 30 vol% were shown in Fig. 1a. It is well known that the plane stretching vibration of epoxide group at 913.25 cm<sup>–1</sup> is the characteristic peak of EPR. Obviously, non-cured EPR in Fig. 1a-1 displayed the characteristic peak of EPR at 913.25 cm<sup>–1</sup>. However, after the materials were cured, the characteristic peaks at 913.25 cm<sup>–1</sup> disappeared as shown in results of Fig. 1a-2 and a-3. Therefore, it could be suggested that the BaTiO<sub>3</sub>/EPR composites had been cured relative completely by mean of our curing process and other materials, such as harder MeTHPA and catalyst 2,4-EMI.

DSC analyses of the cured pure EPR and the composites with different concentration of BaTiO<sub>3</sub> are shown in Fig. 1b. Data obtained from the DSC curves are shown in Table 2. The temperature of glass transition peak ( $T_g$ ) of pure cured EPR is 69.4 °C, glass transition temperature of the composites changes with increase of the volume fraction of BT-07. It can be found that the  $T_g$  decreases firstly when the concentration of BaTiO<sub>3</sub> particles is less than 0.3. The existence of BT-07 in EPR poly-

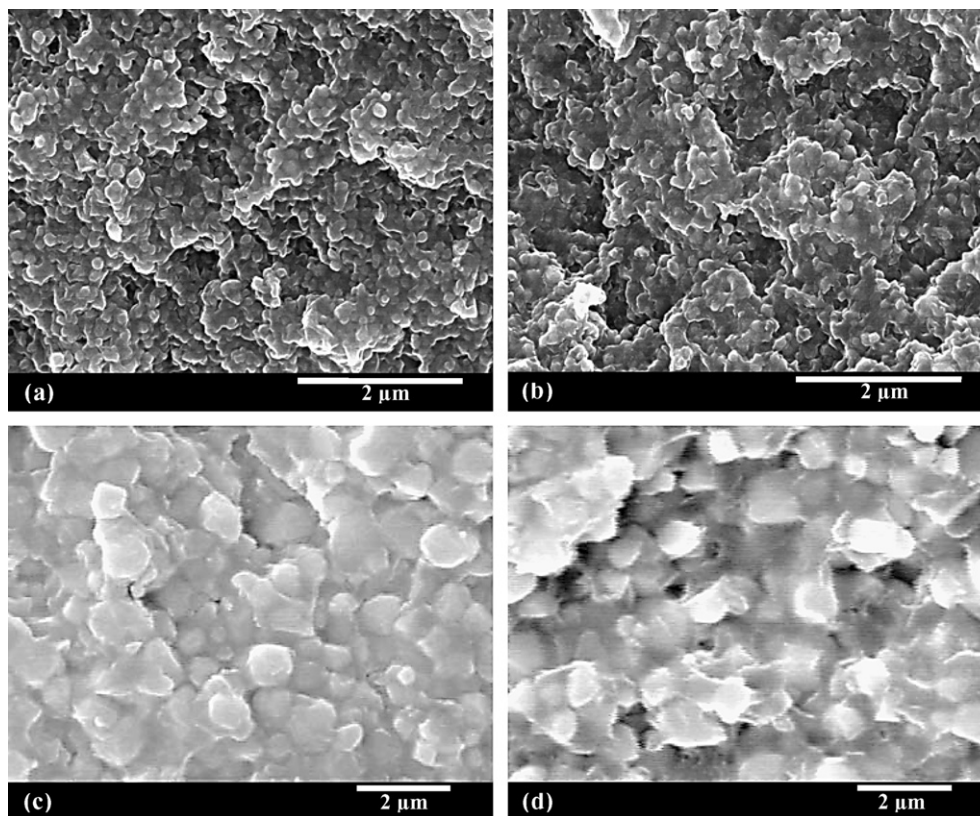


Fig. 2. Microstructures of fractured surface of the composites (loading 0.1  $\mu\text{m}$  or 0.7  $\mu\text{m}$  BaTiO<sub>3</sub> at 60 vol%) (a) BT-01 with 1% KH550 and (b) without KH550, (c) BT-07 with 1% KH550 and (d) without KH550.

mer reduces the degree of cross linking and also the glass transition temperature decreases. However, the result is just opposite when the volume fraction of BT-07 is more than 0.4. The composite with BT-07 at 0.7 contains only a little epoxy and maybe forms a continuous random cluster, which might induce to form small aggregated cluster structure. As a result, because of the appearance of voids, the glass transition temperature of the composites with BT-07 decreases. And the heats of glass transitions ( $\Delta H_g$ ) also decrease with an increase in the content of  $\text{BaTiO}_3$ . The DSC thermograph of Fig. 1b shows that the endothermic heat decreases with increasing temperature, and appears an abrupt decrease at glass transition temperature. Additionally, all of the composites with BT-07 at different fraction appear another peak at nearly Curie temperature (about 130 °C), which is relevant to the crystal phase transition temperature of  $\text{BaTiO}_3$ . The results suggest that the introduction of  $\text{BaTiO}_3$  particles in the composites would change the mobility of the EPR molecules, and therefore, a decrease of  $T_g$  in the composites could be noticed.

### 3.2. Microstructure and dielectric property of the $\text{BaTiO}_3$ /EPR composites with and without coupling agent

Microstructures of fractured cross-section of the composites (loading 0.1  $\mu\text{m}$  and 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  at 60 vol%) with and without KH550 were shown in Fig. 2a–d. It could be found that the KH550 improved the interaction between EPR and  $\text{BaTiO}_3$  particles, and therefore the ceramic particles are homogeneous into EPR. Same results can also reported in our past work and other references [5]. Main factors with being charge of the high dielectric permittivity in the composite with KH550 modifying  $\text{BaTiO}_3$ /epoxy composites is similar to  $\text{BaTiO}_3$ /PVDF composite [5]. Additionally, the dispersant of phosphated ester (BYK-9010) possess some organic acid groups in its molecular structure. The acid groups may induce an interaction with ceramic filler via an acid-base neutralization process, which, in turn, facilitated the dispersion of the ceramic filler within the EPR matrix [10,11]. EPR alone would not take advantage of this interaction process; meanwhile, the anhydride hardener was deficient in stoichiometry against epoxide groups. As a result, as shown in Fig. 3a and b, an increase in dielectric permittivity and a decrease in loss tangent were observed in the  $\text{BaTiO}_3$ /EPR composite with the silane coupling agent. It is clearly that the size of  $\text{BaTiO}_3$  has an effect on the dielectric property of the composites after optimizing the processing conditions. As a result, the dielectric property of the composite with BT-07 is obviously better than that with BT-01. Comparing with Fig. 2c and d, the compatibility between  $\text{BaTiO}_3$  and EPR is improved obviously. The results suggested that the coupling agent as well as the dispersant could improve the composite miscibility and subsequently created the expectable dielectric properties.

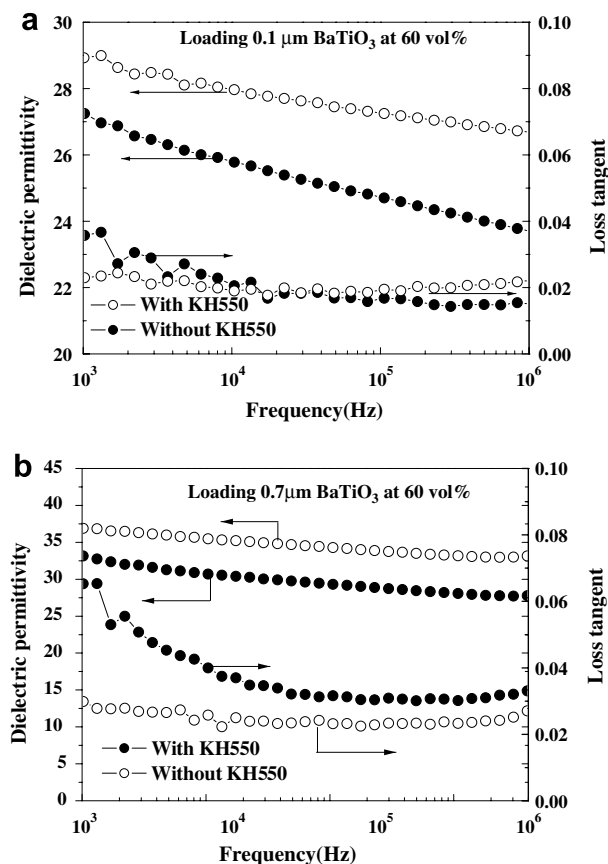


Fig. 3. Frequency dependence of dielectric property of the composite (loading 0.1  $\mu\text{m}$  or 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  at 60 vol%) with and without KH550 (a) BT-01 (b) BT-07 measured at room temperature.

### 3.3. Microstructure and dielectric property of the $\text{BaTiO}_3$ /EPR composites at room temperature

Fig. 4 showed morphologies of fractured cross-section of the composites loading 0.7  $\mu\text{m}$  and 0.1  $\mu\text{m}$   $\text{BaTiO}_3$  at 60 vol% and 75 vol%, respectively. It can be seen from Fig. 4a and b that the EPR is self-connected into a continuous phase while ceramic particles are randomly dispersed in the matrix, and the  $\text{BaTiO}_3$  particles are surrounded by the EPR. Few voids can be observed on the fractured surfaces of the composites at 60 vol% loading. However, it is very clear that the pores appear slowly with an increase of  $\text{BaTiO}_3$  concentration (at 75 vol%), which can be seen in Fig. 4a' and b', and the pores are very remarkable. The observed morphologies would be used to explain the results of dielectric properties as shown in Fig. 5. Namely, we can observe from Fig. 5a that the dielectric properties of the composites with 0.7  $\mu\text{m}$  and 0.1  $\mu\text{m}$   $\text{BaTiO}_3$  at 60 vol% are almost not dependent on frequency. However, the dielectric permittivity of the composite with 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  is significantly larger than that with 0.1  $\mu\text{m}$  one at 60 vol% while keeping almost the same loss tangent. The large dielectric permittivity in the composite with 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  can be attrib-



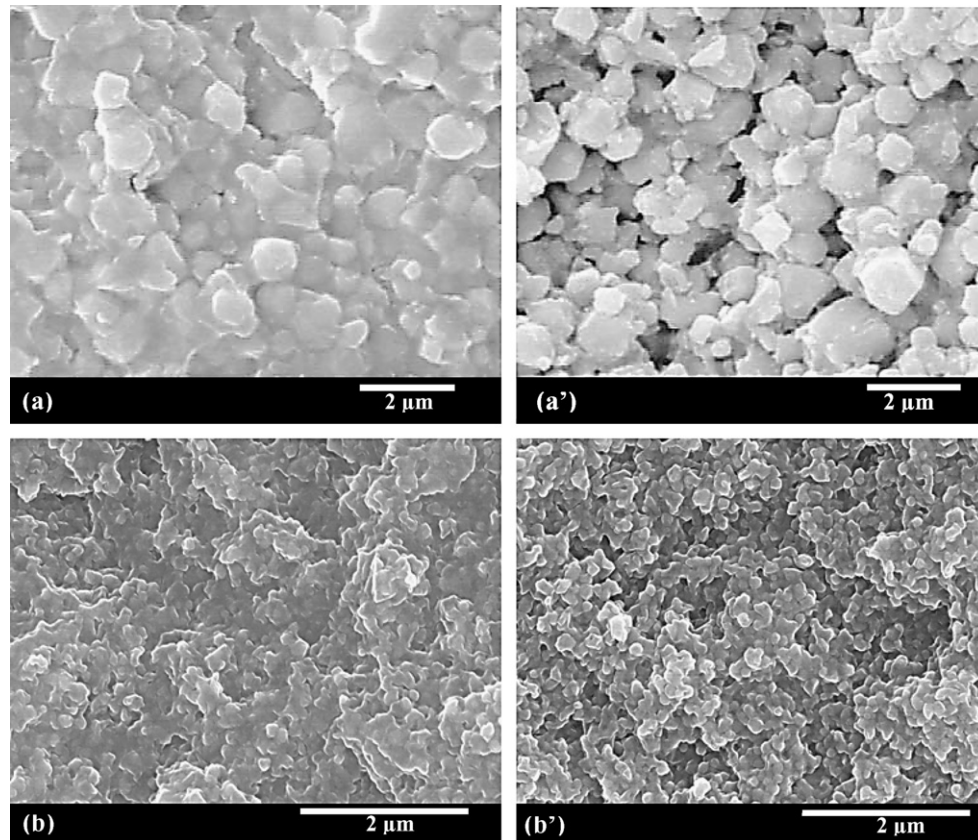


Fig. 4. Microstructures of fractured surface of the composites loading (a, a') 0.7  $\mu\text{m}$  and (b, b') 0.1  $\mu\text{m}$   $\text{BaTiO}_3$  at (a, b) 60 vol% and (a', b') 75 vol%, respectively.

uted to the increase of dielectric permittivity of the ceramic powders resulted from the increase of tetragonality phase and occurrence of clusters structure of  $\text{BaTiO}_3$  [12]. As the ceramic loading volume increase, the dielectric predominance of the composites with 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  is more obvious. However, because of the effect of pores at 70 vol% as shown in Fig. 4a' and b', the dielectric properties of the composites at 70 vol% always decrease with an increase in frequency. The dielectric permittivity of the composite with 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  is only slightly larger than that with 0.1  $\mu\text{m}$  one while displaying a remarkable loss tangent in the composite with 0.7  $\mu\text{m}$   $\text{BaTiO}_3$ . The results suggested that both the size of  $\text{BaTiO}_3$  particles and microstructure of the composites played an important role on deciding the final dielectric property of the  $\text{BaTiO}_3/\text{EPR}$  composites.

#### 3.4. Dependence of dielectric property of the $\text{BaTiO}_3/\text{EPR}$ composites on the concentration of $\text{BaTiO}_3$ at different frequencies

Fig. 6a and b shows the dependence of dielectric properties of the  $\text{BaTiO}_3/\text{EPR}$  composites with 0.1  $\mu\text{m}$  and 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  on the volume concentration of  $\text{BaTiO}_3$  at different frequencies ( $10^3$  Hz and  $10^6$  Hz), respectively.

Whatever frequency it was, in comparison with the dielectric permittivity of the composites with 0.7  $\mu\text{m}$   $\text{BaTiO}_3$ , we could observe that as the amount of  $\text{BaTiO}_3$  powders increased, the dielectric permittivity of the composites with 0.1  $\mu\text{m}$   $\text{BaTiO}_3$  was low when the concentration of  $\text{BaTiO}_3$  was less than 70 vol%. However, when the concentration of  $\text{BaTiO}_3$  arrived the value of 75 vol%, a valuable result appeared. Namely in this case, the dielectric permittivity of the composite with 0.1  $\mu\text{m}$   $\text{BaTiO}_3$  was larger than that with 0.7  $\mu\text{m}$ . Additionally, herein we also had to emphasize that the loss tangent for two kinds of composites kept the same rule. It was assumed that there was more chance for  $\text{BaTiO}_3$  particles to form a continuous random cluster with a decrease in particle size [13]. Therefore, compared with 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  particle, the particles with 0.1  $\mu\text{m}$  in diameter displayed a less chance to form voids and pores in its composites. As a result, the dipole–dipole interaction increased and contributed to higher dielectric permittivity. While at about 70 vol%, the dielectric permittivity of the composites with 0.7  $\mu\text{m}$   $\text{BaTiO}_3$  reached a maximum value and then decreased with further increasing the concentration of  $\text{BaTiO}_3$ . The decrease in dielectric permittivity was mainly due to the formation of voids and pores, which could be clearly found as shown in Fig. 4a'.

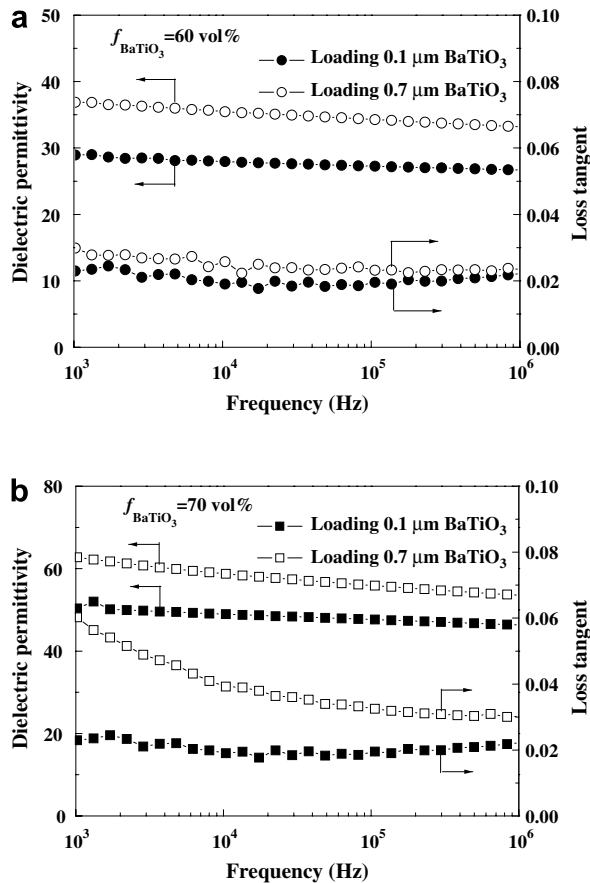


Fig. 5. Frequency dependence of dielectric properties of the composites with BaTiO<sub>3</sub> (0.1  $\mu\text{m}$  and 0.7  $\mu\text{m}$ ) respectively at the volume concentration of (a) 60% and (b) 70% measured at room temperature.

### 3.5. Temperature dependence of dielectric property of the BaTiO<sub>3</sub>/EPR composites

Fig. 7a and b shows respectively temperature dependences of dielectric permittivity and loss tangent of the BaTiO<sub>3</sub>/EPR composites with 0.1  $\mu\text{m}$  and 0.7  $\mu\text{m}$  BaTiO<sub>3</sub> at 70 vol% and  $10^3$  Hz. Both of the dielectric permittivity and loss tangent always increase with the temperature; they increase when the temperature is over 45  $^{\circ}\text{C}$  as shown in Fig. 7a and b. Additionally, the dielectric permittivity and loss tangent of the composite with 0.7  $\mu\text{m}$  BaTiO<sub>3</sub> at 70 vol% are always larger than those with 0.1  $\mu\text{m}$  one. Generally speaking, the change of dielectric property in the composites includes three competitive mechanisms: (a) segmental mobility of polymer is increased with the temperature, which should increase the permittivity, (b) thermal expansion of resin could disrupt the chains of contact BaTiO<sub>3</sub> particles, which should decrease the permittivity, and (c) the structure of BaTiO<sub>3</sub> particles could be changed with an increase in temperature (before Curie temperature), which could generate a modification on the dielectric response of the filler [14].

It is well known that the Curie temperature of pure BaTiO<sub>3</sub> is about 120  $^{\circ}\text{C}$ . However, because of the exis-

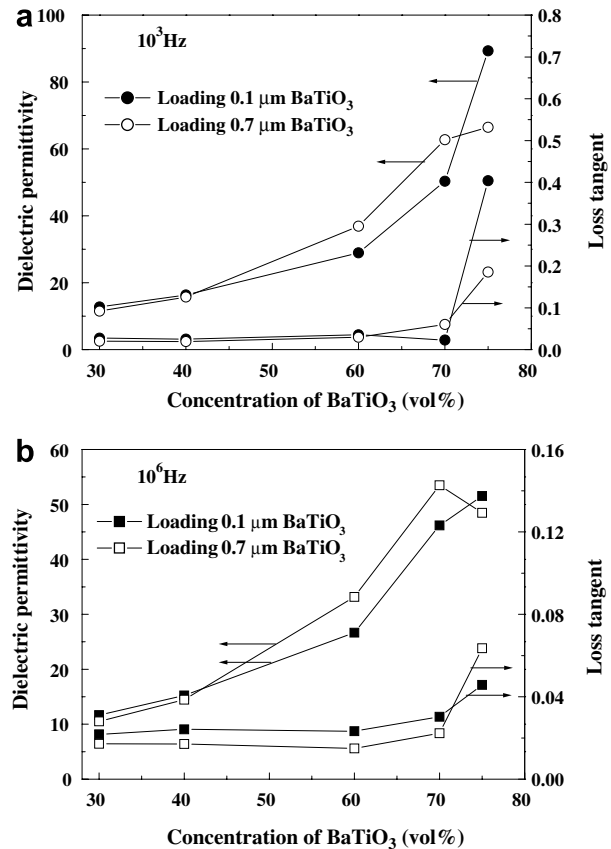


Fig. 6. Dependence of dielectric properties of the composites on the volume concentration of BaTiO<sub>3</sub> (0.1  $\mu\text{m}$  and 0.7  $\mu\text{m}$ ) at (a)  $10^3$  Hz and (b)  $10^6$  Hz respectively, measured at room temperature.

tence of epoxy as matrix and the different size and quality of BaTiO<sub>3</sub> particle, the Curie temperature may shift up or down. As shown in DSC results (see Fig. 1b), a small peak can be seen at around 130  $^{\circ}\text{C}$  because of the existence of phase transition of 0.7  $\mu\text{m}$  BaTiO<sub>3</sub> in the composite. The phase transition becomes a main factor to produce the effect on dielectric properties instead of the EPR matrix. The effect is more effective in high temperature and at low frequency [15]. However, the phase transition in the composite with 0.1  $\mu\text{m}$  BaTiO<sub>3</sub> is not very remarkable because the change rule of dielectric permittivity in the composite with 0.1  $\mu\text{m}$  BaTiO<sub>3</sub> is not different with that in the composite with 0.7  $\mu\text{m}$  one. Below 40  $^{\circ}\text{C}$ , the difference of dielectric permittivity in two kinds of composites is very negligible, which can be seen in the inset of Fig. 7a. The results suggested that the temperature would play a key role on determining the dielectric permittivity of the BaTiO<sub>3</sub>/EPR composites when it was beyond 40  $^{\circ}\text{C}$ . The loss tangent values increase abruptly (Fig. 7b) in the region of 60–80  $^{\circ}\text{C}$ . As the temperature increases, the loss tangent abrupt increases mainly around  $T_g$ . At the temperature near  $T_g$  the dipoles might begin to have enough mobility to contribute to the loss tangent and dielectric permittivity.

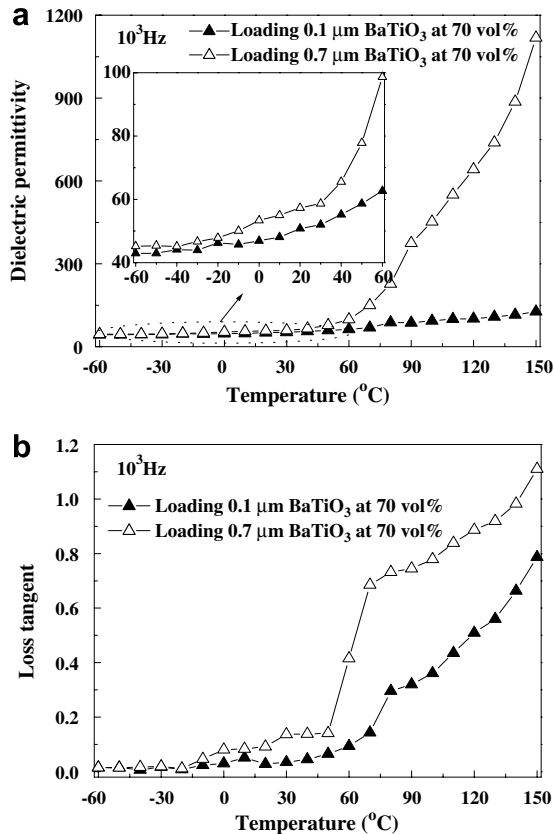


Fig. 7. Temperature dependence of (a) dielectric permittivity and (b) loss tangent of the composites with 70 vol% BaTiO<sub>3</sub> (0.1 μm and 0.7 μm) at 10<sup>3</sup> Hz. The inset in (a) is magnification from -60 °C to 60 °C in order to showing a clear change in dielectric permittivity.

#### 4. Conclusions

The BaTiO<sub>3</sub>/EPR composites with a good miscibility can be prepared by employing the optimum amount of silane coupling agent, and therefore, the dielectric permittivity of the composites can be improved significantly while keeping a low loss tangent. The size and concentration of BaTiO<sub>3</sub> particles also result in obvious effect on morphology and dielectric properties of composites. The use of lar-

ger size BaTiO<sub>3</sub> particles can increase the dielectric permittivity of the composites due to the existence of the tetragonality BaTiO<sub>3</sub>. However, when the amount of the BaTiO<sub>3</sub> particles reach 75 vol%, the dielectric permittivity of the composites with 0.1 μm BaTiO<sub>3</sub> continue to increase, not the case for the composites with 0.7 μm BaTiO<sub>3</sub> because of the existence of voids and pores. Additionally, temperature dependence of dielectric properties of two kinds of composites is different because there is a remarkable phase transition for large size BaTiO<sub>3</sub> particle when the temperature is near its Curie temperature.

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#### References

- [1] Bhattacharya SK, Tummla RR. *J Mater Sci Mater Electron* 2000;11:253.
- [2] Kuo DH, Chang CC. *J Eur Ceram Soc* 2000;21:1171.
- [3] Fan LH, Rao Y, Tison C, Moon KS, Pothukuchi SV, Wong CP. In: *Electronic components and technology conference*, 2002.
- [4] Yagi T, Tatemoto M, Sako J. *Polym J* 1980;12:209.
- [5] Dang ZM, Wang HY, Xu HP. *Appl Phys Lett* 2006;89:112902.
- [6] Rao Y, Yue J, Wong CP. In: *International symposium on advanced packaging materials*, 2001.
- [7] Cho SD, Lee JY, Paik KW. *Mater Sci Eng B* 2004;110:233.
- [8] Dang ZM, Wang HY, Zhang YH, Qi JQ. *Macromol Rapid Commun* 2005;26:1185.
- [9] Dang ZM, Shen Y, Nan CW. *Appl Phys Lett* 2002;81:4814.
- [10] Ogitani S, Bidstrup-Allen SA, Kohl PA. In: *Proceedings of the 1999 electronic components and technology conference*, 1999.
- [11] Cho SD, Lee JY, Paik KW. In: *The first symposium on electronic materials and packaging*, 2001.
- [12] Nan CW. *Prog Mater Sci* 1993;37:1.
- [13] Dang ZM, Wang HY, Peng B, Nan CW. *J Electroceramics*, in press.
- [14] Ramajo L, Reboredo M, Castro M. *Composites A* 2005;36:1267.
- [15] Psarras G, Manolakaki E, Tsangris GM. *Composites A* 2002;33:375.