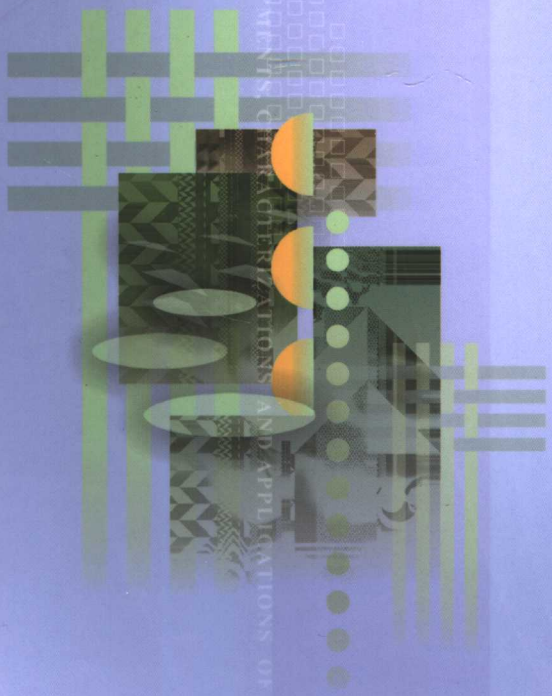
INNOVATIVE DEVELOPMENTS, CHARACTERIZATIONS AND APPLICATIONS OF COMPOSITES

Edited by Yao Zhang Qing-Qing Ni



CHINA AGRICULTURAL SCIENCE & TECHNOLOGY PRESS

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PREFACE

Since the Chinese Society for Composite Materials (CSCM) and the Japanese Society for Composite Materials (JSCM) sponsored the China-Japan Joint Conference on Composites (CJJCC) in 1997, six conferences (CJJCC 1 ~ 6) have been successfully launched in China or Japan, which provided an excellent base for scholars from both sides to present their achievements, exchange innovative ideas and share technical information. Following the steps of earlier joint conferences, the CJJCC – 7 will be held in Dunhuang, China from August 6th to 9th, 2006.

After critical reviews, over 50 high quality papers have been selected for presentation in the conference and for the publication in this book. The full papers selected in this book cover a wide range of topics, as Nanocomposites & Nanomechanics; Material & Processing; Properties & Characterization; Structure, Design & Analysis; Measuring & Computation, etc. It is believed that these current researches will offer us valuable information and will be beneficial to technique exchange among scientists and engineers.

The editorial committee would like to express their appreciation to many organizations and individuals who had contributed to the successful completion of the book. Among them are Chinese Society of Composite Materials (CSMS) and Japanese Society of Composite Materials (JSMS). In addition, we also would like to thank Prof. Hong CAI and the related members for their administrative and technical support.

Editor
Yao Zhang
Professor
Beihang University (China)

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PREPARATION OF FERROELECTRICS/POLYETHYLENE NANOCOMPOSITES BY IN-SITU POLYMERIZATION

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Abstract Nanosized perovskite ferroelectric lead strontium titanate (Pb_xSr_{1-x})TiO_3 (PST) powders were successfully prepared by a simple coprecipitation method. Lead-strontium titanyl oxalate (PSTO) precursor was first synthesized at room temperature, and the precursor was then calcined at a temperature higher than 600℃ for 1h to produce the single-phase perovskite PST powders. The average diameter was ranging from 10 to 200 nm. PST powders with desired composition could be synthesized by adding 25 mol% excess Sr. Then, Ziegler-Natta catalysts were supported on the PST powders and PST/polyethylene (PST/PE) nanocomposites were prepared by in-situ polymerization. PST/PE nanocomposites with different volume fractions of PST were obtained by changing the polymerization time. The dispersion and element distribution of the PST powder in the PST/PE nanocomposite were investigated by analyses and observations of energy dispersion X-ray (EDX) and transmission electron microscopy (TEM). The results indicated that the PST powder homogeneously dispersed in the PE matrix. The dielectric properties and Curie temperatures of the PST powders and PST/PE nanocomposites were also evaluated.

Key words Ferroelectrics; Coprecipitation; In-situ polymerization; Nanocomposite

INTRODUCTION

(Pb_xSr_{1-x})TiO_3 (PST) is a complete solid solution of $PbTiO_3$ (PT) and $SrTiO_3$ (ST), and has a perovskite structure just like (Ba_xSr_{1-x})TiO_3 (BST). The Curie temperature of PST could be adjusted by the ratio of PT and ST from −220 to 490℃, so is called composition-dependent Curie temperature. Due to its large electric field-dependent dielectric constant at a temperature near the Curie temperature, the PST is highly suitable for electronic and microelectronic applications, such as microwave devices, frequency tuning devices, capacitors, sensors, etc[1,2]. For ferroelectrics, the important electromechanical properties are the result of structural and micro structural changes that are incurred at Curie temperature. Size-effect phenomena issues in ferroelectrics have been of interest for many years. However, despite a large number of recent investigations regarding the effect of size on the ferroelectric

transition[3,4], few studies that focused on the nanosized PST powders with various stoichimetric compositions and particle sizes have been reported. Curie temperature of most ferroelectric materials drops remarkably when the particle size decreases to less than 100 nm, so is called the size effect[5,6]. Obviously, the PST is one of the most suitable candidates for nano-ferroelectrics applications in nano-electromechanical-system(NEMS), since its Curie temperature could be compensated by the composition. Therefore, preparation and evaluation of nanosized PST powders have been getting an increasing interest because of their novel physicochemical properties, which might be quite different from those of the bulk materials.

The ferroelectric materials have spontaneous polarization that causes particle agglomeration particularly in these nanosized powders. Dispersing the PST powders in a select polymer is an advantageous way for the solution as well as its applications. Polyethylene(PE) belongs to polyolefin that is one of the fastest growing classes of thermoplastics. Polyethylene/montmorillonite (PE/MMT) nanocomposites had been prepared via in-situ intercalative polymerization of ethylene after supporting Ziegler-Natta catalysts on the silicate MMT[7]. It indicated that ethylene could be polymerized on the surface of oxides to form PE/oxide composites. Therefore, it is possible to prepare (Pb, Sr) TiO_3/polyethylene (PST/PE) nanocomposites by the in-situ polymerization method.

In this paper, the nano-powders of ferroelectric PST were synthesized by coprecipitation processing, and then the PST/PE nanocomposites were prepared via in-situ polymerization. The process, structure and properties of PST powders and PE/PST nanocomposites were examined by various methods.

PREPARATION AND PROPERTIES OF NANOSIZED PST POWDERS

The starting materials were oxalic acid, ethanol, titanium tetrabutoxide, lead nitrate and strontium nitrate. Initially, $H_2C_2O_4 \cdot 2H_2O$ and $Ti(OC_4H_9)_4$ were dissolved ethanol, respectively. The $Ti(OC_4H_9)_4$ solution was then added into oxalic acid solution at room temperature, resulting in a clear oxalatitanic acid solution, $H_2TiO(C_2O_4)_2 \cdot 4H_2O$(HTO). Mixed aqueous solution of $Pb(NO_3)_2$ and $Sr(NO_3)_2$ was dripped slowly into the HTO with a constant stirring. The pH value of the solution was adjusted by adding aqueous ammonia and/or nitric acid. The resulting micro emulsion-derived precursor was kept overnight for the reaction to go to its completion. The precipitate, (Pb, Sr) $TiO(C_2O_4)_2 \cdot 4H_2O$(PSTO) obtained was filtered, washed, dried and calcined. Finally, PST crystalline powders were obtained[8].

Due to the different solubility of constituent components in the coprecipitation system, the final composition in the product is not always consistent with that of the starting materials introduced in the beginning. The pH value has obvious effect on the chemical composition. In this work, the products with starting compositions of PT, ST and $(Pb_{0.5}Sr_{0.5})TiO_3$ (PST5/5) were analyzed by Energy Dispersion X-ray(EDX) and Inductively Coupled Plasma(ICP). The results showed that stoichiometric PT powder could be obtained by this method with pH = 1, but the Sr/Ti ratio of ST powder changed from

0.80 at pH = 1 to 0.95 at pH = 4. Considering all the results from the analyses, it was found that an excess amount of 25 mol% Sr was required to obtain PST powders with desired composition at pH = 1. Hence, an excess of 25 mol% $Sr(NO_3)_2$ was added to starting materials in order to synthesize PST powders with desired composition at pH = 1 for all the further investigation in our work.

The complete reaction process could be expressed as below:

(1) $2H_2C_2O_4 \cdot 2H_2O + (C_4H_9O)_4TiH_2TiO(C_2O_4)_2 \cdot 4H_2O + 4C_4H_9OH$

(2) $H_2TiO(C_2O_4)_2 \cdot 4H_2O + xPb(NO_3)_2 + (1-x)Sr(NO_3)_2(Pb_xSr_{1-x})TiO(C_2O_4)_2 \cdot 4H_2O + 2HNO_3$

(3) $(Pb_xSr_{1-x})TiO(C_2O_4)_2 \cdot 4H_2O(Pb_xSr_{1-x})TiO(C_2O_4)_2 + 4H_2O$

(4) $(Pb_xSr_{1-x})TiO(C_2O_4)2 + O_2(Pb_xSr_{1-x})CO_3 \cdot TiO_2 + 3CO_2$

(5) $(Pb_xSr_{1-x})CO_3 \cdot TiO_2(Pb_xSr_{1-x})TiO_3 + CO_2$

From the above formulas, thermal decomposition of PSTO precursor was the main process by heating it in air/oxygen atmosphere, as represented in reactions(3)-(5). To study this process, thermogravimetric and differential thermal analyses(DTA/TGA), Fourier transform infrared spectrometer(FTIR) and X-ray diffractometer(XRD) were carried out. According to TGA and DTA curves in Fig. 1, there are three stages of weight loss, which appear in the temperature range from room temperature to 250℃, from 250℃ to 400℃, and around 600℃. The experimentally observed weight losses were in good agreement with the theoretically calculated values based on the thermal reactions. Figure 2 shows curves of FTIR for PSTO, $(Pb,Sr)CO_3 \cdot TiO_2$ calcined at 400℃ for 1h and the final PST calcined at 600℃ for 1h. In comparison of the curves(a) and (b), it was clear that the absorption bands of oxalate group around 1 725 ~ 1 633, 1 420 and 1 280 cm^{-1} in PSTO were absent in $(Pb,Sr)CO_3 \cdot TiO_2$[9,10]. In curve(b), there were a band at 2 340 cm^{-1} related to CO_2 adsorbed on a metal cation, and a sharp band at 1 480 cm^{-1} assigned to unidentate carbonate[11]. The FTIR spectrum curve(c) did not show any band between 4 000 and 1 000 cm^{-1}. The room-temperature XRD patterns of PST5/5 calcined in air for 1 h at various temperatures indicated its phase development, as shown in Fig. 3. It also can be seen that PST5/5 powders calcined below 900℃ have a cubic structure while those samples cal-

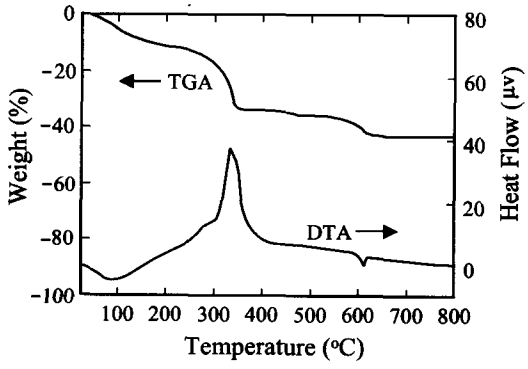

Fig. 1. DTA/TGA curves of PSTO.

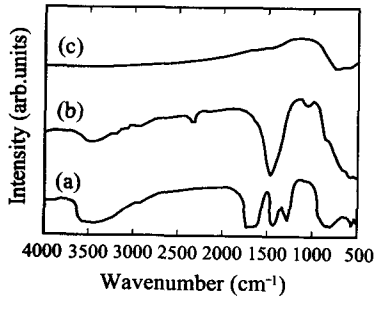

Fig. 2 FTIR spectra of(a) PSTO, (b) $(Pb,Sr)CO_3 \cdot TiO_2$ and(c) PST.

cined at 1 000℃ have a tetragonal one at room temperature.

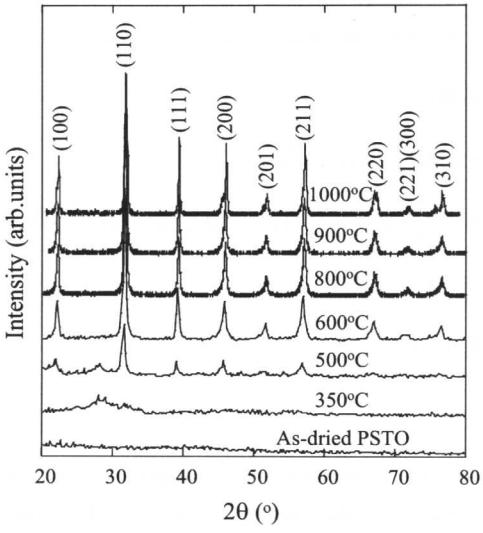

Fig. 3 Room – temperature XRD patterns of PST5/5 powders calcined at various temperatures.

A transmission electron microscopy (TEM) was used to analyze the particle size and morphology of the PST powders. The PST powders were treated with ball milling in ethanol for dispersion before TEM observation. Figure 4 shows the TEM photographs of PST5/5 powders calcined at 600 (a) and 1 000℃ (b) for 1h, respectively. From the pictures, PST5/5 powders were of spherical in nature with average sizes of 10 and 200 nm. In this way, the average particle sizes of PST5/5 as well as($Pb_{0.6}Sr_{0.4}$) TiO_3 (PST6/4) and ($Pb_{0.7}Sr_{0.3}$) TiO_3 (PST7/3) powders were estimated, as shown in Fig. 5. Therefore, the particle size could be controlled in range of 10 ~ 200 nm by varying the calcination temperature from 600℃ to 1 000℃.

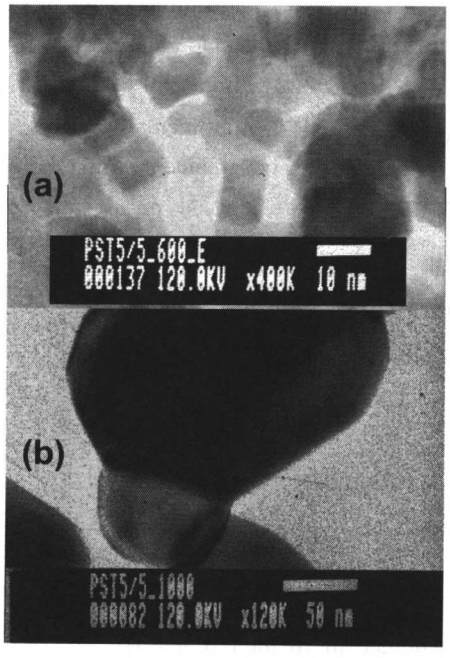

Fig. 4 TEM photographs of PST.

Using high-temperature XRD, the Curie temperatures of PST powders were estimated. The temperature at which the splitting of(002) and(200) refraction peaks around $2\theta = 45°$ disappeared was taken

as the Curie temperature. Figure 6 shows the dependence of Curie temperature on the particle size for PST6/4. The Curie temperature of a sample below 200 nm in size decreased sharply as the particle size decreased. These Curie temperatures are much lower than that of the bulk PST6/4, 230℃[1]. For nanosized powders, the crystalline size is so small that thermal vibrations at a lower temperature may destroy the ordered anisotropic crystalline structure. This results in the disappearance of ferroelectricity and a decrease of the Curie temperature. The surface tension effect has been also used to explain the observations. The large internal pressure caused by the particle size would qualitatively shift the Curie temperature to a lower temperature for ferroelectric materials.

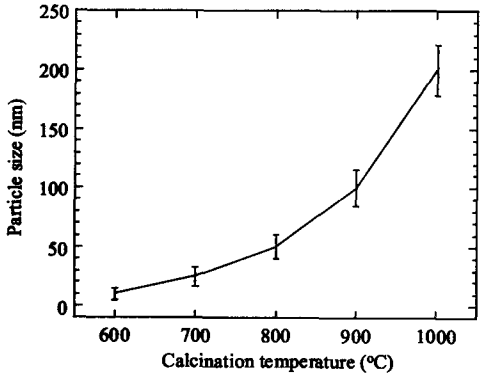

Fig. 5 Size dependence on calcination temperature.

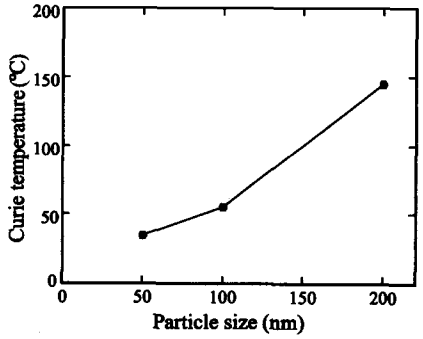

Fig. 6 Curie temperature of PST6/4 dependence on particle size.

PREPARATION AND PROPERTIES OF PST/PE NANOCOM-POSITS

In an N_2-purged 250 ml four-neck glass reactor fitted with a stirrer, the prepared PST6/4 powder 100 nm in size and anhydrous heptane were introduced and the mixture was then stirred to a homogeneous suspension. $TiCl_4$ was added dropwise to the suspension over 1 h at room temperature and the reaction was allowed to continue for another 2 h. The obtained slurry was then separated by filtration, and the residual was washed several times with heptane. The PST-supported catalyst was then stored in ampoules as slurry in heptane.

Slurry polymerization was carried out in a 5 L autoclave reactor equipped with a mechanical stirrer. Alkyl aluminum cocatalyst and the prepared slurry with Zigler-Natta-type catalyst supported on the nanosized PST powder were added in succession into the reactor filled with 2 L of hexane and then ethylene gas was introduced. The polymerization was performed under an ethylene gas pressure of 1 bar at 60℃. After the completion of polymerization, the whole slurry was poured into a large container and the solvent was decanted. The obtained solid polymer was collected and dried in vacuum. During the ethylene polymerization process, PST/PE nanocomposites with different volume fractions of PST were obtained by changing the polymerization time, as listed in Table 1.

Table 1 Ethylene polymerization results

	Polymerization time(min)	PST content(wt%)	Volume fraction of PST(%)
PST/PE-1	20	24.3	4.1
PST/PE-2	10	36.6	7.2
PST/PE-3	5	55.8	14.5
PST/PE-4	3	84.2	41.9

The TEM photograph in Fig. 7 shows the PST/PE nanocomposite. The black particles are the PST powders and the lighter areas belong to the PE matrix. It could be seen that the PST particles in the nanocomposites are dispersed separately. Figure 8 shows the electron diffraction patterns of the PE, PST and PST/PE. PE is a partial crystalline polymer with a spherulite structure, which consists of aggregates of lamellar crystals formed by folding molecular chains. From the figure, the electron diffraction pattern of PE consists of dispersed concentric rings. PST is monocrystalline and its electron diffraction pattern is made up of regularly lined lattices. In the diffraction pattern of PST/PE, dispersed concentric rings and regularly lined lattices are superimposed. The elemental distribution of the PST/PE nano-composite was examined by a scanning electron microscopy(SEM). In Figure 9, the white particles of PST6/4 powders 100 nm in size are dispersed in the black PE matrix. The distributions of elements such as Pb, Sr, Ti and O in PST are clearly observed. All of the above results indicate that PST powders homogeneously dispersed in the PE matrix during ethylene polymerization and that a uniform PST/PE nanocomposite was formed. The phase of PST/PE nanocomposite with various volume fractions was evaluated by XRD, as shown in Fig. 10. Pure PE shows strong X-ray diffraction peaks in the 2θ angle range of $20° \sim 25°$. The PST perovskite structure is visible as soon as PST powders exist in the PE matrix. With increasing volume fraction of the PST powders, the characteristic diffraction peaks of PST6/4 become stronger and those of PE gradually fade out. This corroborated the formation of PST/PE nanocomposites.

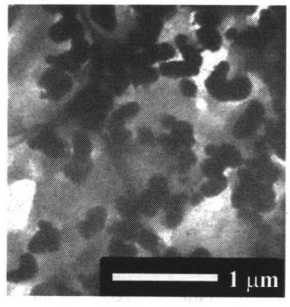

Fig. 7 TEM photograph of PST/PE nano-composite.

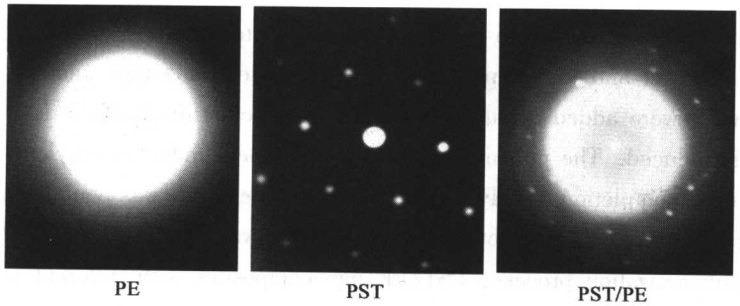

Fig. 8 Electron diffraction patterns of PE, PST6/4 and PST/PE.

In this study, the dielectric constant of PST6/4 powders 100 nm in size was estimated to be 849 at 20℃ by the powder dielectric measurement method[12]. The dielectric constant of PE is known to be 2.3. The dielectric constants of PST/PE nanocomposites with different volume fractions of PST60/40 powders were evaluated at 20℃ and 100 kHz. Figure 11 shows the dependence of the dielectric constant of PST/PE nanocomposites on the volume fraction of PST6/4. From the TEM photograph in Fig. 7, it can be seen that the PST particles are almost separated and surrounded by the PE matrix in the nanocomposite. The 0-3-type composite model is most applicable to the nanocomposites. Yamada et al. proposed a theoretical model to explain the behavior of the dielectric properties for 0 ~ 3 composites[13]. The dielectric constant of

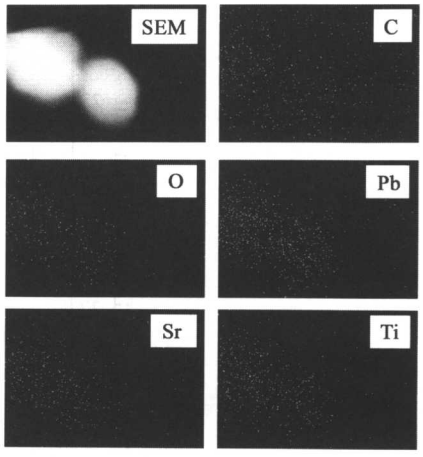

Fig. 9 SEM image and elemental distribution for PST/PE.

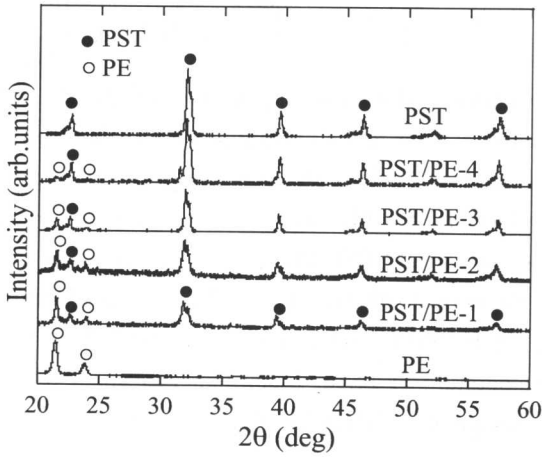

Fig. 10 XRD patterns of PST/PE with various volume fractions of PST6/4.

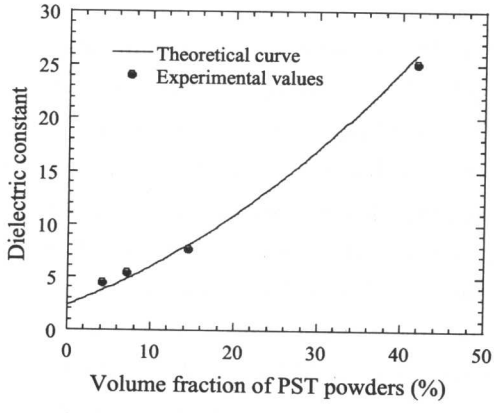

Fig. 11 Dependence of dielectric constant of PST/PE on volume fraction of PST6/4.

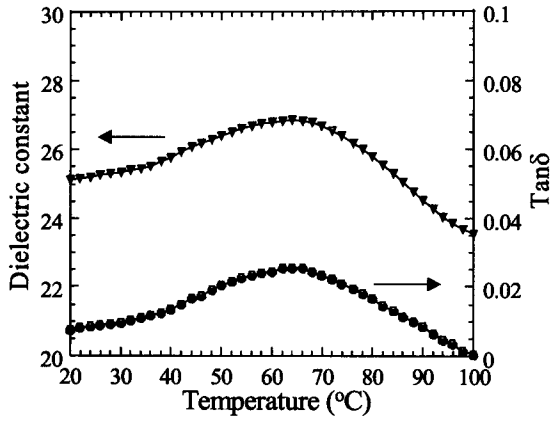

Fig. 12 Dependence of dielectric constant of PST/PE – 4 on temperature.

the composite is given by

$$\varepsilon = \varepsilon^{p}\left\{1 + \frac{\eta\phi(\varepsilon^{C} - \varepsilon^{P})}{\eta\varepsilon^{P} + (\varepsilon^{C} - \varepsilon^{P})(1 - \phi)}\right\}$$

where η is a parameter depending on the shape of particles and $\phi$is the volume fraction of the ceramic. The other symbols ε, ε^{c} and ε^{p} refer to the magnitudes of the dielectric constants of the composite, ceramic and polymer, respectively. In this study, a shape parameter equal to 15.5 was found to fit to our experimental values obtained in PST/PE composites with various ceramic volume fractions. Figure 11 reveals that the dielectric constants of PST/PE appear to have strong concentration dependence and are in good agreement with theoretical values. Figure 12 shows the dielectric constant of PST/PE-4 in the temperature range from 20 to 100℃ and measured at 100 kHz. There is a maximum at 64℃, which implies the Curie temperature of PST6/4 powders was about 64℃. This value corresponded with that estimated by high-temperature XRD(Fig. 6).

CONCLUSION

Nanosized perovskite ferroelectric PST powders were successfully prepared the coprecipitation method. The completed reaction process for the preparation was characterized. The PST powders with desired composition could be synthesized by adding 25 mol% excess Sr. The average diameter was ranging from 10 to 200 nm by means of controlling the calcination temperature. The size effect on Curie temperature showed a sharply decreasing when the particle size decreased below 200 nm. Then, Ziegler-Natta catalysts were supported on the PST6/4 powders and PST/PE nanocomposites were prepared by in-situ polymerization. The volume fractions of PST powder in the nanocomposite could be adjusted by changing the polymerization time. By the SEM analyses and TEM observations, it was known that the PST powders homogeneously dispersed in the PE matrix during ethylene polymerization. The dielectric constant of PST/PE appeared to have strong concentration dependence. By the dependence of dielectric constant of PST/PE on temperature, the Curie temperature of PST6/4 powders was observed at