

# Preparation of BaTiO<sub>3</sub>/Poly(vinylidene fluoride) 0-3 Composite Films for Dielectric Applications

Kyu-Seog Hwang\*, Jong-Min Kang\*\*, June-Ho Lee\*\*\* and Seung-Hwangbo<sup>†</sup>

**Abstract** – Ferroelectric BaTiO<sub>3</sub>/poly(vinylidene fluoride) (PVDF) nanocomposite films were successfully prepared by mixing BaTiO<sub>3</sub> nano-particles into PVDF solution dissolved in dimethylformamide under ultrasonification. The mixture was casted onto glass petri dish and then annealed at 100°C for 12 h in vacuum dry oven. Crystal structure and surface morphology of the samples were analyzed by using an X-ray diffraction analysis and a field emission-scanning electron microscope, respectively. The relative dielectric permittivity and loss tangent were determined in the frequency range of 50 Hz to 1 MHz. For the BaTiO<sub>3</sub>/PVDF nanocomposites, the entire diffraction peaks match those indicated by standard BaTiO<sub>3</sub> perovskite structure. The FE-SEM image reveals the homogeneity of the BaTiO<sub>3</sub> nanopowder distribution and also predominant 0-3 connectivity. All results show that the dielectric properties of the nanocomposite films are desirable and the fabrication technique for preparing the BaTiO<sub>3</sub>/PVDF nanocomposites has a potential in the electronic applications.

**Keywords:** BaTiO<sub>3</sub>, Poly(vinylidene fluoride), Nanocomposite, Dielectric permittivity.

## 1. Introduction

Ferroelectric BaTiO<sub>3</sub> has been applied as an excellent dielectric material in electronic engineering. Nevertheless, these ceramic materials have some shortcomings, such as poor flexibility which is not well fulfilled for production of some electronic devices. Poly(vinylidene fluoride) (PVDF) is the most normally used polymer dielectric materials owing to its good permanency to ultra-violet exposition and destructive chemical atmosphere. However, the low dielectric constant and high dielectric loss of this polymer with the difficulty of poling treatment thick films also limit their use [1].

Hybrid materials of nanocomposites have been fascinated a great deal of attention for their great performance and distinctive property which cannot be accomplished by other simple materials [2, 3]. Ceramic-polymer mixtures organize a new class of structure and functional materials of great application possible in having the joined hardness and stiffness of ceramics and the elasticity, flexibility, low density and high breakdown strength of polymers. The approaches of manufacturing nanocomposites have been done by many researchers aiming at conjoining the high relative dielectric permittivity of ceramic and the high

breakdown strength of polymer.

To accomplish many performance aims, ferroelectric ceramics such as Pb(Zr, Ti)O<sub>3</sub> and BaTiO<sub>3</sub> [3-5] have been used as fillers in polymers. The dielectric properties of PVDF can be enhanced exploiting them as matrixes in composites, in which ferroelectric ceramics with changed composition and morphology are added. Ceramic and polymer-hybrid composites having 0-3 connectivity can be prepared by dispersing ferroelectric ceramics not in contact with each other, therefore having connectivity 0, dispersed in a continuous polymeric network, having connectivity 3 [3, 6]. However, a high volume fraction of ceramic powders, generally above 50 vol%, is required for improved dielectric properties, which always lead to severe deterioration of the breakdown strength [7]. The noteworthy decrease of the breakdown strength in composites is attributed to an inhomogeneous local electric field concentration that is produced by difference in permittivity between the polymer matrix and the ceramic filler [8]. Many processes are used to prepare homogeneous ceramic-polymer composites, e.g. compression molding, solvent casting, or spin-coating. Compression molding and solvent casting results in films with thickness ranging from 30 to 500 μm, while spin-coating generally leads to comparatively thin films of only a few μm.

In this paper, the polymeric material used to prepare the nanocomposite films was PVDF, and the ceramic material was lead-free BaTiO<sub>3</sub> nanoparticles. Crystal structure and surface morphology of the composite films were examined. The frequency dependence of the dielectric permittivity and tangent loss was studied in the frequency range of 50 Hz to 1 MHz.

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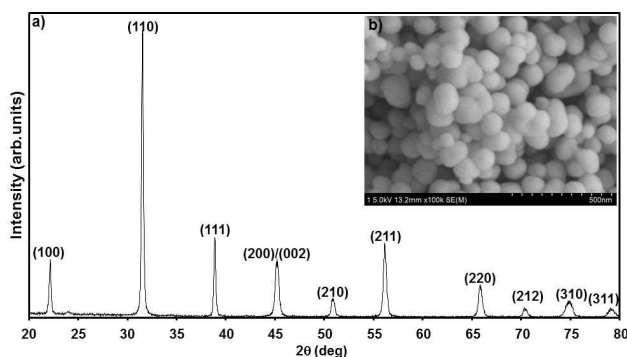
## 2. Experimental Procedure

Samples of BaTiO<sub>3</sub>/PVDF nanocomposites of 0 - 3 type-connectivity were prepared using a solution casting technique. Commercially available BaTiO<sub>3</sub> nano-powders (Sigma-Aldrich, 100 nm, 99%), PVDF (Sigma-Aldrich, M<sub>w</sub>~530,000) and dimethylformamide (DMF, Daejung, 99.8%) were used as starting materials to prepare nanocomposites. PVDF pellets at a 1:10 weight ratio were fully dissolved in DMF under magnetic stirring at 40°C for 50 min. Nanocomposites were prepared by dispersing 20 wt%-BaTiO<sub>3</sub> powders into the PVDF/DMF solution by stirring at 50°C for 6 h, followed by high energy ultrasonic treatment at 40°C for 50 min. Subsequently, the mixture was casted onto a glass petri dish and dried at 100°C for 12 h in vacuum dry oven. For dielectric measurement, top and bottom surfaces of nanocomposite films were coated with conductive silver paste.

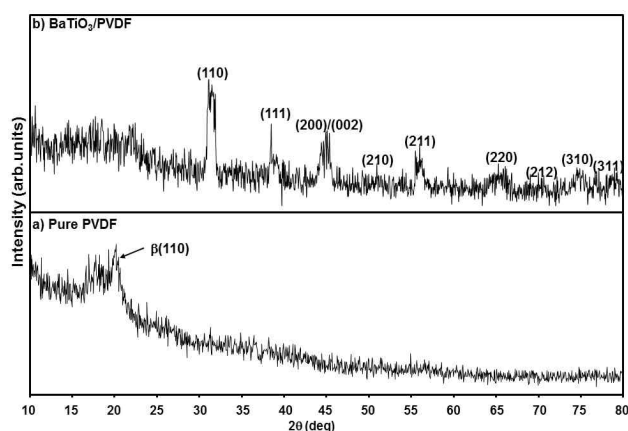
The crystal structure and surface morphology of the BaTiO<sub>3</sub> nanoparticles and nanocomposites were determined using a high-resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands) analysis and field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Jpn.). The relative permittivity ( $\epsilon$ ) and tangent loss ( $D$ ) was calculated from the capacitance measured by means of a LCR meter (PM6306, Fluke, U. S. A.) in the range of 50 Hz to 1 MHz at room temperature.

## 3. Results and Discussion

Fig. 1 (a) and (b) shows typical XRD pattern and morphology of the BaTiO<sub>3</sub> nano-powders. The BaTiO<sub>3</sub> perovskite phases, (100), (110), (111), (200), (102), (211), (220), (212), (310) and (311) reflections at  $2\theta = 22.16^\circ$ ,  $31.53^\circ$ ,  $38.87^\circ$ ,  $45.14^\circ$ ,  $50.83^\circ$ ,  $56.14^\circ$ ,  $65.81^\circ$ ,  $70.33^\circ$ ,  $74.85^\circ$ , and  $79.07^\circ$  respectively, were clearly identified. FE-SEM observation of the as-received BaTiO<sub>3</sub> powder [Fig. 1 (b)] showed large agglomerates, with diameters comparable with the value claimed by the supplier, were identified. From the FE-SEM image, it can be seen that the



**Fig. 1.** XRD patterns (a) and FE-SEM micrograph (b) of the BaTiO<sub>3</sub> nano particles

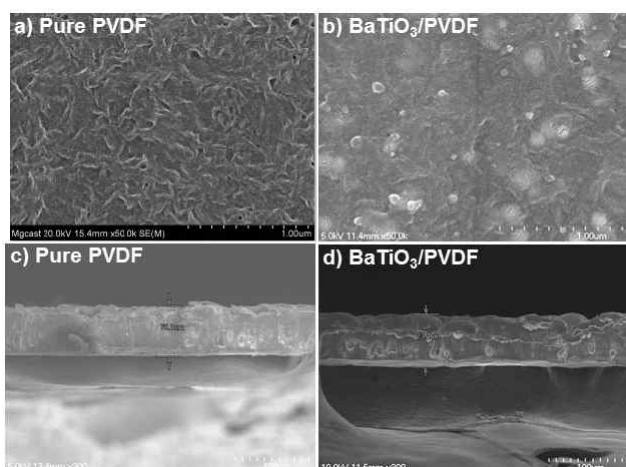


**Fig. 2.** XRD patterns of the pure PVDF (a) and BaTiO<sub>3</sub>/PVDF nanocomposite films (b)

spherical grains are distributed homogeneously and the grain size are found to be about 100 nm.

Fig. 2 shows the X-ray patterns of pure PVDF (a) and the BaTiO<sub>3</sub>/PVDF nanocomposites with 20 wt% BaTiO<sub>3</sub> (b). The single crystal BaTiO<sub>3</sub> nano powder has a pure perovskite phase, as previously shown in Fig. 1 (a). It is evident from Fig. 2 (a) that the peak at  $2\theta$  corresponding to  $20 \sim 21^\circ$  presents in XRD pattern indicates the presence of  $\beta$ -phase PVDF. Thus pure PVDF films developed by solvent casting using solvent DMF showed the presence of  $\beta$ -phase and XRD pattern indicates the semi-crystalline nature of PVDF polymer film. Although BaTiO<sub>3</sub>/PVDF nanocomposites displayed a perovskite phase, as shown in Fig. 2 (b), it is difficult to calculate tetragonality because of low peak intensities of nano BaTiO<sub>3</sub> powder. Generally, the cubic phase shows paraelectric properties with a trivial dielectric constant, while the tetragonal phase shows ferroelectric properties which are more interesting for dielectric applications due to its high dielectric constant. It is known that the dielectric constant decreases with a decrease in particle size and disappears below a certain critical size. This is due to the phase transition from tetragonal to cubic in connection with the particle size decrease, which is called the size effect [9, 10]. Due to the importance of fine tetragonal BaTiO<sub>3</sub> powder with a high dielectric constant, many researchers have been interested in the cubic-to-tetragonal phase transition of this powder. However, all the study reports show different results on a critical particle size. This inconsistency may arise from the different residual elastic strain energy, chemical impurity levels and crystalline defects associated with various powder synthetic methods as well as the resolution of the characterization [9].

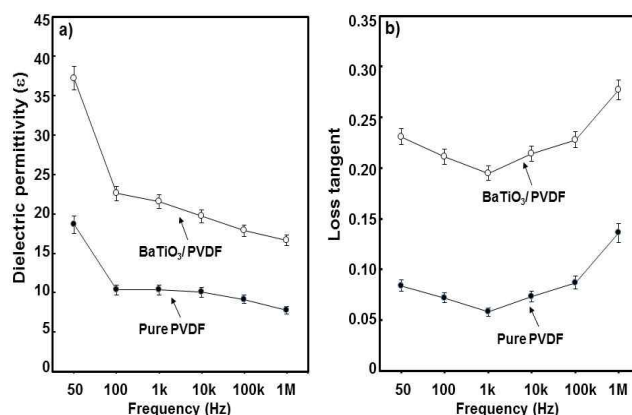
For the BaTiO<sub>3</sub>/PVDF nanocomposites, the entire diffraction peaks match those indicated by standard JCPDS card No. 05-0626 pertaining to perovskite structure. Furthermore, the nanocomposite is free from the pyrochlore phase, which is considered unwanted in the BaTiO<sub>3</sub> system, and it is observed that there is no shift in



**Fig. 3.** FE-SEM micrographs and cross-sectional images of the pure PVDF films (a) and (c), and BaTiO<sub>3</sub>/PVDF nanocomposite films (b) and (d), respectively

BaTiO<sub>3</sub> peaks position owing to the existence of PVDF matrix. However, a change in phase for the PVDF is apparent, as shown in Fig. 2 (a) and (b). The pure PVDF displays the strongest peak around  $2\theta = 19\sim 20^\circ$ , but the diffraction peaks of PVDF in the nanocomposites are negligible with an addition the BaTiO<sub>3</sub> nano powder. We assume that this is since the BaTiO<sub>3</sub> nano powders dispersed in the PVDF matrix might have an important effect on the crystallization of the PVDF polymer [11]. As a result, the amorphous regions of the PVDF polymer are enlarged.

The surface morphologies of fabricated pure PVDF film (a) and BaTiO<sub>3</sub>/PVDF nanocomposite films with 20 wt% BaTiO<sub>3</sub> (b) are shown in Fig. 3. The surface is found flat and dense. Rod-type morphology is detected on the pure PVDF film [see Fig. 3 (a)]. The distribution of rods is random. The uniform distribution of the bright areas (related to the BaTiO<sub>3</sub> nanoparticles) evidences that sample has revealed a uniform dispersion of BaTiO<sub>3</sub> nanoparticles into the PVDF polymer matrix, as shown in Fig. 3 (b). Agglomeration of the ceramic fillers will considerably lower the energy density [12]. Even if a evident agglomeration was present in the as-received powder, BaTiO<sub>3</sub> nanopowders were homogeneously distributed in the PVDF matrix, as shown in Fig. 3 (b). The combination of a suitable concentration of PVDF on DMF and the sonification method were found to be critical for uniform dispersion BaTiO<sub>3</sub> nanopowders in PVDF matrix [12]. The BaTiO<sub>3</sub> nanopowders have average diameter of 100 nm which is consistent with the manufacturer's information. It is well known that the dielectric properties of composites strongly depended on the dispersion of different ferroelectric particles. The FE-SEM image reveals the homogeneity of the BaTiO<sub>3</sub> nanopowder distribution and also predominant 0-3 connectivity. As shown in Fig. 3(d), BaTiO<sub>3</sub>/PVDF nanocomposite films had a thickness about 73.4  $\mu\text{m}$ , as identified by FE-SEM observation of their cross-sections.



**Fig. 4.** Variation in relative dielectric permittivity( $\epsilon$ ) and tangent loss ( $D$ ) of pure PVDF and BaTiO<sub>3</sub>/PVDF nanocomposites films as a function of frequency change

The dielectric constant variation with frequency of nanocomposite films measured at room temperature is present on Fig. 4 (a). Dielectric constant was calculated from  $C = \epsilon_0 \epsilon_r A/d$ , where  $C$  is the capacitance (F),  $\epsilon_r$  is the relative dielectric permittivity,  $A$  is the surface area (m<sup>2</sup>),  $d$  is the sample thickness (m) and  $\epsilon_0$  is the permittivity of vacuum ( $8.854 \times 10^{-12}$  F/m). Once the capacitance is calculated, the relative dielectric permittivity can be determined. To measure the capacitance, five samples were tested using an LCR meter at different frequency levels ranging from 50 Hz to 1 MHz. Commonly, the capacitance of a dielectric material is influenced by the volume fraction of the ceramic filler and frequency. As shown in Fig. 4 (a), at 50 Hz testing frequency, sample displayed high relative dielectric permittivity; however, a sudden decrease on dielectric permittivity occurs within the lower frequency level range from 50 Hz to 100 Hz due to the nature of ferroelectric materials, i.e., materials phase and lattice structure. At high frequency, the electric response of a sample lags behind the applied field and creates loss [12]. After 100 Hz frequency, relative dielectric permittivity linearly decreased with the increase of frequency from 100 Hz to 1 MHz. This phenomenon can be described with Clausius-Mosotti relation, which states that the dielectric constant is related to polarizability of the material. Polarizability of a dielectric material changes with the frequency of the applied electric field which contributes to the variation of the capacitance as well as the relative dielectric permittivity. At low frequency, the dipole orientation of the nanocomposites is not as affected as it does at high frequency, thus, contributing to high capacitance value. At higher frequency, the dipoles cannot maintain their orientation with the alternating field, resulting in a lower relative dielectric permittivity [12]. The dependence of dielectric loss of the nanocomposites on frequency is present in Fig. 4 (b). The dielectric loss was unchanged in the frequency range of 100 Hz to 1 MHz. The nanocomposites showed good dielectric stability over a wide frequency

range.

By incorporating the outstanding dielectric properties of BaTiO<sub>3</sub> and PVDF, researchers have developed the dielectric properties of the electronic devices. Inclusion of high dielectric constant ceramic fillers in the polymer matrix shows improved dielectric property and piezoelectric reaction of the polymer-ceramic composite material in comparison to ferroelectric polymer. Polymer-ceramic composite system combines high dielectric constant ( $\epsilon$ ) and stiffness of ceramics and flexibility, elasticity and high dielectric breakdown of ferroelectric polymers [13].

#### 4. Conclusions

Ferroelectric BaTiO<sub>3</sub>/PVDF nanocomposite films were successfully prepared by mixing BaTiO<sub>3</sub> nano-particles into PVDF solution dissolved in DMF under ultrasonification. Pure PVDF films developed by solvent casting using solvent DMF showed the existence of  $\beta$ -phase and XRD pattern indicated the semi-crystalline nature of PVDF polymer film, although BaTiO<sub>3</sub>/PVDF nanocomposite films showed perovskite structure with a pseudo-cubic phase. The FE-SEM image revealed the uniformity of the BaTiO<sub>3</sub> nanopowder distribution and also predominant 0-3 connectivity. At 50 Hz testing frequency, BaTiO<sub>3</sub>/PVDF nanocomposite films displayed higher relative dielectric permittivity than that of pure PVDF. The dielectric loss of nanocomposites was unchanged in the frequency range of 100 Hz to 1 MHz. The combination of a suitable concentration of PVDF on DMF and the sonification method were found to be critical for uniform dispersion BaTiO<sub>3</sub> nanopowders in PVDF matrix, resulting in good dielectric stability over a wide frequency range.

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