

Frequency-Dependent Dielectric Properties of Polymer-Based BT Nanocomposites with High Energy Density

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ABSTRACT

Nanodielectric materials become one of the key materials to play an important role in sustainable and clean energy production, energy transformation, energy storage, and end usage in terms of energy storage capabilities due to the trade-off between dielectric constant, dielectric loss and voltage breakdown. Based on our recent research on BaTiO₃ (BT) nanoparticles, BT/Parylene and BT/P(VDF-HFP) nanocomposites, frequency dependent dielectric properties of such material systems with high energy density have been investigated as a function of the volume fraction of nanoparticles at room temperature by several theoretical models. For single domain and single crystals of BT a Debye type of dissipation and soft mode theory has been developed to obtain more precise frequency dependent dielectric spectrum of BT. For nanodielectric composites, among the others, Lichtnecker model, Maxwell-Wagner model, Yamada, and modified Kerner model were adopted to evaluate frequency dependent dielectric spectrum of nanocomposites. A simple rule of mixture for the dielectric loss tangent was obtained using Lichtnecker logarithmic rule. The results from theoretical calculations are compared with the experimental data. For dielectric constant, Lichtnecker model, Maxwell-Wagner model and Yamada model show reasonable agreements with the experimental data up to 50% volume fraction of the nanoparticles. For dielectric loss, the simple rule of mixture gives good predictions for a wide frequency range and showed reasonable agreements with experimental data. This theoretical study provides an essential information on dielectric properties of polymer-based BT nanocomposites with a wide frequency range instead of trial-and-error strategy of experiments and can be used for designing high energy density dielectric materials in the future.

Keywords: Nanodielectrics, Dielectric Properties, BT, Nanocomposites, Frequency-Dependent

1 INTRODUCTION

Unique dielectric properties of barium titanate (BaTiO₃) offer increasing broad range of applications in many fields, such as in green energy storage devices, gate dielectrics and frequency modulation in communication devices and also potential new applications at nanoscale [1-3]. A fundamental study and exact interpretation of the intrinsic

dielectric behavior of single domain BT is important for the determination of the limitation in designing dielectric devices, especially those built from nanodielectrics with intended higher dielectric constants, lower loss and reduced equivalent series resistance (ESR) at applied frequency and temperature range. As nanoparticles have a larger surface to volume ratio, unique physical and chemical properties compared to the corresponding bulk material, nanodielectrics contain potential to improve the performance of traditional dielectrics in wide applications ranging from capacitors, dielectric resonators to cable insulators and provide key dielectric components in MEMS and NEMS systems and devices which cannot be achieved by the traditional dielectric materials.

Thin films of BT are good candidates for a wide range of applications: for example, as high-density dynamic random access memories, large-scale integrated capacitors, pyroelectric detectors, and phase shifters [6, 7]. It is a challenge to develop a composite material thin film with compatible high dielectric constant which can be integrated into capacitor technology. Due to the excellent process ability of polymers and high dielectric constant of BT-based ceramic powders, BT-based polymer-matrix composite can be produced as a high-k nanodielectric with high energy density. Several researchers have investigated mostly epoxy/ceramic composites due to the good compatibility with printed writing boards (PWB) [8-14].

Understanding the dielectric properties of ceramic particles is very important for composite material design. Several methods and models, with a number of numerical rules, have been developed to predict the effective dielectric constant of a two-phase composite based on each phase dielectric properties and the volume fraction, i.e., both ceramic and polymer [5, 15,16]. Though several models have been developed, most of them are frequency independent and cannot be used for evaluation of dielectric loss. Subsequently, uncertainty still prevails in which model is more convenient for the prediction of the effective dielectric constant of the composites.

In this work, first, frequency dependent dielectric spectrum of single domain BT at c-axis was obtained based on our recent publication [18]. Then dielectric properties of BT/Parylene layered thin films and BT/P(VDF-HFP) particle reinforced nanocomposites were examined in a wide-range frequency at room temperature. Among the others, Lichtnecker model [5], Maxwell-Wagner model [5], Yamada rule [15] and modified Kerner model [16] were

used to study the frequency dependent nanocomposites dielectric spectrum. A simple mixture rule derived through Lichtnecker model for dielectric loss was used to examine the dielectric loss tangent in terms of frequency and the volume fraction of the nanoparticles. The predicted results are compared with the experimental data [1, 4] and show reasonable agreement between each other.

2 THEORETICAL BACKGROUND

Very few studies have been completed concerning frequency dependent spectrum of single domain BT [14, 17] as well as BT based composites. Liu et al [18] have studied the intrinsic dielectric frequency-dependent spectrum of single domain tetragonal. Both dielectric spectra of *a*- and *c*-axes of BT were obtained. Here we adopted the dielectric properties of the single domain BT [18] and the published dielectric properties of the polymer matrix as our individual phase properties to evaluate the effective dielectric properties of the nanodielectric composite in terms of frequency and the volume fraction of the nanoparticles. The effective permittivity in complex form can be written as, $\epsilon_{eff} = \epsilon' + i\epsilon''$ where the real and imaginary parts are positive means of the dielectric constant and loss, respectively.

Many models have been established to study the effective dielectric behavior of static systems. Here we adopt Lichtnecker model, Yamada model, Maxwell-Wagner model, Wiener mixture rule, modified Kerner model to find frequency dependent BT based nanocomposite dielectric spectrum. The most commonly used model is the Lichtnecker logarithmic law [5] of mixing and is written for a two-phase system such as a polymer/ceramic system as

$$\log \epsilon_{eff} = v_p \log \epsilon_p + v_c \log \epsilon_c \quad (1)$$

where ϵ_{eff} , ϵ_p and ϵ_c are dielectric permittivity of the composite, polymer and ceramic, respectively. And v_p and v_c are the volume fraction of the polymer and ceramic, respectively.

Jayasundere and Smith [16] have also developed a model which was modified from the well-known Kerner model. The modified Kerner equation is shown as follows

$$\epsilon_{eff} = \frac{\epsilon_p v_p + \epsilon_c v_c \left[\frac{3\epsilon_p}{\epsilon_c + 2\epsilon_p} \right] \left[1 + \frac{3v_c(\epsilon_c - \epsilon_p)}{\epsilon_c + 2\epsilon_p} \right]}{v_p + v_c \left[\frac{3\epsilon_p}{\epsilon_c + 2\epsilon_p} \right] \left[1 + \frac{3v_c(\epsilon_c - \epsilon_p)}{\epsilon_c + 2\epsilon_p} \right]} \quad (2)$$

Maxwell and Wagner [5] applied the Maxwell-Garnett mixing rule by consideration of the frequency. Maxwell-Garnett mixing rule can be shown as follows.

$$\epsilon_{eff} = \epsilon_p \frac{2\epsilon_p + \epsilon_c + 2v_c(\epsilon_c - \epsilon_p)}{2\epsilon_p + \epsilon_c - v_c(\epsilon_c - \epsilon_p)} \quad (3)$$

Yamada has proposed a model to predict the dielectric constant for the polymer/ceramic binary system by means

of the properties of its constituents and the shape of the inclusions [15].

$$\epsilon_{eff} = \epsilon_p \left[1 + \frac{\eta v_c (\epsilon_c - \epsilon_p)}{\eta \epsilon_p + (\epsilon_c - \epsilon_p)(1 - v_c)} \right] \quad (4)$$

Where $\eta = 0.2$, morphology factor depending on the shape of ellipsoidal particles on the surface of the film in his model.

According to Wiener [19,20], for any two-phase composites can be treated as parallel or series and these two extremes represent bounds for its effective dielectric function as lower bound

$$\frac{1}{\epsilon_{eff}} = \frac{v_p}{\epsilon_p} + \frac{v_c}{\epsilon_c} \quad (5)$$

and upper bound

$$\epsilon_{eff} = v_p \epsilon_p + v_c \epsilon_c \quad (6)$$

Equations (1) to (6) are, in general, only suitable for frequency independent effective dielectric constant or the real part of the complex dielectric permittivity. The proposed formula for loss tangent can be derived from Lichtnecker logarithmic law. In that law putting the complex dielectric as

$$\epsilon_{eff} = \epsilon'_{eff} + i\epsilon''_{eff}, \epsilon_p = \epsilon'_p + i\epsilon''_p \text{ and } \epsilon_c = \epsilon'_c + i\epsilon''_c \text{ and then, simplified with } \tan \delta_{eff} = \frac{\epsilon''_{eff}}{\epsilon'_{eff}}, \tan \delta_p = \frac{\epsilon''_p}{\epsilon'_p} \text{ and } \tan \delta_c = \frac{\epsilon''_c}{\epsilon'_c}.$$

We found the final form of dielectric loss follows a simple rule of mixture and can be written as

$$\tan \delta_{eff} = v_p \tan \delta_p + v_c \tan \delta_c \quad (7)$$

Where $\tan \delta_{eff}$, $\tan \delta_p$, and $\tan \delta_c$ are loss tangent of composites, polymer and ceramics, respectively

3 RESULTS AND DISCUSSIONS

We first reconstruct the dielectric spectrum of BT single domain using Liu's formula [18]. The obtained clamping dielectric constants of ϵ_c is about 80, which match very well with Kim's data [4], and the frequency response is shown in Figure 1. Different models as described above have been applied to analyze the dielectric properties of BT/P(VDF-HFP) - thin film as a function of frequency and also the volume fraction of nanoparticles and compare with the experimental data [4]. Thin films of the nanocomposites were fabricated by spin-coating dispersions on an aluminum-coated glass substrate as the base electrode.

Figure 2 are the plots of the effective dielectric permittivity calculated using a matrix material of PVDF and BT nanoparticles in terms of the volume fraction of BT. From Fig.2, it is observed that Maxwell and Wagner formula predicted the lowest composite permittivity values up to 50% volume of BT in both frequencies of 100Hz and 10kHz. The experimental dielectric constant of BT/P(VDF-HFP) at 100 Hz and 10 kHz agreed well with the predicted values up to 50% volume fraction of BT. Both Lichtnecker Log Law and Modified Kerner model gave high

permittivity levels for a composite with volume fraction of BT up to 60%. It is also observed that the dielectric constant of nanocomposites is increasing with the volume fraction of BT up to 50% of BT for all models as well as experimental results. Experimentally, there was a depression of the effect for higher volume fraction of BT. This may have occurred due to air trapped voids during the curing of the samples, which would have produced lower permittivity. All models show discrepancy after 70% volume fraction, as it should reach pure BT value when the volume fraction is 1.

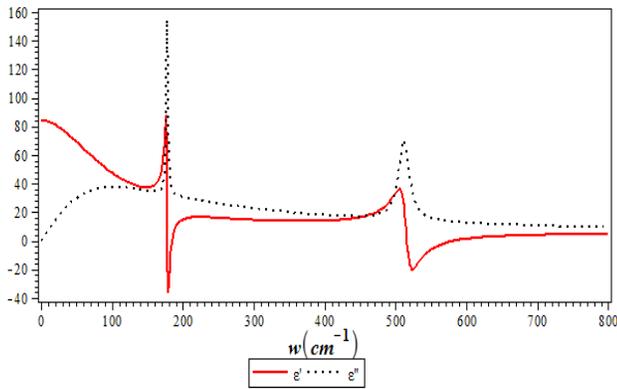


Figure 1. Dielectric frequency response curves at room temperature parallel to the ferroelectric *c*-axis

In the case of BT/Parylene layered composites [1], the permittivity of the BT/Parylene composite has been predicted according to the lower bound of Wiener Mixture Rule which gives the exact solution of the lamina structure. Figure 3 shows the comparison between theoretical models and experimental data [1] for 80% of BT nanoparticles. Since all the models except Wiener mixture rule are for particle-reinforced composites and cannot be used for layered structure, they do not agree with the experimental data. Our research group [1] has fabricated high-*k* BT/Parylene thin films as the gate dielectric on glass and flexible PEN substrates. A thin layer of parylene-C is evaporated in chemical vapor deposition (CVD) system to solve the incongruity between inorganic BT gate dielectric and the organic semiconductor active layer. The real part of the permittivity of pure BT decreases with frequency and also the permittivity of BT/parylene composite slightly decreases with frequency, which agrees well with the lower bound of Wiener Mixture rule [13, 20].

Figure 4 shows the frequency-dependent dielectric constant of BT/P(VDF-HFP) particle-reinforced nanocomposites at 40% volume of BT nanoparticles [4]. The prediction by the Lichtenecker logarithmic law gives best result comparing to the experimental data [4]. For other volume fractions of BaTiO₃ particles up to 50%, the Lichtenecker law also provides the best prediction of the system. Therefore, the Lichtenecker logarithmic law is constructive for predictions of the frequency-dependent

effective dielectric constant of polymer based ceramic particle nanocomposites, although there are limitations that this law can be useful only if the dielectric constant of polymer matrix varies somewhat from the dielectric constant of ceramic particle inclusions [5].

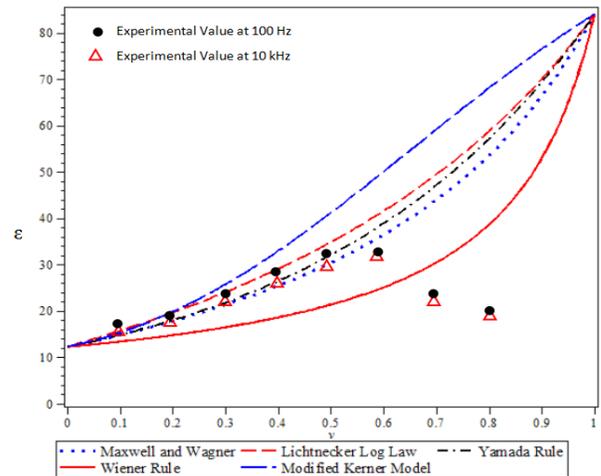


Figure 2: Theoretical predictions and Experimental values of BT/P(VDF-HFP) Nanocomposites in terms of volume fraction of BT

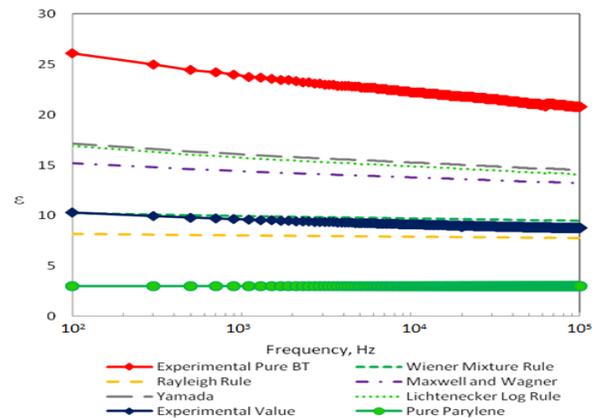


Figure 3: Comparison of experimental and calculated frequency-dependent dielectric permittivity of BT/Parylene layered composite with 80% of BT.

Dielectric loss of BT/P(VDF-HFP) nanocomposites were predicted by the proposed rule derived from Lichtenecker logarithmic law given in equation (7). As shown in Figure 5, the theoretical predictions and the experimental values [4] of the loss tangent of BT/P(VDF-HFP) composites in terms of frequency agree well for the volume fraction from 5% to 20%. The loss tangent of pure nanocomposites increases with frequency and also the difference increases in loss tangent of BT/P(VDF-HFP) composite from 100 kHz to 1 MHz. This sudden increase in loss tangent was dominated by the loss tangent of polymer.

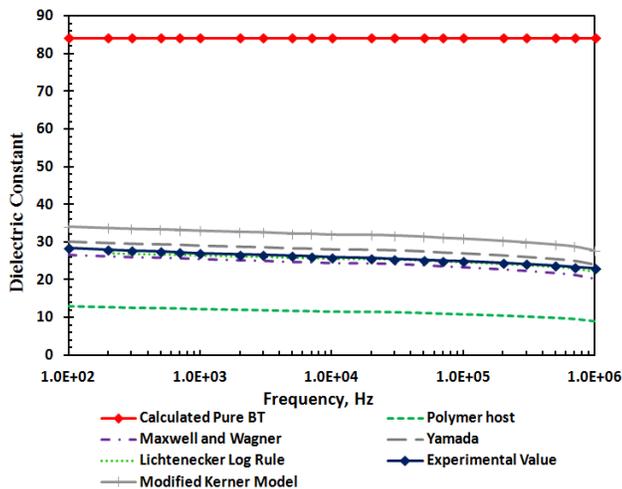


Figure 4: Theoretical predictions and Experimental values of BT/P(VDF-HFP) Nanocomposites in terms of frequency at 40% of BT by volume

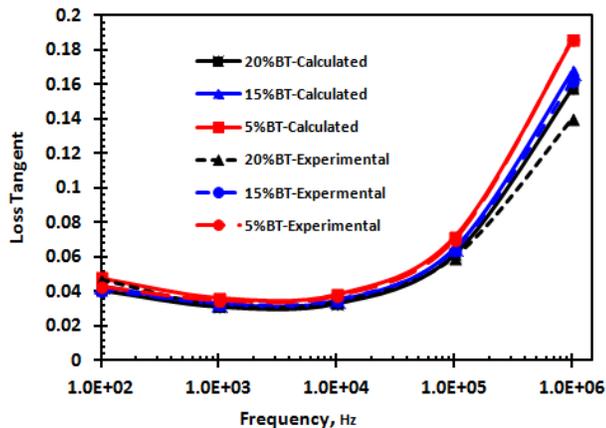


Figure 5: Theoretical predictions and the Experimental values of the loss tangent of BT/P(VDF-HFP) composites in terms of frequency.

4 CONCLUSIONS

Frequency-dependent dielectric spectrum of single domain tetragonal barium titanate (BT) was studied by considering phonon vibrations and a model was established for the frequency range up to the THz regime. Then the dielectric properties of BT/P(VDF-HFP) composites at room temperature were studied in terms of frequency as well as the volume fraction by several theoretical models. It has been found that the predicted results by Lichtenecker logarithmic law agree well with the experimental data for particle reinforced nanocomposites. While the lower bound of Wiener Mixture rule can be adopted to study the frequency-dependent permittivity of BT/parylene layered composite. Dielectric loss of BT/P(VDF-HFP) nanocomposites were investigated by the proposed rule which is similar to the simple rule of mixture. The predicted

results in terms of frequency with a wide volume fraction agreed well with the experimental values. This proposed model provides the essential information on dielectric properties with a wide frequency range instead of trial-and-error strategy of experiments for the future development of energy storage applications.

5 ACKNOWLEDGEMENTS

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