Simulation of the Effects of Nano-filler Interactions in Polymer Matrix Dielectric Nanocomposites

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Abstract: The finite element method was used for simulating the dielectric response of polymer matrix dielectric composites with randomly and evenly distributed fillers. The dielectric simulation of the composite materials was conducted using a time harmonic-electric current solver in the AC/DC module of COMSOL Multiphysics® 5.2. The calculations were performed for a wide range of filler contents and filler permittivities, in order to investigate the influence of these important parameters on the effective permittivity of the dielectric composites. The interaction between the fillers was evaluated using an interaction field that resulted in calculated values that agreed with previous experimental measurements on a series of PVDF/BT composites with and without MWNT additives.

Keywords: COMSOL Multiphysics®, Polymer composite, Finite element method, Dielectrics

1. Introduction

Polymer matrix flexible dielectric composites with high permittivity and low loss can be used as potential materials for gate dielectrics [1], embedded passive components [2], high energy density electrical energy storage [3, 4], piezoelectric generator [5] and electromechanical transducers [6]. Poly (vinylidene fluoride) (PVDF) based polymers have been widely investigated, due to their higher permittivity than other polymers [7-12]. Some high dielectric constant ceramics, such as barium titanate (BT), barium strontium titanate (BST) [9, 11] and calcium copper titanate (CCTO) [13, 14] have been used as fillers. It has also been reported that the dielectric properties of PVDF matrix nanocomposites were improved by optimizing the synergistic effects between the ferroelectric phase and the conductive added phase [11].

There are many theoretical models used to predict the effective dielectric permittivity of dielectric PMCs. However the current existing models do not predict the dielectric properties well enough, due to complexities in the microstructure, composition, and interfaces of the dielectric PMCs [15]. In recent years, the finite element method (FEM) has been extended to nanoscale electrical characterization of materials. However, to the best of our knowledge, numerical simulations have not yet been widely employed in the study of the electrical/dielectric properties of composites. In the literature, the vast majority of impedance and dielectric related work is experimental in nature, and simulation studies are very limited. However, several approaches for impedance simulations have been reported. For example, the roles played by geometric parameters of thin films and electrodes were studied using FEM [16, 17]. The effects of mixed ionic electronic conductors (MIECs) thin film electrodes in solid oxide fuel cell were studied using FEM [18]. FEM was also used to simulate the dielectric response of a composite [19].

In this study, a finite element method (FEM) was used to improve the predictability of the dielectric properties of polymer matrix composites.

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2. Use of COMSOL Multiphysics®

Dielectric polarization and relaxation mechanisms in polymer matrix nanocomposites can be largely affected by the interfaces between the matrix polymer and the filler and interaction between the fillers. Dielectric simulation was conducted in polymer matrix nanocomposites, with respect to filler volume fraction, permittivity and interactions between the fillers. In the case of impedance measurements, the potential/current is time varying and usually harmonic. Impedance measurement setups involve small length scales (orders of mm) and low frequencies (mHz-MHz range). Hence, the electric field wavelength is typically several orders of magnitude larger than the dimensions of the sample that is measured. In such a situation, the quasi-static approximation can be used [20]. The impedance response of dielectric composites was calculated in the frequency

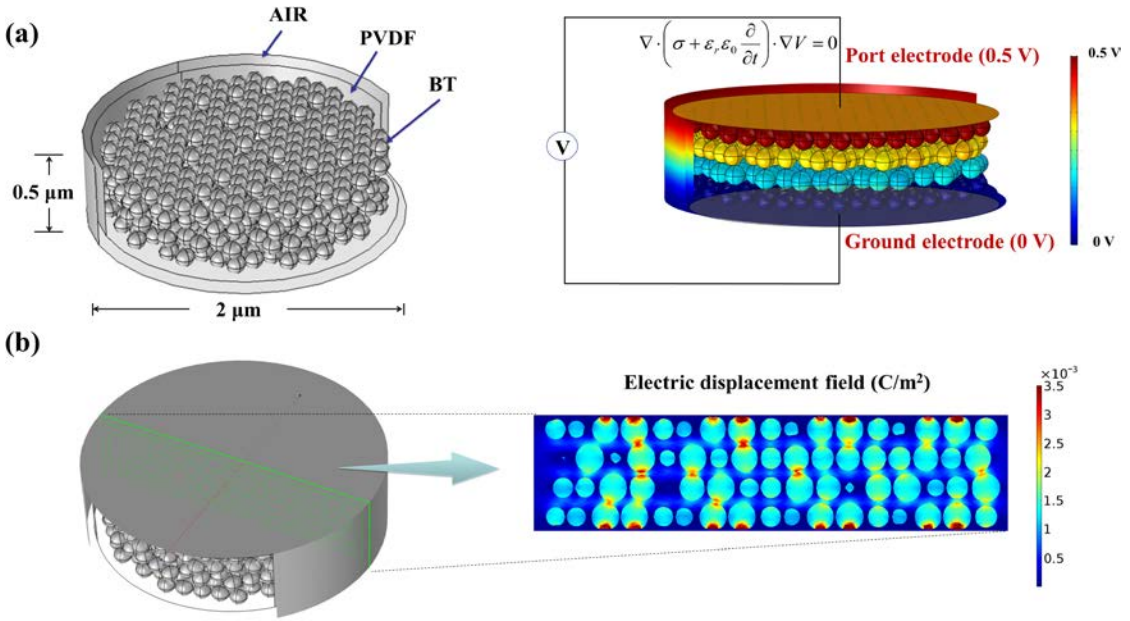

Figure 1. (a) Schematic of the configuration for dielectric simulation and (b) calculated electric displacement field map of a composite containing 47.9 vol % barium titanate (BT) nanoparticles (NPs).

domain using the AC/DC module of COMSOL Multiphysics® version 5.2. Dielectric properties were calculated from obtained impedance data according to the following equations:

$$\varepsilon' = \frac{-Z''}{2\pi f\varepsilon_0[(Z')^2+(Z'')^2]}\cdot\frac{l}{A} \qquad (1)$$

$$\varepsilon'' = \frac{-Z'}{2\pi f\varepsilon_0[(Z')^2+(Z'')^2]}\cdot\frac{l}{A} \qquad (2)$$

where ε_0 is the permittivity of free space (8.854×10^{-12} F/m), Z' and Z'' are the real and imaginary impedances of the dielectric medium respectively, A is the area of electrodes and l is the distance between the electrodes.

The objective was to solve the quasi-static form of Maxwell's equations for the electric potential and electric displacement in the 3D geometry as in equation (3)

$$\nabla\cdot\left(\sigma+\varepsilon_r\varepsilon_0\frac{\partial}{\partial t}\right)\cdot\nabla V=0 \qquad (3)$$

When voltage is applied to the port electrode, the current that flows through it is extracted. The total current flowing from the port electrode to the ground electrode is calculated by integrating the current density. The complex impedance can be calculated from the electric potential distribution. Then the other dielectric functions such as admittance (Y), electric modulus (M), permittivity (ε) can be calculated using the following relationships[21]:

$$Z^* = 1/Y^* = Z' - jZ'' \qquad (4)$$

$$Y^* = Y' + jY'' \qquad (5)$$

$$Y^* = j\omega C^* = j\omega C_g\varepsilon^* \qquad (6)$$

$$\varepsilon^* = 1/M^* = \varepsilon' - j\varepsilon'' \qquad (7)$$

$$M^* = M' + jM'' \qquad (8)$$

where the term j *is* $\sqrt{-1}$ and C_g is geometric capacitance.

Nano-sized fillers with different properties, and volume fractions were used in the simulation

to describe interactions between fillers. Figure 1(a) shows a schematic of the simulation configuration and geometry. Figure 1(b) shows the calculated electric displacement field map for a PVDF polymer matrix composite containing 47.9 vol % barium titanate (BT) nanoparticles (NPs). It can be seen that in order to maintain some physical distance between the fillers, it is not possible to add any more into the simulation space.

3. Results

3.1. Dielectric Responses from Interactions of Fillers

The interaction between fillers is more important at the higher concentration of fillers, because the inter-particle distance decreases as the concentration is increased. Moreover, the induced electrical field from the distribution of dipole moments is no longer negligible when calculating overall field locally experienced in the matrix [15].

Figure 2(a) shows the effects of inter-particle distance of nanoparticles on the electric displacement field. The electric displacement in between 2 adjacent nanoparticles increased by more than 200 % as the inter-particle distance decreased from 60 nm to 10 nm when the BT particle size was 78 nm. A schematic in Fig. 2(b) shows that the interaction zone becomes stronger as the inter-particle distance decreases, in other words, filler concentration increases [15].

The interactions between the ferroelectric filler and the conductive filler were also simulated. Figure 3 displays maps for the electric displacement of nanocomposites containing only BT NPs and BT NPs with MWCNTs. Perfect alignment of the MWCNTs perpendicular to the electric field vector and a repeating geometry was assumed. The electric displacement field between adjacent BT NPs was increased by up to 5 times with the presence of effectively separated

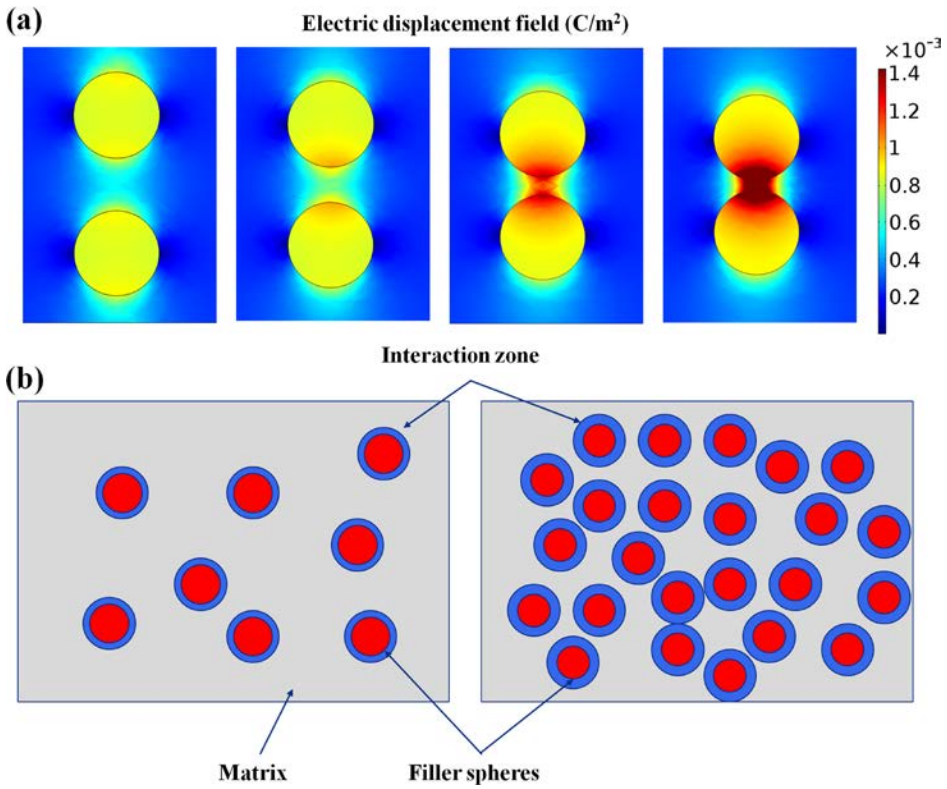

Figure 2. (a) Effects of inter-particle distance in electric displacement field in between BT NPs (60, 40, 20, and 10 nm from the left) and (b) schematic of interaction zone with respect to inter-particle distance; image redrawn from Ref. [15]

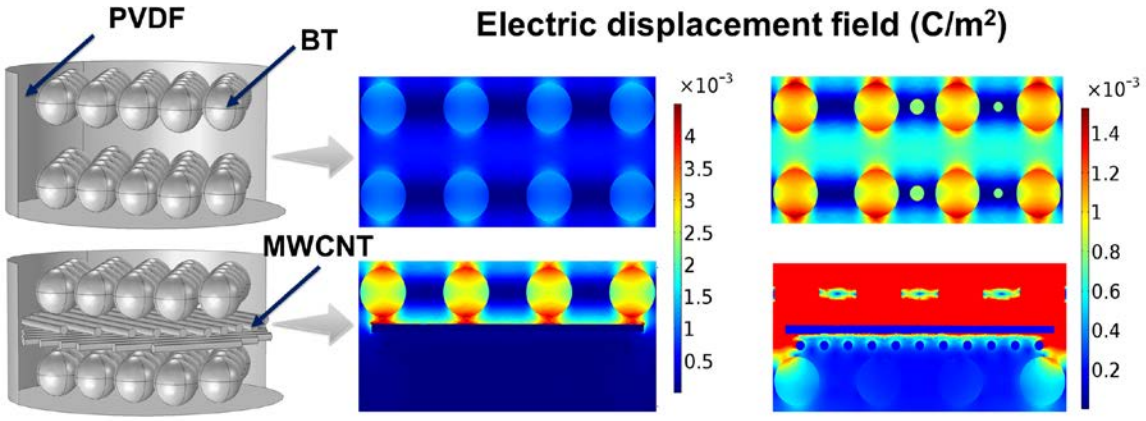

Figure 3. Cross-sectional electric displacements field maps of composites containing 22.8 vol % BT and 0 to 3 vol % MWCNT (shown in 2 different scales).

MWCNTs. These results were compared with real measured dielectric properties and will be described further below[11].

3.2. Dielectric Response as a Function of Concentration of Fillers

Figure 4 shows the experimental and FEA simulated real permittivity of composites as a function of filler content and calculated values using some existing numerical models. When the filler concentration was less than 20 vol %, existing numerical models were able to predict the overall dielectric property well; however, at filler concentration above 20 vol %, many numerical models showed lower values than the experimentally measured real permittivity. The Maxwell-Garnett model, which is based on mean field theory predicted the lowest effective permittivity [22]. Another mean field theory, known as the Bruggeman model can predict more sharply increased effective permittivity for the filler volume fraction above 20 % as was previously reported [23]. Among the existing numerical models, the Jaysundere-Smith (J-S) model showed better prediction of the real permittivity obtained from the PVDF/BT nanocomposites. In the J-S model, an additional electric field was introduced as follows [24]:

$$E_{Interaction} = \frac{3\varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} 2 f_2 E_0 \qquad (9)$$

where ε_1 and ε_2 are the permittivities of the matrix and the filler respectively, f_2 is the fraction of filler, E_0 is the initial electric field. However, it is only applicable to isolated spherical dielectric fillers. A realistic geometry-based simulation was needed to better account for the complexities in the morphology and the arrangement of the fillers as well as varying the compositions of such components.

The FEA model, that included the additional interaction field originally proposed by Jaysundere and Smith [24], helped improve the predictability of the effective permittivity of the composites. There was good agreement between the experimental and the simulation results shown in Figure 4. Note that there was no more physical space in the matrix beyond 47 % of the BT filler to include more fillers, when the distance between the fillers was 10 nm. The geometry based FEA simulations can be used to predict and to analyze dielectric properties of polymer matrix dielectric nanocomposites.

3.3. Dielectric Response as a Function of the Permittivity of the Fillers

The increase in the effective permittivity of PMCs is generally assumed to be due to the relatively high permittivity of the inorganic fillers used compared to the polymer matrix. However, increased permittivity is often accompanied by high dielectric loss. In order to minimize dielectric loss and maximize breakdown strength for a given filler concentration, this can be achieved by: (1) effective dispersion of fillers, (2) minimizing pores, (3) improving the interfaces in the composites as well as (4) developing novel ceramic fillers with colossal permittivity [15].

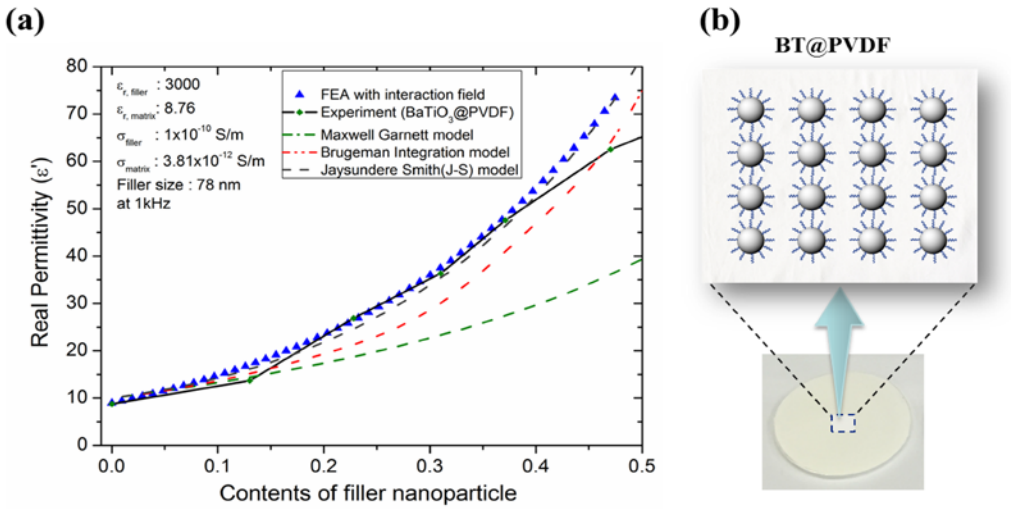

Figure 4. (a) Experimental and FEA simulated real permittivity of composites as a function of BT contents and calculated values by some numerical models and (b) experimental sample.

Some ceramics with colossal permittivity (CP) have been widely investigated as fillers in polymer matrix dielectric composites such as calcium copper titanate (CCTO) [13]. However, there is a limit on how to improve the dielectric properties of composites by simply incorporating fillers with higher intrinsic permittivity into polymer matrices. Figure 5 illustrates the simulated real permittivity of composites at 1kHz as a function of filler permittivity. It is clear that not much is gained by going above permittivity of 1000.

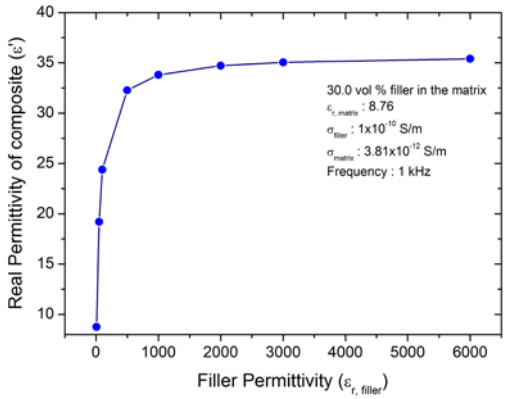

Figure 5. Steady state real permittivity of composites at 1kHz as a function of filler permittivity.

Additionally, Jin et al.[11] recently reported a detailed equivalent circuit model for polymer matrix dielectric composites that takes into account all of the polarization mechanisms present in the composites. It was found that the interfaces play a more important role in determining the dielectric properties of the nanocomposites than the intrinsic permittivity of the fillers used [11].

4. Conclusions

This work highlights the usefulness of utilizing FEM analysis to incorporate the effect of materials microstructure and interfaces for improving the predictability of the dielectric properties of polymer matrix nanocomposites The presented 3D simulation was able to reasonably predict the effective real permittivity of PVDF/BT composites with and without MWNT fillers. There was good agreement between the experimental and the simulation results. This simulation model can be applicable to many different kinds of nanocomposite systems with different fillers, because this model is based on real geometric arrangement of nano-fillers, which is one of the most important factors in improving the effective permittivity of composite materials.

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6. Acknowledgements

Research funding from the National Science Foundation (NSF) under DMR-1207323 is acknowledged and appreciated.