

Dielectric properties and charge storage optimization in poly(vinylidene fluoride) polymer matrix hybrid nanocomposites with BaTiO₃ and multi-walled carbon nanotubes

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ABSTRACT

Polymer matrix hybrid nanocomposites featuring uniformly dispersed barium titanate (BT) nanoparticles and multi-walled carbon nanotubes (MWCNT) in the poly(vinylidene fluoride)(PVDF) were fabricated by miscible-immiscible coagulation method followed by hot pressing. Dielectric properties of the polymer matrix hybrid nanocomposites were improved using a MWCNT content near the electrical percolation with consequent optimum synergistic effects between the charge storage effects of the ferroelectric phase and the charge transport effects of the conductive phase. The real permittivity was 71.7 and the dielectric loss was 0.046 at 1 kHz for composites containing 37.2 vol % of BT and 3 vol % of MWCNT. Due to the simplicity of the processing method, reliable dielectric properties and flexibility, this composite may be useful in many electronic applications such as high energy density capacitors and flexible high-k dielectrics.

Keywords: polymer matrix composites (PMCs), dielectric composite, carbon nanotubes, dielectric properties

1 INTRODUCTION

Flexible dielectric materials have gained special attention due to high permittivity, light weight and good processability. Their many potential applications include gate dielectrics [1], PCB board applications [2], energy storage devices [3, 4] and electromechanical transducers [5].

Many ceramic materials and metals can show high dielectric constant, high stiffness and good thermo-mechanical stability; however, they show poor processability and their brittle nature limits their use in high voltage applications, as well as next-generation microelectronics and high energy density capacitors. In contrast to metals and ceramics, polymer materials can have easy processability, mechanical flexibility, low density and high breakdown strength. However, their intrinsic dielectric permittivity and energy density are low, typically in the range of 2-5 [6] and 1-3 J cm⁻³ [7] respectively. Thus, polymer matrix composites (PMCs) filled with functional nanofillers can be an ideal solution to combine the advantages of inorganic fillers and matrix polymers.

A common approach is to incorporate high-k ceramic fillers into a polymer matrix. Many polymeric materials have been used as a matrix. In particular, PVDF based polymers [8-11] have been investigated due to higher permittivity than other polymers. Some high dielectric constant ceramics, such as barium titanate (BT), barium strontium titanate (BST) [12] and calcium copper titanate (CCTO) [10] have been used as fillers. Uniform distribution of high-k ceramic fillers into the hosting polymers effectively increases dielectric permittivity of the composites. However, a high loading of the ceramic nanoparticles (often over 40-50 vol %) is often required to achieve a permittivity value about 50 in the ceramic/polymer composites. Degradation in the mechanical properties and processability due to such a high filler loading is one of the problems in PMCs made with ceramic fillers. In addition, the non-uniform distribution of fillers or their aggregation into large clusters may decrease the effective surface area of filler particles per unit volume, resulting in a lower dielectric permittivity. It has also been reported that large clusters of fillers can cause leakage current pathways resulting in high dielectric loss [13]. Therefore, how to achieve a high permittivity with low loss and high flexibility obviously by effective dispersion of nanofillers is the key problem in flexible dielectric materials.

Another approach is to incorporate conductive 0D/1D/2D fillers in the polymer matrix. Based on percolation theory, the effective permittivity of a dielectric composite containing MWCNT can be expressed as

$$\epsilon_{\text{eff}} = \epsilon_m (f_c - f_{\text{MWCNT}})^{-s} \quad (1)$$

where ϵ_m is the dielectric constant of the polymer matrix, f_c is the percolation threshold of the composites, f_{MWCNT} is the volume fraction of MWCNT component and s is a critical exponent, which has a universal value in the range of 0.8-1.0 [14]. The percolation threshold of MWCNT/polymer composite was reported to be around 0.015 for randomly distributed MWCNT [15], and even lower than 0.006 for phase segregated dispersion of MWCNT in the polymer matrix [16]. The effective permittivity experiences sharp increase when the MWCNT concentration reaches the percolation threshold, however, 3D percolation networks make the composite a conductor instead of a capacitor

when the filler concentration exceeds this critical value. And even before the percolation threshold is reached, dielectric loss abruptly increases near the percolation threshold due to high leakage current from aggregated CNT bundles and phase inhomogeneity between the matrix and the fillers. Therefore, the dielectric properties have to be tuned within so-called “adjustable windows” near the percolation threshold, where the real permittivity of the composites can be maximized while the dielectric loss is suppressed [15]. However, it is not easy to control the dielectric properties in this window, because conductive phases provide very narrow adjustable windows. To overcome this problem and find practical applications of CNT based dielectric nanocomposites, homogeneous, uniform dispersion of MWCNT without aggregated bundles is crucial. A lot of recent works have been reported including advanced fabrications of core-shell structure [17], surface modification of CNT [18] and inclusion of other functional fillers in the composites [19].

In this article, we demonstrate a simple and effective fabrication method to disperse BT and MWCNT together in the PVDF matrix. The effective dispersion of fillers can be achieved by quick phase separation using miscible-immiscible coagulation [20]. Free standing thin composites can be obtained with easy controllability of the final thickness. A synergetic increase of the dielectric permittivity of the composite with very low loss is achieved.

2 EXPERIMENTAL DETAILS

2.1 Fabrication of Polymer Matrix Hybrid Nanocomposites

BT was obtained from Sigma-Aldrich. The particle size was 77.8 ± 5.9 nm. PVDF and 3-(Methacryloyloxy) propyltrimethoxysilane (MPS) were obtained from Alfa Aesar. MWCNT was obtained from cheaptubes.com with the following specifications: 0.5–2.0 μm in length, 8–15 nm in diameter, > 95 wt % purity with <1.5 wt % ash. PVDF was dissolved in DMF by ultrasonication and the solid to solvent weight ratio was 1:10. Different amounts of BT were added on the basis of the desired concentration of BT in the final composites. Homogeneous dispersion of nanoparticles can be achieved by ultrasonication and speed mixing (DAC 150 Speed Mixer) for 10 min. MWCNT was added to the mixture and dispersed in the ultrasonicator and speed mixer for another 20 min. Prior to blending, the surfaces of BT nanoparticles and MWCNT were modified by 0.5 wt % silane coupling agent (MPS) in 1:99(v/v) acetone/H₂O mixture to improve the interfaces between the matrix and the fillers and to prevent sub-microscopic agglomeration of nanofillers. The surface modified fillers were rinsed repeatedly to remove un-reacted MPS.

It is not uncommon for the nanofillers to re-aggregate during the processing; especially carbon based 1D material [2,15,19]. To minimize re-aggregation of the filler, quick

phase separation based on miscible and immiscible coagulation method was used. First, a thin layer of composite suspension was dispersed on the glass substrate. Second, a thin DI water layer was applied in between the composite and the glass substrate. PVDF was extracted from the composite immediately, preventing re-aggregation of nanofillers. Free standing thin films were dried on a hot plate at 80 °C for 10 min. For void-free dense composite samples, dried composites were stacked and hot pressed at 175°C for 20 min. The thickness of samples was controlled as 100 μm for microstructural and dielectric analysis and 10 μm for high voltage breakdown strength tests.

2.2 Microstructural and Dielectric characterization

A Hitachi (Dallas, TX) SU8230 cold field emission scanning electron microscope (SEM) was used for microstructural characterization. A Solartron 1260 impedance analyzer was used together with a Solartron 1296 Dielectric Interface (Farnborough, Hampshire, U.K.) for the dielectric characterization of the nanocomposites. Prior to impedance measurements, a Denton Vacuum Desk II Turbo Sputter Coater (Denton Vacuum, Moorestown, NJ) was used to coat the samples with Ag (nominal purity of 99.9%) for contact electrodes. A RK2674 high voltage supplier was used for breakdown strength measurements.

3 RESULTS AND DISCUSSION

3.1 Microstructural Analysis

Figure 1 contains SEM images of fractured cross-sections of BT/MWCNT/PVDF hybrid nanocomposites. BT nanoparticles were uniformly dispersed in the matrix. There was no evidence of macroscopic filler clustering. The immediate phase separation prevented macro clustering of the nanofillers. Surface modification of the fillers helped to prevent sub-microscopic filler agglomeration and improve the interfaces between the matrix and fillers. The composite thin films were highly flexible after hot pressing, even those with the highest concentration of fillers. The uniformly dispersed nanofillers showed excellent dielectric properties because of their enhanced interfaces with the matrix. However, the presence of MWCNT is not clearly detected in these images, due to the small fraction of MWCNT used.

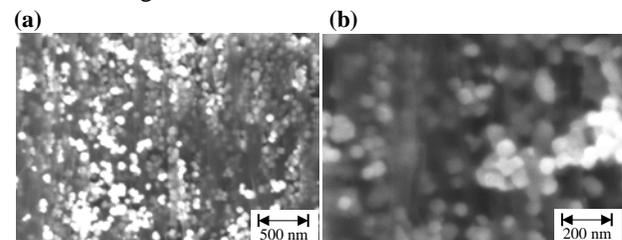


Figure 1: SEM images of polymer matrix hybrid nanocomposite with 37.2 vol % BT and 3 vol % MWCNT.

3.2 Dielectric Properties

Impedance measurements were conducted to systematically investigate dielectric properties of the nanocomposites. The real and imaginary permittivity values were calculated from the measured impedance data according to the following equations:

$$\epsilon' = \frac{-Z''}{2\pi f \epsilon_0 [(Z')^2 + (Z'')^2]} \cdot \frac{l}{A} \quad (2)$$

$$\epsilon'' = \frac{-Z'}{2\pi f \epsilon_0 [(Z')^2 + (Z'')^2]} \cdot \frac{l}{A} \quad (3)$$

Figure 2(a) and (b) show frequency dependent real permittivity and dielectric loss of polymer matrix hybrid nanocomposites respectively. The real permittivity of the nanocomposite containing 37.2 vol % BT was 47.5, which is 5.4 times higher than that of pure PVDF. The dielectric loss was as low as 0.050 due to uniformly dispersed BT nanoparticles in the matrix. Because BT has much larger dielectric constant than PVDF, the effective permittivity of the composites comes from the average increase of the electric field in the matrix.

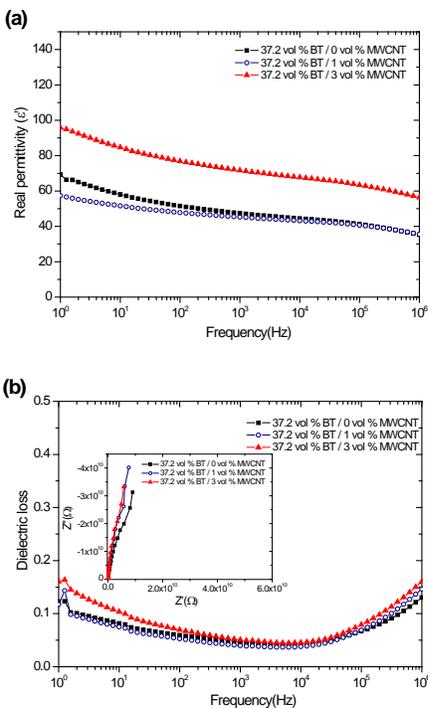


Figure 2: (a) Real permittivity, (b) dielectric loss of polymer matrix hybrid nanocomposites. Inset shows impedance complex plots.

The capacitance of a parallel plate capacitor configuration can be expressed as,

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad (4)$$

where ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity of the dielectric medium, A is the area of the electrodes and d is the distance between electrodes. According to the capacitor model, which in this case are formed by dispersed filler nanoparticles, the dielectric permittivity of the composites can be improved by the presence of many BT nanocapacitors. Permittivity of the composites is further increased either by increasing the relative permittivity of the matrix region in between the BT nanoparticles or decreasing the distance between the BT nanoparticles [21]. The former can be achieved by adding a third phase, especially conductive 0D/1D/2D materials and the later can be achieved by increasing the BT content if the fillers are uniformly dispersed. The real permittivity of the hybrid nanocomposites containing 37.2 vol % BT and 3 vol % MWCNT was 72.4, which is 8.3 times higher than that of pure PVDF and more than 50 % higher than that of composites with 37.2 vol % BT alone. The dielectric loss was 0.042, which was even lower than composites without MWCNT. This illustrates that homogeneous dispersion of each phase was achieved in the hybrid composites. Impedance complex plots (0.1 Hz – 10 MHz) of hybrid composites containing 37.2 vol % BT with 0 to 3 vol % of MWCNT are shown in the inset of Figure 2(b). It is obvious that all samples are highly insulating and that MWCNT did not form electrical percolation paths. BT nanoparticles were effectively dispersed first, then each BT nanoparticle works as an insulating barrier in between the adjacent MWCNT without adversely affecting the conductive nature of MWCNT, even near the percolation threshold. The electrical charges coming from the external current collectors will be migrating and accumulating near the interfaces or interaction zones of the different phases, due to charge storage effects of the ferroelectric phase and the charge transport effects of the conductive phase and the different relaxation time of each phase [15].

The dielectric properties of hybrid nanocomposites as a function of MWCNT content at 1kHz are shown in figure 3. There was substantial increase in the real permittivity with respect to MWCNT. The real permittivity of composites containing 22.8 vol % BT increased from 26.9 for 0 % MWCNT to 78.4 for 5 vol% MWCNT. However, composites containing 5 vol % MWCNT also showed high dielectric loss up to 0.2. The inset in figure 3(b) shows the complex impedance plot of the composite with 5 vol % MWCNT. Unlike the other samples, it shows a semi-circle, which represents the formation of percolation networks that lead to an electrical conductivity of $1.72 \times 10^{10} \text{ Sm}^{-1}$. It is common that dielectric composites containing conductive fillers show narrow adjustable windows near the percolation threshold. The dielectric properties can be tuned up in this window, until the conductive fillers form percolation networks. In this case, the window is in between 3-5 vol % of MWCNT with 22.8 vol % BT. Uniformly dispersed BT nanoparticles not only increase the average field in the surrounding matrix but also help to disperse MWCNT. The fast phase separation used to make

the composites prevented re-aggregation of the MWCNT, which is a common phenomenon in CNT containing composites [2]. Thus, the dielectric loss of the hybrid composites can still be very low (<0.05) in the vicinity of the percolation threshold, which illustrates the effective dispersion of the nanotubes until they physically percolate. Nanocomposites containing 37.1 vol % of BT showed shifted adjustable windows toward lower MWCNT concentration. The real permittivity was 72.4 with 3 vol % of MWCNT and it sharply increased with further increase of MWCNT, resulting in high dielectric loss. However, dielectric loss was still very low (< 0.05) in the adjustable window. Interestingly, the dielectric permittivity decreased with increasing MWCNT contents in the adjustable window below the percolation threshold, when BT concentration was 47.0 vol %. Although, MWCNT didn't form percolation networks in this case, the average field in the matrix was adversely affected by the high BT concentration. This can be explained by local bundling of MWCNT and neutralization of the relaxation time difference between the phases due to physical contacts between the BT and MWCNT.

The breakdown strength of the hybrid composites was in the range of 200-250 V/ μm depending on the concentration of BT and MWCNT used (not shown in this article).

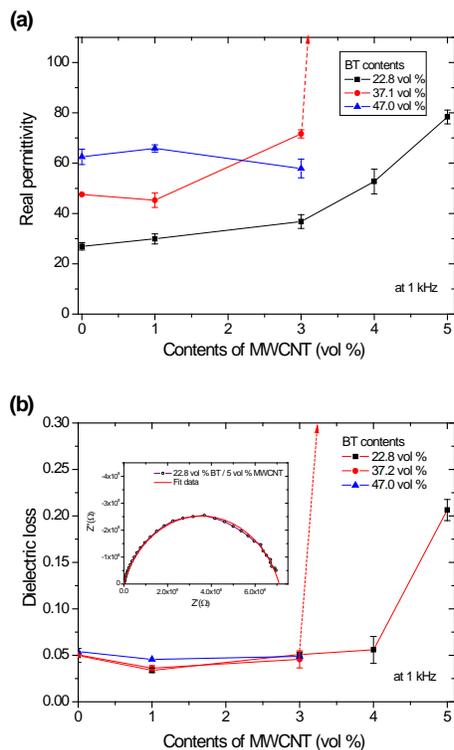


Figure 3: Steady state dielectric properties of polymer matrix hybrid nanocomposites at 1 kHz (a) real permittivity (b) dielectric loss. Inset shows complex impedance plot for the composite containing 22.8 vol % BT and 5 vol % MWCNT.

4 CONCLUSIONS

We demonstrated a simple fabrication method to disperse multiphase hybrid fillers in the PVDF polymer matrix. The uniformly dispersed BT and MWCNT fillers have shown synergetic effects on the dielectric permittivity. The maximum value achieved was above 70 with very low loss (<0.05). Easy processability and flexibility as well as excellent dielectric behavior make BT/MWCNT/PVDF hybrid nanocomposites attractive as potential candidates for embedded devices and high charge storage applications.

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