Enhanced Dielectric Properties of Thick PVDF Composite Films with Small Loading of Barium Titanate

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Abstract. Polymer-based composites with high dielectric performance and superior discharge energy capability are highly desirable for advanced electrostatic capacitor applications. Herein, polymer-ceramic thick composite films with high dielectric permittivity were successfully fabricated by blending poly (vinylidene fluoride) (PVDF) polymer and barium titanate (BaTiO\textsubscript{3}/BT) particles (5 wt% and 10 wt% loading) using tape-casting. Structural and dielectric properties of the PVDF-BT nanocomposite films at room temperature have been investigated. X-ray diffraction studies indicate the evolution of the $\beta$-phase of PVDF in the nanocomposite films. Scanning electron micrographs show the homogeneous dispersion of BT nanoparticles within the PVDF polymer matrix with small agglomeration in some confined areas. With the increasing weight fraction of BT, the dielectric permittivity increases while the tangent loss decreases. At 1 kHz, the dielectric permittivity and tangent loss values for nanocomposite with 10 wt% loading of BT nanoparticles are ~21 and ~0.05, respectively. Also, the value of the dielectric constant remained approximately constant in the frequency range of 1 kHz to 100 kHz.

Keywords: PVDF-BT composite films, dielectric study.

INTRODUCTION

The high energy density capacitors are used as embedded electronic components in weapons, sensors, lasers, etc. [1]. Usually, the capacitor based on ferroelectric ceramics such as PbZrTiO\textsubscript{3}, PbTiO\textsubscript{3}, BaTiO\textsubscript{3}, etc. possesses high dielectric constant [2]. However, the dielectric strength of these ceramics is low due to their brittle nature. On the other hand, polymers such as poly (vinylidene fluoride) (PVDF), PVDF-TrFE, PVDF-HFP, etc. are flexible, easy to process and have high dielectric strength and low dielectric constant (i.e. $<$ 10) [3]. The high dielectric constant of ceramic materials can be combined with high breakdown strength of polymer by appending the ceramic material into a 3-dimensional continuous polymer matrix, leading to the formation of polymer-ceramic nanocomposites. The incorporation of barium titanate (BT) fillers has been extensively studied for a variety of polymeric matrices including poly (vinylidene fluoride) (PVDF) [4], polymethylmethacrylate (PMMA) [5], and polyimides [7], as it is one of the most commonly used high dielectric constant materials. Kobayashi et al. [4] incorporated 30 vol% BT nanoparticles in the PVDF matrix to get a dielectric constant of 32 and a low dielectric loss of 0.05. Abe et al. [5] synthesized polyimide-BT nanocomposite films with 59 vol% loading of the BT powder. It was observed that the dielectric constant of the synthesized film was 37 with a refractive index of 1.85. Nagao et al. [6] synthesized PMMA-BT nanocomposites having 53 vol% BT nanoparticles modified using silane coupling agent (KH550) as the surface modifier. The nanocomposite showed a dielectric constant of 0.05 with a low refractive index of 1.85. It was also found that polyvinylpyrrolidone (PVP) linker layer acts as an adhesive in the multilayered BaTiO\textsubscript{3} nanofiber/PVDF nanocomposites, resulting in homogeneous surfaces, which further leads in the enhancement of the dielectric properties of the synthesized nanocomposites [7].

The present work reports the enhancement in the structural and dielectric properties of tape-cast thick PVDF composite films with 5 wt% and 10 wt% loading of the barium titanate powder at room temperature. By using this technique, nanocomposites can be tuned and modified to perform better in terms of dielectric behavior.

METHODOLOGY

BaTiO\textsubscript{3} powder was prepared by hydrothermal method [1]. Titanium chloride (TiCl\textsubscript{3}), barium chloride dihydrate (BaCl\textsubscript{2}·2H\textsubscript{2}O) and sodium hydroxide (NaOH) were used as precursors. These precursors were dissolved in DI water according to stoichiometric ratio and mixed under vigorous stirring till the solution became clear. To this mixture, NaOH solution was added drop wise to get white precipitates which were then transferred to a Teflon lined autoclave. The autoclave was put in an oven at 180 °C for 16 hrs. and later allowed to cool at room temperature. The obtained powder was washed 6 times with DI water and dried at 80 °C in a vacuum oven. After drying, the sample was calcined at 800 °C for 12 hrs. to get BT nanoparticles.

PVDF-BaTiO\textsubscript{3} thick composite films (~100 μm) were synthesized using the tape casting method. For this, the poly (vinylidene fluoride) (PVDF) powder was dissolved in dimethylformamide (DMF) at 60°C under mechanical stirring, and different wt% (5% and 10%) BaTiO\textsubscript{3} powder was added to the PVDF solution followed by sonication for 2 hrs. The crystal structure and phase identification of samples were carried out by the X-ray diffraction (XRD) technique (PANalytical XPert Pro MPD).
dieractometer). Scanning electron microscopy was used to analyze the surface of the composite films and BT powder. The dielectric response was measured by Wayne Kerr 6500B Precision Impedance Analyzer in the frequency range from 100 Hz to 1 MHz at room temperature by making silver electrodes of 5mm diameter on both sides of the composites.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) pattern of barium titanate (BaTiO$_3$/BT) powder prepared by hydrothermal method and PVDF-BT nanocomposites prepared by tape casting method, respectively. The peaks present at 22.11°, 31.51°, 38.84°, 45.18°, 50.87°, 56.14° and 65.83° confirm that the powder formed is BaTiO$_3$, which matches the ICDD card no. 01-075-0461 [8,9]. It can also be observed from the XRD pattern that the peaks of both BaTiO$_3$ and PVDF are present distinctly in the thick composite films, which confirms the complete incorporation of BaTiO$_3$ in the PVDF matrix. The increase in the relative intensity of the β phase (polar in nature) [10] peak observed at 20.1° indicates that with increasing wt% loading of the BT powder, the β phase fraction increases in the PVDF-BT composites [10]. The peak at 31.52°, along with the other peaks, shifts toward the lower angle side, which can be due to the effect of tension (strain) in BaTiO$_3$ grains when embedded in the PVDF matrix [11].

![XRD pattern of barium titanate powder and PVDF-BT thick composite films.](image)

The scanning electron micrographs (SEM) of the BaTiO$_3$ powder and PVDF-BT thick composite films are shown in Fig. 2. As observed from the SEM images, it is seen that there is an aggregation of particles in the powder sample. Also, some particles have faceted geometry which can be due to some localized inhomogeneity present during the reaction time. This leads to a distortion in the spherical morphology of the particles [12]. The lognormal distribution of particle size gives an average particle size of 275 nm (0.275μm) for the obtained BT powder. The composite films with 5 wt% and 10 wt% of BT powder have uniformly distributed BT particles in the PVDF matrix (as seen in Fig. 2 (c) and 2 (d)). The image for PVDF-10BT specifies that BT particles are well distributed in the PVDF matrix with little agglomeration in some confined areas. So, it can also be deduced here that the extent of agglomeration increases with an increase in BT content in the films.
Figure 2. SEM images of (a) BT powder, (b) particle size distribution curve, (c) PVDF-5BT thick composite film and (d) PVDF-10BT thick composite film.

Figure 3 shows the Fourier transform infrared (FTIR) spectra of the PVDF-BT thick composite films. The signature peak of the $\beta$-phase is detected at 526 cm$^{-1}$, which is associated with CF$_2$ bending mode [13]. Due to CF$_2$ rocking and CH$_2$ bending vibrations, peaks are witnessed at 695 cm$^{-1}$ and 912 cm$^{-1}$, respectively [14]. Because of the collaboration of PVDF with metal oxide (Ti–O), a peak of $\beta$-phase is also observed at 620 cm$^{-1}$ [13]. The peak at 794 cm$^{-1}$ corresponds to the rocking or skeletal bending of CF–CH–CF [10].

Figure 4 shows the variation of dielectric constant and tangent loss of the PVDF-BT thick composite films with frequency. It can be seen from Fig. 4 (a) that the dielectric constant increased with increasing wt% of BT powder in the PVDF matrix for both the composites. The dielectric constant value for the PVDF-5BT and PVDF-10BT composites at 1 kHz are ~12 and ~21, respectively. The value of the dielectric constant is maximum in the low-frequency region (100 Hz-1 kHz) and decreases with increasing frequency (>100 kHz) with a stable trend in the moderate frequency region (1 kHz-100 kHz). A significant decrease in the dielectric constant is observed after 1kHz due to the dipole relaxation processes, which include dipole orientation relaxation.
polarization and interface polarization caused by the composites inner structure [15]. Since the space charge polarization does contribute to the dielectric constant at high frequencies, so, due to this, the dielectric constant has low values in the higher frequency region [16].

**Figure 4.** Variation of (a) dielectric constant and (b) tangent loss for PVDF-BT thick composite films.

Figure 4 (b) shows that the tangent loss (\(\tan \delta\)) also follows the same trend as the dielectric constant in the lower and moderate frequency regions at room temperature. The \(\tan \delta\) for PVDF-5BT and PVDF-10BT at 1 kHz is \(\sim 0.08\) and \(0.05\), respectively. The tangent loss for both the PVDF-BT composite films is maximum in the lower frequency region (due to Maxwell-Wagner effect), with a decrease up to 100 kHz, and after 100 kHz, it again increases. This can be due to the reversible confirmation rearrangement in the crystals, molecular motions in chain folds of crystalline lamellae, and defects in the crystalline phase of the PVDF. The peak in \(\tan \delta\) near 1 MHz can be due to the glass transition relaxations found in the PVDF matrix at higher frequencies [13].

**CONCLUSION**

PVDF-BT thick composite films with 5 & 10 wt% loading of BT in the PVDF matrix have been fabricated using the tape casting method. The XRD studies reveal that the \(\beta\) phase fraction increases with an increase in the BT wt%, which further leads to the enhancement in the dielectric properties of the thick composite films. SEM studies reveal that the average particle size of synthesized BT powder is 275 nm, and with an increase in the wt% of BT, agglomeration of the BT powder in the thin films increases. The dielectric studies show that there is an increase in the dielectric constant of the PVDF-BT composites with increasing BT filler content. Also, the values of dielectric constant and tangent loss follow the same trend in the low frequency (100 Hz-1 kHz) and moderate frequency (1 kHz-100 kHz) region. The dielectric constant and tangent loss values at 1 kHz for the thick composite films are \(\sim 12\) & \(\sim 21\) and \(\sim 0.05\) & \(0.08\), respectively. The dielectric loss follows the Maxwell-Wagner effect leading to higher loss in the low frequency region.

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