Correlation of enhancement of $\beta$-phase with improved dielectric properties of ferroelectric ceramic polymer composites

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Introduction

- Ferroelectric poly (vinylidene fluoride), (PVDF) ([CH$_2$CF$_2$])$_n$, a semicrystalline polymer crystallizes in to five types of phases, viz. α, β, γ, η and ε.
- The α phase did not possess piezo- and pyroelectric properties and hence not ferroelectric as well. The electro-active β phase is highly preferable due to their highest dipolar moment per unit cell as compared to rest of the phases. This makes the material with high permittivity, large piezoelectric coefficients and better ferroelectric properties.
- PVDF and its copolymers have been mostly utilized in electronic industries owing to their relatively high dielectric permittivity as compared to other polymer matrix.
- Improvement of electroactive β-phase of PVDF can be achieved by various methods: (i) application of high DC field (poling), (ii) electrospinning (synthesis), (iii) stretching the α-phase of PVDF film (strain) and (iv) addition of different fillers like metal nanoparticles, different inorganic ceramic oxides, clays, carbon nanotubes, salts, organic molecules.
- The motivation behind the choosing of particular composition 0.94 (Na$_x$Bi$_{0.5}$TiO$_{3-x}$)·0.06(BiOCl)$_x$ (BNBT) as ceramic filler is that, the morphotropic phase boundary (MPB) between NBT-BT solid solutions which shows highest dielectric constant.

Sample Preparation

- Magnetic stirring (Overnight)
- Ultra sonication (1hr)
- Solution Casting
- Dried at 60°C
- Filler modified PVDF film

Characterisation Technique

- Structural and Vibrational: XRD, Raman, FTIR
- Microstructural: FESEM
- Dielectric and Ferroelectric properties: Impedance analysis (IM3570) and Broadband Ferroelectric Loop Tracer

Results & Discussions

A close look on the XRD pattern shows that with increase in the filler concentration the intensity of the β-phase (located at 20.2°) increases initially up to 35 wt. % of filler and after that it decreases.

With increase in filler wt.%, Spherulite size increases and maximum spherulite observed for 35 wt. % of filler.

Using Lambert-Beer law $F(\phi)$% is Calculated from 0-50 wt.%. With increase in filler concentrations $F(\phi)$% enhanced and peaked for 35 wt. % of the ceramic filler.

The dielectric constant changes with filler concentration is explained using percolation theory. The equation is $\varepsilon_r = \varepsilon_{r0} f_0 (1 - f_0)^{-\gamma}$, for $f_{\text{sat}} > f_c$

The fitting parameter is found to be $f_c = 0.336$, and $q = 0.311$. At this critical volume concentration $f_c = 0.336$, the dielectric constant abruptly increases.

Conclusions

- Solution-casting technique was successfully used for the synthesis of polymer-ferroelectric composite film.
- Structural and morphological characterization of the free-standing film confirms composite nature of the same.
- UV-VIS absorption and vibrational spectra indicated the interaction between the polymer and filler at the molecular level. This confirmed the ion-dipole interaction between ferroelectric ceramic and polymer and explained the enhancement of β-phase.
- The dielectric and ferroelectric properties were maximum for the fractional filling (35 wt.%) of ferroelectric ceramic which is due to the enhancement of β-phase. The changes in the dielectric properties with filler concentrations have also been explained using percolation theory.

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Publications