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Applications of Pvdf/Batio3 Composites & Polymer Films as Separator for Supercapacitors

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Abstract:

This section provides a summary of the work presented in the research through chapters three to six. The behaviour of multiphase PVDF in (1-x)PVDF/(x)$BaTiO_3$ nanocomposite films is discussed via structural, morphological, dielectric and ferroelectric properties. The dielectric properties are investigated over the wide range of frequency (20 Hz–2 MHz) and temperature (80–425 K). To study the effect of swift heavy ion irradiation of the structural, morphological, dielectric and ferroelectric properties of PVDF and (1-x)PVDF/(x)$BaTiO_3$ nanocomposites, the samples are irradiated with 80 MeV O^{6+} ion and 40 MeV Li^{3+} ion beams. The irradiation-induced modifications in the samples are discussed in detail. Further, the 80 MeV O^{6+} ions and 40 MeV Li^{3+} ions irradiated PVDF and (0.8)PVDF/(0.2)$BaTiO_3$ nanocomposite films of thickness 0.06 mm are proposed as a separator for supercapacitor applications. The piezoelectric behaviour of the flexible polarized separator films is analyzed for different deformations.

Keywords: Application, Polymer films, Separator

Introduction: Barium Titanate ($BaTiO_3$) belongs to perovskite group of materials having the general formula of ABO_3 with atomic parameters being as, 2-valent cation (A), (0,0,0); 4-valent cation (B), (½, ½, ½); oxygen (O) atoms, (0, ½ , ½), (½ , 0, ½), (½ , ½ , 0). Depending on the temperature, $BaTiO_3$ exists in four different phases, cubic, tetragonal, orthorhombic and rhombohedral (Figure 1.4) [39]. The tetragonal phase of $BaTiO_3$ is ferroelectric and results in a high dielectric constant [40]. The tetragonal crystallographic geometry of $BaTiO_3$ is ferroelectric between 0 °C to $T_C \approx 120$ °C (Curie temperature) and shows spontaneous polarization due to the displacement of the Ti^{4+} and Ba^{2+} relative to the O^{2-} ion (Figure 1.5), which further leads the formation of electric dipoles. Above T_C, $BaTiO_3$ shows paraelectric cubic geometry. Below 0 °C, the symmetry of barium titanate becomes orthorhombic, and below −90 °C, it becomes rhombohedral [41]. $BaTiO_3$ nanoparticles can be synthesized via the hydrothermal method, co-precipitation method, sol-gel processing, flame assisted spray pyrolysis, and electrochemical route [42–46].

APPLICATIONS OF PVDF/BaTiO3 COMPOSITES

PVDF/$BaTiO_3$ composite materials have been used in several important applications (figure 1.7) in different fields [75–79]. The remarkably high piezoelectric, pyroelectric coefficients, and high dielectric susceptibility etc. make PVDF/$BaTiO_3$ composites very promising for many applications such as pyroelectric thermal imaging, biochips, photoreceptor, capacitors, EMI shielding, gate insulators in transistors, pressure sensors, filters, memory elements, bone scaffolds, nanogenerators, etc. [80]. Some reported applications of PVDF/$BaTiO_3$ composites are discussed below.

DIELECTRICS IN EMBEDDED MICROCAPACITORS

The enhanced dielectric properties of PVDF/$BaTiO_3$ composites, as compared to the polymer PVDF, greatly depend on the concentration and dispersion of the ceramic filler in the PVDF matrix. The content and homogeneous dispersion of $BaTiO_3$ offers the application of the composite as a dielectric material in embedded micro capacitors [81].

TRANSDUCERS

Due to the piezoelectric nature of the composite, the flexible PVDF/$BaTiO_3$ composite produces large electricity on stretching and bending. Also, depending on the requirement, its

size and shape can be tailored easily. Thus, this composite can be used as transducers for vibrational energy harvesters [82].

PRESSURE SENSORS

The $BaTiO_3$ filler has excellent dipole moment, high dielectric constant, very high electromechanical coefficient. When $BaTiO_3$ is incorporated in PVDF, the ferroelectric β – phase content of PVDF also increases, which overall enhances the piezoelectric property of the composite. This facilitates the fabrication of low-cost piezoelectric devices for sensor applications [83].

ELECTROMAGNETIC INTERFERENCE (EMI) SHIELDING

The electrical conductivity is a significant characteristic that affects the shielding effectiveness as well as the shielding mechanism of a material. With the incorporation of the $BaTiO_3$ in the PVDF matrix, both the dielectric constant and the conductivity of the composite material increase. Pure PVDF has shielding effectiveness of about 0.3 dB, whereas, the shielding effectiveness of PVDF/micro-sized $BaTiO_3$ and PVDF/nano-sized $BaTiO_3$ is found to be 7 and 9 dB, respectively [84].

BIOCOMPATIBLE BONE SCAFFOLDS

The β -phase of PVDF enhances with the incorporation of $BaTiO_3$. The polydopamine functionalized $BaTiO_3$ particles disperse uniformly in PVDF due to the formation of active sites in $BaTiO_3$ particles. This further remarkably promotes cell adhesion, differentiation and proliferation. Also, it improves the mechanical and piezoelectric properties of the scaffolds. Hence, this piezoelectric composite is a promising scaffold material for bone reconstruction applications [85].

PHOTORECEPTOR

The $BaTiO_3$ ferroelectricity changes when radiated optically and show a photo- ferroelectric property. The electro-photographic properties of PVDF/$BaTiO_3$ composite were first observed by P.K.C. Pillai et al. The localization of photo-excited free charge carriers at different trapping sites gives the idea of dark (photo) polarization in these materials. The photoreceptors have applications in the area of optical memory, and holography etc. [86].

The remarkably high piezoelectric, pyroelectric coefficients and high dielectric susceptibility etc. make PVDF/$BaTiO_3$ composites very promising for other applications such as pyroelectric thermal imaging, biochips, gate insulators in transistors, filters, memory elements, nanogenerators, etc. [80].

POLYMER FILMS AS SEPARATOR FOR SUPERCAPACITORS

Supercapacitors are electrochemical capacitors with very high electric capacitance value. It comprises two electrodes, electrolyte, separator and current collectors. The structure of the supercapacitor is represented in figure 1.8. These all elements of supercapacitor assist its final characteristics, which determine its ability to charge and discharge. Besides the electrode-electrolyte framework, the separator is also a key component. It accomplishes various crucial tasks, like physically separating the two oppositely charged electrodes to prevent short circuits, at the same time assuring the good electric conductivity of electrolyte accommodated in its porosity. However, the properties that define the separator material are very challenging and often incompatible with each other. The thickness, porosity, electrical and mechanical properties of separator must support its functions efficiently. Several natural and synthetic materials studied as separators are discussed below.

The natural macroporous eggshell membrane has been investigated as a separator for supercapacitor by H. Yu et al (2012). It has been observed that the eggshell membrane has excellent electrochemical performances, like low resistance, fast charge-discharge ability and good cycling stability of ~92% after ten thousand cycles [87]. Similarly, D. Dahlan et al (2015)

studied duck eggshell membrane as separator and examined the effect of TiO_2 coating on the same and observed a maximum specific capacitance ~ 2.3 F/g for TiO_2 wt% = 5% [88]. However, these natural eggshell membranes are not reliable where the flexibility of the separators is considered as one of its prime tasks.

Several researchers have considered the polymers as the best material for separators with desired characteristics, for example, fluorinated ethylene propylene, poly (vinylidene fluoride), poly(vinylidene fluoride-co-hexa fluoropropene) (PVDF-HFP) and sulfonated poly(ether-ether-ketone) etc. [89–91].

C. Y. Bon et al (2018) examined the PVA-Ceramic composite as separators with three different ceramics, aluminium oxide (Al_2O_3), silicon dioxide (SiO_2), and titanium dioxide (TiO_2). It has been found that ceramics help in increasing ionic conductivity when incorporated in the polymer as the ceramic particles introduce the porosity within the PVA matrix by increasing the amorphous regions in the crystalline polymer [93]. In another study, $BaTiO_3$/PEDOT: PSS composite separator has been investigated with the graphene electrodes on a paper substrate and PVA as an electrolyte. High performance has been shown by the graphene supercapacitor with ceramic/polymer composite separator [94]. Highly efficient disulfonated poly (arylene ether sulfone) (SPAES) /poly(ethylene oxide) (PEO) composites with good mechanical and thermal stability were analyzed as separators by R. Na et al (2016) [95].

Electrospinning is considered as a promising method for producing the porous nanofibers of polymers. A. Jabbarnia et al (2015) investigated electrospun PVDF/PVP with carbon black nanopowder reinforcement as separators. The presence of functional oxygen and nitrogen groups has been observed in separator samples, which significantly enhanced the total capacitance values [96]. T. He et al (2017) also synthesized a separator-cum-electrolyte ultrafine meso/macroporous PVDF fibre via electrospinning method. They observed a high electrolyte uptake (~360 wt%), low ionic conductivity (~1.8 mS cm^{-1}) and good electrochemical stability (~ 0.0–3.3 V) for the ultrafine PVDF fibres [97]. Moreover, A. Laforgue et al (2011) prepared nanofibrous polyacrylonitrile (PAN) and microporous polyethylene terephthalate (PET) separator mats using electrospinning and melt blowing methods, respectively. It has been observed that the %porosity for PAN and PET separators was found to be ~90 and 84%, respectively. They further concluded that the separators do not affect the capacitance of the supercapacitor cell rather has an impact on the internal resistance [98].

Q. Xie et al (2018) studied the coin cells of carbon electrodes and hydrophilic PVDF separator. It has been concluded that the prepared coin cells shown all excellent specific capacitances, exceptional rate performance and good cyclability [99]. D. Karabelli et al (2011) also investigated macroporous PVDF based separators. They observed that among the fluorinated polymers, the homopolymer PVDF separator provided higher conductivities than the commercial separator cellulose and above all Celgard™ [100]. D. Karabelli et al (2015) further extended their investigation for the gamma-irradiated crosslinked PVDF based polymers as a separator. It has been analyzed that the crystallinity of the polymer increases due to chain scission with increasing gamma irradiation dose. The PVDF/ macromonomer of ethylene oxide/propylene oxide (MEP) separators have been resulted in high flexibility even after the irradiation [101].

In the present research work, (1-x)PVDF/(x)$BaTiO_3$ nanocomposite films (with x = 0.1 to 0.5) were aimed to synthesized via solution mixing method. The behaviour of multiphase PVDF in (1-x)PVDF/(x)$BaTiO_3$ nanocomposite films is studied via structural, optical, dielectric and ferroelectric properties. The effect of 80 MeV O^{6+} ion and 40 MeV Li^{3+} ion irradiation on the structural, morphological, dielectric and ferroelectric properties of (1- x)PVDF/(x)$BaTiO_3$ nanocomposite films are investigated. Furthermore, ion irradiated uniformly porous PVDF and

(0.8)PVDF/(0.2)BaTiO3 films are proposed as a separator for supercapacitors. The outlines of the studies presented in this research are given below.

In the first study, the synresearch of BaTiO3 nanoparticles and (1-x)PVDF/(x)BaTiO3 nanocomposite films has been reported via co-precipitation and solution-mixing methods, respectively. The structural, morphological, dielectric and ferroelectric properties of synthesized BaTiO3 nanoparticles and (1-x)PVDF/(x)BaTiO3 nanocomposite films are analyzed. The pristine PVDF when incorporated with BaTiO3 nanoparticles, its α-phase diminishes while the β-phase enhances. Moreover, the significant increase in dielectric constant with increasing content of BaTiO3 in nanocomposite films is due to the enhancement in the interfacial polarization. It has been observed by the temperature- dependent dielectric studies that both the PVDF and BaTiO3 become non-polar in the region 80 – 200 K owing to the fact that below some critical temperature, the dielectric materials behave like non-polar solids, where 200 K is the critical temperature. The value of polarization is highest (0.093 μCcm^{-2}) for (0.6)PVDF/(0.4)BaTiO3 nanocomposite film as compared to pristine PVDF (0.020 μCcm^{-2}) and shows an increase in the charge storage ability of the (0.6)PVDF/(0.4)BaTiO3 nanocomposite film.

The second study represents 80 MeV O^{6+} ion irradiation-induced modifications in the structural, morphological, dielectric and ferroelectric properties of PVDF and PVDF/BaTiO3 nanocomposites as compared to the un-irradiated samples. The PVDF and PVDF/BaTiO3 nanocomposite films are irradiated at fluences 5×10^{10}, 2×10^{11} and 2×10^{12} ions/cm^2. SHI irradiation induces the contraction in the PVDF chain, which resulted in the α→β phase transition due to chain-folding and crosslinking in the polymer. Almost complete amorphization in BaTiO3 filler in (1-x)PVDF/(x)BaTiO3 nanocomposite is observed after irradiation. For irradiated PVDF samples, the dielectric constant (ε′) increases at lower fluence (~13 at 1 kHz) while decreases at higher fluence (~5 at 1 kHz) as compared to the pristine samples. While, in (1-x)PVDF/(x)BaTiO3 nanocomposite, there is an overall decrease in dielectric constant (ε′) after irradiation as compared to the un-irradiated samples.

In the third study, the effects of 40 MeV Li^{3+} ion irradiation (with fluences 5×10^{10}, 2×10^{11} and 2×10^{12} ions/cm^2) on the structural, morphological, dielectric and ferroelectric properties of PVDF and PVDF/BaTiO3 nanocomposites have been examined as compared to the un-irradiated samples. From SRIM calculations, the Li^{3+} ion projected ranges are found to be 0.229, 0.284 and 0.214 mm for PVDF, (0.8)PVDF/(0.2)BaTiO3 and (0.5)PVDF/(0.5)BaTiO3, respectively. The 40 MeV Li^{3+} ion irradiation also resulted in α→β phase transition in PVDF, while complete amorphization in BaTiO3 filler of nanocomposite after irradiation. The dielectric constant (ε′) decreases for all the samples after 40 MeV Li^{3+} ion irradiation due to amorphization and crosslinking effects in BaTiO3 and PVDF, respectively. The remanence polarization decrease for all the samples while, the coercive field increases due to the irradiation-induced modification in the crystal structure of BaTiO3 filler.

In the fourth study, the SHI irradiated PVDF and PVDF/BaTiO3 nanocomposite films have been proposed as a separator for supercapacitors. The piezoelectric behaviour of the flexible polarized separator films has been analyzed for different deformations. Further, the electrochemical performances in the presence of a liquid electrolyte have been examined. The Cyclic Voltammetry (CV) curves retain its shape without obvious distortion with the increase of scan rate 20 – 180 mA s^{-1}, demonstrating the excellent high rate performance of the separators. The performance of the SHI irradiated PVDF and (0.8)PVDF/(0.2)BaTiO3 separator films has been compared with previously reported and commercially available separators. The Rbe values was found to be 1.4 and 0.7 Ω for Li^{3+} ion irradiated PVDF and (0.8)PVDF/(0.2)BaTiO3

separator films, respectively; while 0.9 and 0.4 Ω for O^{6+} ion irradiated PVDF and (0.8)PVDF/(0.2)BaTiO3 separator films, respectively. The calculated values of conductivity (σ) are in the range of 41.5 – 14.1 mS cm^{-1}, which is higher than the conductivities of commercially available cellulose separators (10 mS cm^{-1}) and Celgard™ 2500 separators (4 mS cm^{-1}).

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