Swift Heavy Ions Irradiated PVDF/BATIO$_3$ Nanocomposit Films

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Abstract: Swift heavy ion (SHI) irradiated PVDF and (0.8)PVDF/(0.2)BaTiO$_3$ films (thickness ~ 0.06 μm) have been studied as a separator for supercapacitors. Samples were irradiated by O^{6+} and Li^{3+} ions at fluence 2×10^{11} and 2×10^{12} ions/cm^2, respectively. The irradiation-induced $\alpha \rightarrow \beta$ phase transition in the PVDF polymer matrix, whereas complete amorphization in BaTiO$_3$ filler is observed in nanocomposite films. The estimated value of percentage porosity (P%) for the irradiated composite films is comparable to the P% values for commercially available Cellulose separators. The flexibility is retained even after irradiation owing to irradiation-induced cross-linking in the PVDF matrix. The Cyclic Voltammetry (CV) curves retain their shape without distortion with increasing scan rate (20–180 mA s^{-1}) showing the high rate performance of the separators. The electrochemical impedance spectra of Ni/separator/Ni blocking cells after the 1st and 200th cycles are analyzed to evaluate the bulk electrolyte resistance (R$_{be}$) and conductivity under the cyclable performance of the separator films. The R$_{be}$ for the 1st cycle for irradiated PVDF and (0.8)PVDF/(0.2)BaTiO$_3$ separator films are ranged from 0.4–1.4 Ω, which is much lower than R$_{be}$ for commercially available non-porous Celgard™ 2500 (88.2 Ω) and micro-porous Celgard Ez 2090 (47.1 Ω) separators. However, the conductivity values are higher than that of commercially available Cellulose and Celgard™ 2500 separators.

[Thakur, R. **Swift Heavy Ions Irradiated PVDF/BATIO$_3$ Nanocomposit Films**. *The International Journal of Interpretation, Observation and Analysis*, 2024; Volume 4, Issue 1:7-10 (October-December). ISSN 2349-0713, Peer-reviewed (online/offline), Refereed, Indexed and International Journal (Since 2013), Global Impact Factor: 5.776

Keywords: Swift Heavy Ions, Irradiated PVDF/BATIO$_3$, Nanocomposit Films

Introduction:

Recently the Polyvinylidene fluoride (PVDF) is studied extensively due to its interesting piezoelectric and pyroelctric properties. PVDF based composites found application in lithium ion batteries, capacitors, hydrophones and variety of sensors [1,2,3]. The most attractive property of PVDF is polymorphism. It exists in five α, β, γ, δ, ϵ phases but the first two phases are dominate phases [4,5,6]. The piezoelectric and pyrolectric properties are mainly governed by α and β phase. So researchers are investigating the various methods to promote these phases. Fillers/dopants are used to make PVDF composite film so as to improve the dielectric, magnetic and mechanical properties. The addition of dopant in polymer enhances the physical properties, thus widening the application are of PVDF polymer. In various studies, the researchers confirm the changes in the morphology and crystalline structure of PVDF doped with different types of fillers/dopant [7,8]. For PVDF film having dominated α, and β phase the prepared films were to be mechanical stretched as well as poled [9]. This technique enhances the piezoelectric response which is desirable for sensing applications. Plasma treatment was also used to enhance the hydrophilic property of PVDF membranes [10]. Different types of organic and inorganic fillers were utilized to investigate the effect on various physical and chemical properties of PVDF. The degree of crystallinity and electrical response of PVDF also depends upon the weight percentage of fillers [11]. Few researches have added nanoclay as filler to PVDF so as to study the changes in structure PVDF matrix [12,13]. Some groups focused on use of high polarity solvent used for casting the PVDF film. Recently Zeolite was actively used as filler to develop a Zeolilite/PVDF composite. Additions of Zeolite improvise the tensile strength as well as mechanical properties of PVDF thin films, thus widening the application are of these composites [14]. Some of the common fillers used as dopant includes Ba, Co, Mn, Fe, Cr, Ti, Li and so on [15–18]. In this research work, the MgCl2 is selected as dopant material. It was revealed that addition of MgCl2 significantly modifies the crystalline structure and reduction in crystalline structure was observed. The other objective was to evaluate the effect of MgCl2 on the dielectric constant and application of sensing properties of PVDF composite films.

Direct printing with nanomaterial inks has gained much interest lately due to its potential in fabricating flexible electronic components such as sensors [1], actuators [2], batteries [3], supercapacitors [4], transistors [5], etc. Generally, printing techniques can be classified into two categories, namely “contact” and “non-contact” printing. In contact printing, patterns are formed inside the printer (on engraved rollers or a stencil) and transferred directly onto the substrate; however, in non-contact techniques, the patterns are deposited onto the substrate through one or a series of computer-controlled nozzles. Flexography, gravure, offset, and screen printing are the most well-known contact printing techniques, while inkjet, aerosol jet, and electrohydrodynamic jet printing are the most prominent non-contact methods.

Nanomaterial inks used in inkjet printing play a crucial role in imparting functionality to the printed pattern. Hence, a lot of impetus has been put on building a library of new nanomaterial inks for flexible electronics. For satisfactory inkjet printing, inks have to meet certain fluid mechanical requirements, otherwise printing may suffer from satellite drops, splashing, the coffee-ring effect, and nozzle clogging. To quantify fluid mechanical requirements, Fromm et al. introduced a dimensionless Z value, which is defined by dividing the Reynold number (Re) number by the square root of the Weber (We) number [6].

According to Reis and Derby, the interval of $1 < Z < 10$ is the inkjet-printable window [7], where the lower limit demonstrates the minimum Z value below which the drops cannot be ejected from the nozzles and the upper limit is the starting point of satellite drop formation. In other research, Jang et al. reported the interval of $4 < Z < 14$ as the inkjet-printable range [8], which was more consistent with the results achieved in this research. Much focus has been put on synthesizing conducting inks that can replace interconnects and electrodes in devices. However, multifunctional devices require multilayers of semiconducting, conducting, insulating, and piezoelectric materials. Thus, there is a need to develop novel functional inks for printing functional devices.

This work was a step forward in preparing piezoelectric inks for inkjet printing employed for fabricating sensing devices. Polyvinylidene difluoride (PVDF), a thermoplastic polymer, was the material of choice due to its high chemical and mechanical stability and outstanding ferroelectric, piezoelectric, and pyroelectric properties in comparison with other organic materials [9]. These interesting properties lead to its wide application in electronic devices such as sensors, actuators, and capacitors [10,11]. PVDF can crystallize at five different phases of α, β, γ, δ, and ε based on the processing method; however, ferro-, piezo-, and pyroelectric properties of this polymer only stem from polar phases of β and γ. Several methods have been reported to increase the ratio of β-phase crystallinity to other non-polar phases, such as annealing [12], mechanical stretching [13], electrical poling [14], electrospinning [15], solvent casting [16], and addition of nucleating fillers [17]. So far, several fillers have been used to enhance the performance of PVDF films. Maity et al. [18] introduced molybdenum disulfide (MoS_2) into PVDF using a polyaniline (PANI) interlinker. They reported that the incorporation of 10% filler led to 86% of β-phase crystallinity. Li et al. [19] enhanced the performance of PVDF-based nanogenerators by using ZnO nanorods as filler, coupled with electrospinning. The obtained membrane demonstrated promising open circuit voltage of ~85 V and short circuit current of ~2.2 μA. Pariy et al. [20] reported the incorporation of 0.1 w% reduced graphene oxide to enhance the piezoelectric constant (d_{33}) of PVDF to 87 pm/V.

In this paper, we reported a method that uses $BaTiO_3$ as nucleating filler to enhance β-phase crystallinity of PVDF for inkjet printing. Typical inkjet ink comprises four main components, namely (I) solvent, (II) functional particles, (III) binder, and (IV) additives. Solvent is used for dissolving binders and additives and tuning the final viscosity of ink. Furthermore, the solvent has crucial influence on the drying behavior of deposited droplets. The coffee-ring effect and slow/fast drying are typical problems associated with the improper selection of solvent. In this work, DMF (*N*,*N*-dimethylformamide) was used as the solvent of choice as it showed good solubility towards PVDF (with a dipole moment of 3.86 D) and promising surface wettability ($\gamma = 37.1$ mN/m) on a variety of substrates, including Kapton polyimide films. In the majority of inks, functional particles are the most crucial part of the ink, since they determine the final properties of printed patterns. In graphical inks, pigments are used as functional particles to endow different colors to printed images, while in functional inks the desired electrical properties such as conductivity, semi-conductivity, and piezoelectricity are provided by the particles (metal, carbon, ceramic, etc.). Here, $BaTiO_3$ nanoparticles were used as functional particles to endow the ink with piezoelectric properties. $BaTiO_3$ could also enhance polar-phase crystallinity of PVDF by acting as a nucleating agent, which resulted in enhancing the final piezoelectric performance of the obtained film. Polymeric binder is the other component of inkjet ink that brings about stable dispersion of functional particles and prevents their aggregation. PVDF is a polymer with good binding ability and demonstrates promising piezoelectric properties. Unlike metal inks, which require a sintering step to remove the binders, fabricated piezoelectric ink does not require any post-processing steps, since both the binder and the particles are piezoelectric, thus enabling printed devices on substrates with low thermal resistivity.

Swift Heavy

Ions By Swift heavy ions irradiation in the polymers, it seems large variation in the properties of polymers like structural, optical and electrical properties. The SHI irradiation in the polymer, the energy transmits to the material by electrical loss. The energy transfer show that the creation of reactive groups like radicals, gases, and defects in the polymers. Properties of polymer can be changed by using nanotechnology i.e., by embedding any suitable ion beam to the polymer. Ion beam technology provide tailoring to the properties of material as per our need and obtaining the new kind of material. This nanomaterial creates a bridge which has potential to cross the difference between silicon electronics and polymeric electronics. Ion beam is an effective technique to the enhancement of the electronic, optical, electrical and biological properties of the polymers. Ion beam creates impurity inside the polymers and thus the properties of the polymers and thus properties of the polymers can be enhanced. Nowadays, there are large number of benefits of ion beams, before this ion beams were used to study the structure of the substance, but ion beam somehow destroys some intrinsic properties of the material, so it was the best innovation to modify the material properties. In undoped form the band gap has more than 2 eV which is very high for the thermal excitation of electron which means less electrical conductivity of around the order of 10-10 S/cm, by very small doping of ion beam this conductivity rapidly to 10-1S/cm. Many experiments of ion irradiation with low energy (80 MeV) and intensification of electrochemical stability of polypyrrole electrodes after SHI irradiation have been reported for the first time by the present authors [17]. The low energy ion irradiation is in fact ion implantation and an electroactive ion is implanted in the target material, which may be referred to as doping by ion implantation. In high energy ion irradiation, due to the electronic energy loss mechanism, the huge energy of the incident ions is released into (i) radiative decay and (ii) production of new reactive species (radicals, gases) and defects (instauration, scission and crosslinking) and heat. In certain cases, amorphous samples become modified into crystalline phases after ion irradiation. Fink et al. [18] studied the polyvinyl alcohol (PVA) exposed by 160 MeV electrons and found that for the same transferred energy density heavy ions were more efficient for the damage in polymers than the low energetic ions. Hussain et al. [19] studied the 160 MeV Ni+12 bombarded polypyrrole supercapacitor and found that stability of the supercapacitor increases after irradiation. However, changes in crystallinity under high-energy ion irradiation in conjugated polymers have not been studied in detail till now.

Applications of Swift Heavy Ions:

Ion Track Nanotechnology: It is a wide range of application in specific material areas. It can be attacked to suitable chemical etchant; each damage track converts into an individual nanopores. The pore size, geometry, and shape also determine. By electrodeposition technique, ion track is used for nanofibers fabrication to fill the pore of ion -track membrane. Electrochemical deposition, Surface modification, Chemical etching technique is used to modify the nanostructure compound properties. By ion-track membrane technique control geometry, size, shape and surface morphology of the nanowire. This technique is used in the nanofluidic devices like desalination, electrochemical energy storage in batteries, Fuel cells, and batteries.

Cosmic Radiation Simulations: SHI technique become the most important at large accelerator facilities. Electronic components are sensitive in space mission. High energy particles produce charge and electron that generates the leakage current, memory error, multiple type error. Galatic radiations forms a large molecular compound such as aromatic hydrocarbons and fullerenes are observed. SIMS with KeV ions beams released particles and molecules driven by electronic excitations. The liberation of large molecules from cryogenic films by desorption and sputtering and is explore by in situ mass spectrometry in sequence with time-of-flight measurements

Conclusion

Swift heavy ion (SHI) irradiation is an effective method for modulating the properties of thin oxide films by introducing defects, strains, and structural transformations. Here, we applied 516 MeV Xe^{31+} irradiation to BaTiO$_3$ (BTO) thin films grown on Nb:SrTiO$_3$ substrates to induce the generation of tracks and nanohillocks. Memristors with BTO films irradiated at a fluence of 5×10^{10} ions cm^{-2} displayed excellent retention and endurance characteristics. Moreover, the memristors exhibited highly stable synaptic plasticity functions such as excitatory/inhibitory post-synaptic currents (E/IPSC) and paired-pulse facilitation/depression (PPF/D). The memristors achieved a discrimination accuracy of 92.5% on given handwritten digit data by an artificial neural network with supervised learning. These results verify that the judicious application of SHI irradiation on thin oxide films is a viable strategy for exploring neuromorphic computation.

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