



Hierarchical nanostructured polyaniline functionalized graphene/poly(vinylidene fluoride) composites for improved dielectric performances



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ABSTRACT

Hierarchical nanostructured polymeric dielectric composites (PGP) based on semicrystalline poly(vinylidene fluoride) (PVDF) matrix are fabricated by incorporating polyaniline-grafted-graphene oxide (G-graft-PANI). HR-TEM images show uniform dispersion of GO within PVDF matrix. FE-SEM micrographs of PGP composites indicate fibrillar morphology produced from supramolecular organization of G-graft-PANI with PVDF chains resulting hierarchical nanostructure. The dipolar interaction between the filler and PVDF is established from FTIR spectra and Raman spectroscopy indicates reduction of GO during fabrication process. The interaction ability and high surface area of G-graft-PANI cause nonpolar α -phase PVDF to polar β -phase transformation to 91% for 5 wt% filler. PGP composites show higher melting and crystallization temperatures. It exhibit spectacular increase of dielectric permittivity, dielectric loss, and dc-conductivity relative to that of neat PVDF films. The values of dielectric permittivity and dielectric loss are 264 and 1.125 at 10^2 Hz frequency and dc-conductivity increases 8 orders from that of pristine PVDF for loading of 5% G-graft-PANI.

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1. Introduction

Polymer nanocomposites produced by inserting nanomaterials into a polymer matrix lead to dramatic improvement in the mechanical, electrical, optical and thermal properties from the host polymers. These high-performance light-weight composites lead to develop multifunctional materials whose properties can be tailored with composition suitable for different applications [1–3]. Ferroelectric polymers are the most important for its applications in sensors, actuators, energy resources and in the field of biomedical research [4]. Poly(vinylidene fluoride) (PVDF) is a ferroelectric polymer that caters good electro-active (piezoelectric, ferroelectric, dielectric), properties which can be tailored to meet various requirements [5]. PVDF exists in five different crystalline phases (α , β , γ , δ and ϵ) depending on the conformation of the polymer chain in the crystal lattice and amongst them β -phase is the most important possessing an “all-trans” (TTTT) conformation having piezo-electric

property making it suitable for different technological applications [6]. The polar β -phase in PVDF thin films can be produced by adding a variety of nucleating fillers, such as BaTiO₃, hydrated ionic salt, clay, CNTs, PMMA, TiO₂ and nanoparticles such as palladium, ferrite, silver, gold etc [6–10]. Other ways to produce β -phase from melt under specific conditions are application of high pressure, mechanical stretching, with functional carbon nanotubes and graphene etc [11]. Even these techniques are appropriate to produce polar β -PVDF, they are not superior in all aspects considering the aspect ratio of nanomaterials, geometry control, uniform dispersion in matrix and device integrability. Triggering of greater amount of polar β -phase of PVDF depends upon the strength of specific interactions (i.e ion-dipolar, dipole-dipole etc.). This type of interaction and the surface pattern of the nanofillers affect the structure of the polymer matrix which is most important in order to fabricate the flexible, large area and low cost devices.

Graphene, a monolayer sp²-bonded carbon of two-dimensional sheet structure, is an attractive material due to its outstanding electron mobility, thermal stability, mechanical strength, and flexibility [12]. These striking features render graphene extremely promising candidates for electrochemical energy storage. Due to processibility problem a great deal of work has been performed using its oxidized form, graphene oxide (GO) [13,14]. GO has also

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sheet like structure with high aspect ratio bearing hydroxyl and epoxide functional groups at their basal planes, and carboxylic acid groups located mostly at the edges making it dispersible in polar media. The existence of various surface functionalities give opportunities for further modification of GO to fabricate composite materials for different targeted applications [15,16].

In PVDF/graphene nanocomposites, surface functionalization of GO sheets improves its dispersion in PVDF matrix which promotes the formation of the β -phase significantly [17]. Recently, Bose et al. used poly (ethylenimine) functionalized GO to induce β -phase of PVDF with the highest dielectric permittivity of 39 measured at a frequency of 100 Hz [18]. Jang et al. fabricated a ternary nanocomposite system, composed of PVDF/ NH_2 -treated graphene nanodots/reduced graphene oxides (RGO) and they have noticed a great impact on the $\alpha \rightarrow \beta$ phase transformation of PVDF with a dielectric constant (ϵ') ≈ 60.6 at 10^2 Hz for 10 vol % NH_2 -treated graphene nanodots/RGO co-fillers [12]. There is some relation between the polar β phase and dielectric constant of the system. It is well known, that the dielectric properties originate from the polarization of dipoles, thus methods facilitating the polarization of dipoles can modify the dielectric properties of the materials substantially [19]. β phase PVDF is the most polar crystalline form, hence β phase PVDF formation can increase the dielectric constant of the material. It is reported that PVDF nanocomposite with thermally reduced GO also improves the dielectric properties [20].

Polyaniline (PANI) is one of the most promising intrinsically conducting polymers (ICPs) having reversible redox behavior, good electrical conductivity and high dielectric constant ($\epsilon' \approx 10^2\text{--}10^3$) and hence it finds uses in chemical sensors, dielectric materials etc [21–23]. The graphene functionalized PANI are prepared by in situ electro polymerization, noncovalent functionalization [24], and also by covalent grafting method [25]. These graphene-based conducting materials are prime candidates for energy and optoelectronic applications due to enhancement of the intriguing properties which has triggered great scientific area of research and also industrial applications [26]. So, the graphene-PANI nanomaterials would be suitable candidates for other polymer matrices as conducting fillers for fabrication of composite materials. Therefore, it is necessary to develop a simple approach to prepare ternary nanocomposites comprising of GO grafted PANI-PVDF system that can utilize the synergistic effect of GO-graft-PANI for homogeneous dispersion yielding good conductivity and dielectric properties.

Here, we present a novel and facile route to prepare PANI anchored graphene based PVDF composites involving the covalent functionalization of paraphenylenediamine to acylated GO which is subsequently used to polymerize aniline monomer in presence of *p*-toluenesulfonic acid. Concomitantly GO undergoes in-situ reduction to a certain extent thereby yielding highly conducting fibrillar networks. It is expected that radical cations of the doped PANI and the $>\text{C}=\text{O}$ group of amide linkage would interact with the polar $>\text{CF}_2$ groups of PVDF to make a good dispersion of PANI grafted GO (G-graft-PANI). This interaction helps to generate fibrillar porous network morphology by swallowing the spherulitic morphology of PVDF and causes a major β phase formation with a significant increase of dielectric property. The synergetic effect of PANI functionalized GO sheets on PVDF causes the transformation from nonpolar α phase to 91% polar β phase, dielectric permittivity increases from 10 in PVDF to 264 in the composite at a frequency of 10^2 Hz with an eight order increase of dc-conductivity from PVDF for the loading of 5% G-graft-PANI. We have compared the results with the composites of paraphenylenediamine grafted GO (G- NH_2) and it is observed that G-graft-PANI/PVDF composite is superior to G- NH_2 /PVDF composites in respect of β phase formation and dielectric properties. Attempt has been made to co-relate dielectric properties with the % β phase content of PVDF in both the composites.

2. Experimental

2.1. Synthesis of graphene oxide (GO)

GO was prepared from graphite powder using Hummer's method [27]. (SI).

2.2. Synthesis of amine functionalized GO (G- NH_2)

In a 250 ml round bottom flask, 500 mg GO with catalytic amount of N,N-dimethylformamide (DMF) and 100 ml SOCl_2 were taken and were kept in a reflux condition at 80°C for 24 h under nitrogen atmosphere, to convert the carboxylic acids of GO to acyl chlorides. The excess SOCl_2 was removed by distillation under reduced pressure; the obtained product was re-dispersed in 30 ml dry DMF and was stirred for 30 min. Then 500 mg of *p*-phenylenediamine (PPDA) was added to this dispersion and the reaction was continued for 72 h at 120°C under nitrogen atmosphere. The mixture was centrifuged by washing with DMF, distilled water and methanol, respectively and was dried under vacuum at 80°C for two days.

2.3. Synthesis of PANI on G- NH_2 (G-graft-PANI)

100 mg of G- NH_2 was first dispersed in a beaker containing 50 ml of distilled water and ultrasonicated for about 20 min to obtain a homogeneous dispersion. Then 80 ml of 1(M) *p*-toluenesulfonic acid (PTSA 13.776 g) was added in this dispersion and was sonicated for 15 min. This suspension was cooled in an ice bath to 0°C and then, aniline monomer (400 μL) was added to the G- NH_2 suspension with continuous stirring using a magnet. A freshly prepared solution of 1.369 gm of ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) in 10 ml of water was slowly added to the mixture while stirring in the cool conditions. This stirring was continued for 8 h and the cooling condition was maintained to ensure the proper polymerization. The resulting dark green material was then filtered and the residue was washed several times by deionized water, methanol and acetone followed by vacuum drying at 60°C for 24 h (Scheme 1).

2.4. Fabrication of PGP and PGN nanocomposite films

10 mg G-graft-PANI nanofiller was initially dispersed in 10 ml DMF by sonication at 30°C . PVDF (500 mg) was dissolved in 10 ml DMF by heating and magnetic stirring. Different amounts of G-graft-PANI dispersion were mixed with the PVDF solutions and were kept on magnetic stirring for 7 h. The solutions were cast on petridishes at 100°C for DMF evaporation in air for 5–6 h. The composite films were finally dried in vacuum at 70°C for 3 days for complete removal of DMF to make the PGP composites (Scheme S1). These composite films thus produced are named as PGPx where x represents the wt% of G-graft-PANI. In a similar way G- NH_2 /PVDF composites were produced and are named as PGNx where x represents the wt% of G- NH_2 .

2.5. Measurements techniques

To understand the physical and electrical properties of the PGPx composites various instrumental techniques e.g. Fourier transform infrared (FTIR), Raman and X-ray photoelectron spectroscopy (XPS); thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXS), high-resolution transmission electron microscopy (HR-TEM), field emission scanning electron microscope (FE-SEM) dc-conductivity and dielectric property measurements were used and the details

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