

Research paper

The effect of reduced graphene oxide intercalated hybrid organoclay on the dielectric properties of polyvinylidene fluoride nanocomposite films



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ABSTRACT

In present investigation, reduced graphene oxide sandwiched organoclay (Clay@r-GO) was introduced as conductive nanofillers to promote the electroactive β -phase as well as conducting network within polyvinylidene fluoride (PVDF) via solution casting technique. The composition of Clay@r-GO nanohybrid filler was formulated in the weight ratio of 1: 20 of graphene oxide and organoclay after observing the independent contribution of r-GO and organoclay to the dielectric property of PVDF. PVDF/Clay@r-GO nanocomposite films were designed with various wt% of Clay@r-GO filler. The fabricated PVDF/Clay@r-GO nanocomposite film was characterized with SEM, TEM, FTIR and XRD. Electron microscopic results revealed that only 5 wt% of Clay@r-GO hybrid nanostructures was effective to inhibit the formation nonpolar α crystal, whereas; FTIR analysis showed the \sim 80% transformation of β -phase in PVDF/Clay@r-GO nanocomposite film with incorporation of only 2 wt% Clay@r-GO hybrid filler. With 2 wt% of nanohybrid filler, thermal stability of PVDF/Clay@r-GO nanocomposite film was highly improved with a char residue of 41.37% at 700 °C. Dielectric study reveals that only 2 wt% hybrid nanofillers was effective to impart high dielectric permittivity ($\epsilon' \sim 102$ at 1 Hz) as well as low dielectric loss (< 1), whereas; a optimum permittivity ($\epsilon' \sim 433$ at 1 Hz) is observed for 15 wt% loading. Therefore, the fabricated PVDF/Clay@r-GO nanocomposite film may be used as advanced dielectric materials for real life application.

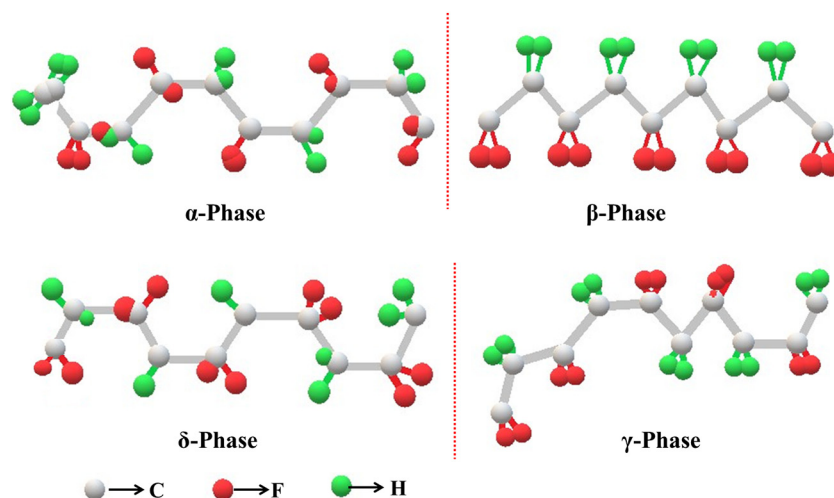
1. Introduction

The development of micron- or nano-sized hybrid architectures of polymer nanocomposites with various morphologies has offered new possibilities in the field of high charge storage capacitors (Shen et al., 2017), electro-active materials (Ehsani et al., 2017), gate dielectrics (Faraji et al., 2016) etc. Although ceramic materials are considered to have ultrahigh dielectric permittivity and low dielectric loss (Liu et al., 2016), the realistic applications are limited by their high temperature sintering, production cost and brittle nature (Yuan, 2017). The increasing demand of polymer in electronics is due to their easy processability, flexibility and low dielectric losses (Kang et al., 2015). The direct use of polymer for dielectrics is limited by their low dielectric constants (Huang and Jiang, 2015). Polyvinylidene fluoride is highly non reactive and pure thermoplastic fluoropolymer, obtained through the polymerization of vinylidene difluoride (McCrum et al., 1967). PVDF gives both, high flexibility and the stereo chemical constraints with four distinct crystalline forms such as α , β , γ and δ (shown in Scheme 1) (Kabir et al., 2017). The α phase is the most stable nonpolar phase having trans-gauche (TG \overline{G} ; T = trans, \overline{G}/G' = gauche)

conformation; while the highly polar β -phase with planer all-trans (TTTT) conformation is assumed to be superior owing to its largest polarization per unit cell (8×10^{-30} Cm) (Roy et al., 2016) as compared to other two polar phases, i.e. γ (T $\overline{3}$ GT $\overline{3}$ G') and δ (TG \overline{G} G') phase (Martins et al., 2014). The β -phase enhancement in PVDF has recently earned a great interest because of its superior performance in piezoelectric, pyroelectric, ferroelectric and dielectric applications (Jahan et al., 2018; Sagar et al., 2017). The most well-known technique to achieve high dielectric constant of polymer is to prepare polymer composites with dispersing high weight % of different ceramic particles. Different ceramic particles like BiFeO $_3$ (Moharana et al., 2016), BaTiO $_2$ (Moharana et al., 2017)[14], CaCu $_3$ Ti $_4$ O $_{12}$ (Zhang et al., 2016), Li $_{0.05}$ Ti $_{0.02}$ Ni $_{0.93}$ O (Wu et al., 2002), PbZr $_x$ Ti $_{1-x}$ O $_3$ (Chang et al., 2015) and PbMg $_{1/3}$ Nb $_{2/3}$ O $_3$ (Wang et al., 2017) are widely used for dielectric applications. But the high concentration of these inorganic filler into polymer matrix inevitably deteriorates the flexibility and break-down voltage of the resultant composites. In other methods, conducting components such as metals [(i.e. Au, Ag, Cu, Al) (Ginsburg et al., 2006; Lu et al., 2006a, 2006b; Dang et al., 2004; Singh et al., 2003)] or carbon allotropes [CNTs (Du et al., 2017), GNPs (Song et al., 2016; Sharmila

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Scheme 1. Structural representation of different crystalline forms of PVDF.

et al., 2016)] or conducting polymers [polyaniline (Molberg et al., 2010; Yu et al., 2016), polypyrrole (He et al., 2018)] are widely used to achieve high dielectric constants in composite materials. Incorporation of conductive fillers can show very high dielectric in polymer composites, but they are prone to high dielectric loss and low-breakdown strength.

Graphene analogous materials are widely used in sensing (Xia et al., 2016), biomedical (Lee et al., 2016), packaging (Sharma et al., 2017) and energy storage applications (Ambrosi and Pumera, 2016; Chua and Pumera, 2016). Graphene sheets are structurally distinguished as honeycomb structure with sp^2 hybridized carbon atoms. It possesses ultrahigh aspect ratio (up to ~ 1000 – 1300) and high electron mobility (Meyer et al., 2007). Due to strong Vander Waals interactions between graphene sheets (Huang et al., 2014), uniform distribution of these sheets to polymers is still a challenging task and therefore, graphene oxide (GO) is used as the intermediate phase to produce reduced graphene oxide (r-GO) based polymer nanocomposites upon chemical reduction. However, chemical reduction leads to an irreversible agglomeration of r-GO in polymer nanocomposites allowing high dielectric permittivity as well as high dielectric loss. Researchers are currently motivated to stabilize the nanostructural phase in polymer nanocomposite to minimize the dielectric loss. Other nanostructures like metal and semiconductor nanoparticles are used to avoid the re-stacking of r-GO sheets during chemical or thermal reduction (Pendashteh et al., 2013; Shayeh et al., 2015; Ma et al., 2014).

The concept of multi-component hybrid filler in designing of advanced functional materials is a recent trend in material chemistry. Moreover, the 2D-2D interactions to stabilize the r-GO phase as well as restoring the electrical conductivity is recently reported in fabricating clay-graphene conductive composites (Ruiz-Hitzky et al., 2016). In another report, boron nitride surface is modified with r-GO to achieve high dielectric constant and low loss of epoxy nanocomposites (Wu et al., 2016). In present times, clays have attracted significant attention in preparation of polymer nanocomposites to improve thermal (Carvalho et al., 2013), fire retardance (Fina et al., 2014), mechanical (Wang et al., 2015) and controlled delivery properties (Lvov et al., 2016). In order to introduce dielectric properties, montmorillonite (Mt) are efficiently incorporated within polyvinyl alcohol (PVA)/polyethylene oxide (PEO) hybrid polymer (Sengwa et al., 2010), polypyrrole (Madakbaş et al., 2013) and cyanoethylated cellulose (Madasanka et al., 2017). Negatively charged Cloisite®30B is basically organically modified Mt. $[M_y^+(Al_{2-y}Mg_y)(Si_4O_{10}(OH)_2 \cdot nH_2O)]$ with quaternary ammonium salts [methyl tallow bis(2-hydroxyethyl) quaternary ammonium chloride]. The basic framework of organoclay (layer thickness ~ 1 nm; aspect ratio: 100–1000) is comprised with

tetrahedral (T_d) silica phase; sandwiched between two octahedral (O_h) alumina phase. Recently, organoclay is incorporated within electrospun PVDF-MWCNT nanocomposite to enhance the β -phase transformation (Qamar et al., 2017). The intriguing combination of montmorillonite, nickel hydroxide and their negatively charged surfaces are proven to be in strong interaction with the positive $-CH_2$ dipoles of $(-CH_2-CF_2)$ unit to nucleate the electroactive β -phase in PVDF-HFP copolymer by Roy et al. (Roy et al., 2016). Moreover, the properly modified CNTs are proved to be effective for the conversion of 100% β -phase of PVDF by Kabir et al. (Kabir et al., 2017). Recently, the nanohybrid of organo-montmorillonite and graphenes are investigated to increase the mechanical (Rahmaoui et al., 2017) and flame-retardant (Wang et al., 2018) behaviors of polymer nanocomposites. Moreover, the synergistic effect epoxy functionalized graphene with modified organo-montmorillonite is used to increase the rheological and mechanical performances of poly (lactic acid)/poly(butylene adipate-co-terephthalate) blend (Adrar et al., 2018).

Therefore, we are motivated to enhance the nucleation of electroactive β -phase within the commercially available PVDF with incorporation of organoclay (OC) stabilized reduced graphene oxide (Clay@r-GO). Well dispersed graphene oxides (GO) and organoclays are sonomechanically allowed to interact with each other in order to avoid agglomerations between r-GO layers during chemical reduction. Present manuscript deals with the incorporation of Clay@r-GO hybrid nanostructure in PVDF films along with the detailed study of dielectric behaviors of PVDF/Clay@r-GO with an aim to evaluate the synergistic contributions of r-GO and organoclay with respect to their individual counterpart.

2. Experimental

2.1. Materials

Polyvinylidene difluoride, (PVDF) was purchased from Sigma-Aldrich, India. *N,N*-Dimethyl formamide (DMF) was purchased from Himedia Laboratories Pvt. Ltd., India. The organically modified Cloisite®30B (Modified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium; cation exchange capacity: 90 meq/100 g clay; moisture content: 2 wt%; d-spacing (001): 1.85 nm) was supplied by Southern Clay Products, Austin, TX, USA. Graphite powder (average diameter 500 nm) was purchased from Loba Chemical Pvt. Ltd., Mumbai, India. All the chemicals were used as received.

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