The effects of conductive nano fillers alignment on the dielectric properties of copolymer matrix

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ABSTRACT
This research focuses on the improvement of the dielectric and energy harvesting properties of piezoelectric P(VDF-TrFE) copolymer matrix by the alignment of conductive reduced graphene oxide nano fillers. The dispersion and the morphology of the conductive nano fillers on the co-polymer matrix were characterized by scanning electron microscopy which showed a configurational phase transition due to highly conductive nano channel formation, steric hindrance, excluded volume interaction van-der-walls forces between adjacent reduced graphene oxide sheets. Five different piezoelectric nanocomposites were prepared by varying the reduced graphene oxide contents in P(VDF-TrFE) matrix to realize its optimum concentration in the matrix. From our analysis, we observed that, an optimized morphological structure plays a vital role in the formation of polar electroactive $\beta$ phase on the co-polymer matrix through the good dispersion, filler alignment and interfacial interaction of reduced graphene oxide nano fillers. The as prepared nanocomposite film showed an enhanced crystallinity (50 ~ 52%), dielectric constant (72 at 1 kHz), piezoelectric charge constant ($\epsilon_{33}$ ~ 23 pC/N) with an output power of 3.2 $\mu$W at 1.8 M$\Omega$ load for 2 N mechanical force. All the outputs were observed without applying poling process. We expect that our synthesized self-poled nanocomposite can be a useful candidate for energy harvesting applications.

1. Introduction
Now-a-days functional electroactive polymers/ copolymers are intensively investigated by many researchers for having potential applications in several fields such as pressure sensor, vibration measurement, ultrasonic imaging in medical instruments, and most importantly energy harvesting [1–3]. Ferroelectric polymers such as poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-co-trifluoroethylene-chlorofluoroethylene)(P(VDF-TrFE-CFE)) have great potential for converting mechanical energy into electrical energy [4]. However, due to low coupling between electrical and mechanical properties it is highly desirable to substantially improve the dielectric response of such polymers [4, 5]. Up to now, several works has been done on the preparation of 0–3 type composites based on polymers and ceramics of high dielectric constant, and the resultant composites usually possess a relatively high dielectric permittivity (about 100) [5–7].
Nevertheless, the high wt % of ceramics, which was necessary to achieve the high dielectric constants, presents a number of limitations, in terms of high weight, low flexibility, and poor mechanical performance, as a result of the weak matrix-filler bonding and agglomeration of ceramic nanoparticles [8, 9]. Furthermore, most ceramics of high dielectric constant are lead-based, and potentially harmful to our health [9]. To overcome these challenges, conductive fillers such as graphite, graphene, reduced graphene oxide, carbon nanotubes (CNTs) have been proposed to tune the polymer microstructure for enhancing the dielectric and piezoelectric properties [10]. Among these fillers, zero band gap based single layer graphene sheet with delocalized electron from PZ orbital perpendicular to the basal plane of graphene, plays an important role for its electronic structure [11]. Lian et al. reported a band opening formation (reduced graphene oxide) happens with the presence of oxygen containing functional groups (such as epoxy, hydroxyl, carboxylic) on the basal plane and edge of the graphene [11]. Furthermore, These oxygen functional groups dominate to provide a electroactive structural formation of PVDF and P(VDF-TrFE) polymers by aligning all the fluorine atoms in one side and thus improving the crystallinity [12]. Among four types of crystalline phases, i.e. α, β, γ, δ, of PVDF, “β” phase has received much attention because of its piezoelectric potential and polar electroactive phase which can be obtained by various treatments such as mechanical deformation [13], poling under large electric fields [14], crystallization under high pressure, or applying high cooling rates to a solution [15]. Oliva-Aviles et al reported, an application of 7 kV/m at a frequency of 60 Hz was applied to align the 0.1~0.75 wt % MWCNT into polysulfone polymer for improved electrical and piezo-resistive properties [16]. However, there weren’t the findings of smallest wt/vol % of the conductive filler with self-aligning properties. Moreover, recently Ladani reported carbon nanofibers reinforced-plastic (CFRP) composites to improve its cyclic fatigue resistance and the detectability of disbonding in adhesively-bonded structure with alternating electric field aligned process [17]. Although, electric field aligned carbon nanofibers show better fatigue resistance and crack growth monitoring, functional conductive fillers such as rGO with self-aligned percolated network could have eliminated the post processing experiments. Multifunctional properties based epoxy nanocomposites reinforced by carbon nanofibers or two dimensional graphene nanoplatelets was also reported recently [18]. However, higher amounts of filler contents such as 0.5, 1, 1.5, 2 wt % make this a complex process to align by applying an external electric field in the epoxy resin [18]. Meanwhile, numerable studies have been conducted on the P(VDF-TrFE) copolymer, which can be formed by adding trifluoroethylene (TrFE) units to PVDF [19, 20]. This extra (TrFE) units stabilize the all trans chain conformation which directly crystallizes similar to the β electroactive structure [21]. However, the dipole moment of the PVDF is reduced by the TrFE units because of the introduction of a third fluorine atom per unit. Therefore, to exclude time consuming treatments, complex experimental steps, and enhancing the polar electroactive crystal morphology, we reported here the conductive fillers (reduced graphene oxide) nano-alignment effect by carefully controlling the filler wt % on the copolymer matrix. Subsequently, macroscopic analysis using X-ray diffraction and the Fourier transform infrared spectroscopy techniques to investigate the effects of reduced graphene oxide fillers alignment on the dielectric and energy harvesting properties of P(VDF-TrFE)-reduced graphene oxide nanocomposite film was analyzed.

2. Experiments section

Materials: P(VDF-TrFE) (75:25 mol%) pellets were purchased from Manufacturer and Measurement Specialties Inc., USA. reduced graphene oxide was obtained from Chengdu Organic Chemicals Co., Ltd. All other chemicals and solvents were analytical grade and were used without any further purification.

2.1. Nanocomposite fabrication

According to the typical process, P(VDF-TrFE) pellets (3 g) were dissolved in 20 ml N-N dimethylformamide (DMF, anhydrous 99.8%) solution under vigorous magnetic stirring at 700 rpm for 5 h at 50 C. Appropriate amount of reduced graphene oxide concentration was separately added in 2 ml DMF solution in order to obtain four different
kinds of reduced graphene oxide solutions. Different reduced graphene oxide – DMF solutions were then continuously ultra-sonicated individually for 2 h followed by 3 h magnetic stirring at 700 rpm (90 °C) to break the strong π-π stacking between reduced graphene oxide flakes. Then all four reduced graphene oxide solutions were mixed dropwise into the appropriate amount of P(VDF-TrFE) to obtain 0 wt% (P(VDF-TrFE)), 0.05 wt% P(VDF-TrFE) - reduced graphene oxide, 0.1 wt% P(VDF-TrFE) - reduced graphene oxide, 0.15 wt% P(VDF-TrFE) - reduced graphene oxide, 0.2 wt% P(VDF-TrFE) - reduced graphene oxide nanocomposites. After that, all the samples were further stirred at 700 rpm for 5 h. Finally, the samples were kept in a vacuum chamber for 30 min to remove the bubbles.

Figure 2. SEM images of (a) copolymer, (b) copolymer-reduced graphene oxide fillers 0.05 wt %, (c) copolymer-reduced graphene oxide fillers 0.1 wt %, (d) copolymer-reduced graphene oxide fillers 0.15 wt %, and (e) copolymer-reduced graphene oxide fillers 0.2 wt %. The inset in (c) shows enhanced due to reduced graphene oxide fillers phase changing.

Figure 3. Cross sectional SEM images of reduced graphene oxide fillers phase changing (isotropic to nematic) in (a) copolymer-reduced graphene oxide 0.05 wt % to (b) copolymer-reduced graphene oxide 0.1 wt %.

Figure 4. Fourier-transform infrared spectroscopy analysis.
energy harvesting study, first the Si substrate was placed on a hot plate at 75°C. All the five samples (copolymer-reduced graphene oxide 0, 0.05, 0.1, 0.15, 0.2 wt %) were then drop casted carefully on the PET-ITO substrate, followed by a heat treatment at 75°C for 5 h. After the heating process gold (Au) coating was deposited on upper surface of the thin films by using magnetron sputtering technique. Afterward, platinum (Pt) wire was attached to the both electrodes using silver (Ag) paste as adhesive. Finally, for the packaging purpose the polydimethylsiloxane (PDMS) solution was drop casted over the whole device. For checking the AC conductivity, metal mask was used for depositing gold on the top surface and gold thin layer was coated on the bottom surface of the nanocomposite (Figure 1) by RF magnetron sputtering technique.

3. Results and discussions

The surface morphology of the as prepared nanocomposite was analyzed with the help of a field emission scanning electron microscope (FSEM. JEOL-JSM-7600F). The effects of ultra-sonication and magnetic stirring to exfoliate the rGO sheets can also be observed from the surface SEM images (Figure 2(b,c)) and cross sectional images (Figure 3(a,b)) where the exfoliated rGO layers homogenous dispersion on the copolymer matrix can be seen. Similar kinds of experiments to exfoliate the rGO sheets were also followed by Loryuenyong et al. [22] and Soltani and Kyu Lee [23]. However, with the homogeneous dispersion an increasing of conductive channel (reduced graphene oxide fillers) throughout the copolymer matrix from Figure 2(a–e) can be observed. At higher wt % (Figure 2(d,e)) the reduced graphene oxide fillers tend to aggregate in the matrix because of its large specific surface energy [12]. The presence of various functional groups such as OH, COO−, C−O, C=O makes the reduced graphene oxide intrinsically charged which interact with the fluorine groups in the P(VDF-TrFE) chain [9, 10, 12, 24]. This interaction helps the nanocomposite for forming the β phase which can be observed from Fourier transform infrared spectroscopic analysis (Figure 4) for different rGO weight %. It proves the existence of rGO functional groups and their interaction with P(VDF-TrFE) [21, 25]. The Fourier transform infrared spectroscopy analysis also shows the dominance of functional groups on the intensity of the electroactive β phase of the as prepared nanocomposites samples (Figure 4). A reduction in the transmittance of the functional groups with the increased amount of reduced graphene oxide filler may be due to the less intermolecular interaction among reduced graphene oxide and P(VDF-TrFE). SEM images at Figure 2(d,e) show that higher amount of non-uniformity in the nanocomposite’s morphology beyond percolation threshold of reduced graphene oxide fillers (0.09 wt %) which agree with the FTIR analysis. The interfacial layer between the conductive fillers and copolymer act as a space charge center which stimulate the crystallinity of the matrix [25]. These interactions of conductive fillers cause the copolymer matrix phase transformation which was carefully investigated by using an X-ray diffractometer with Cu Kα (λ = 0.154056 nm) radiation in the 2 theta scanning range of 10°–30°. From Figure 5 it can be clearly seen that the amount of alpha phases at 49°= 18.3° (nonpolar) corresponding to a reflections planes (020) of P(VDF-TrFE)-reduced graphene oxide nanocomposites whereas 2 theta = 20.5°, 42.6° is indicating the polar electroactive β phase having planes of (110/220), (111/220) [24]. It was observed that, highly exfoliated reduced graphene oxide fillers which were accomplished by the ultra-sonication technique were randomly distributed during the solution cast flow. However, due to the gravitational force and the solvent evaporation process, reduced graphene oxide fillers tend to align parallel to the film surface that induces some phase
transformation of copolymer matrix [26]. After incorporating 0.05 wt % reduced graphene oxide fillers in the copolymer matrix, the amount of nonpolar electroactive phase tends to reduce and electroactive β phase portion was found to be increased in X-ray diffraction analysis. From Figure 6, we can see the β phase intensity which keeps increasing in magnitude toward 0.1 wt % fillers loading. This also agrees with the Fourier transform infrared spectroscopy analysis at Figure 4. Similar findings were also observed by Alamusi et al. [10]. By increasing the fillers ratio, the amount of specific interaction with the copolymer and the excluded volume interaction, van der Waals force between adjacent reduced graphene oxide sheets tend to increase which results in an optimized crystalline electroactive phase of the nanocomposite [27]. Eventually, a self-aligned ordered structured of nematic phase from randomly oriented fillers isotropic phase can be observed (Figure 3(a,b)) as a result of excluded volume interactions between the conductive fillers and the high affinity between polymers wrapped amphiphilic reduced graphene oxide fillers [28]. The (%) crystallinity and crystallite size of the as prepared nanocomposites was calculated from X-ray diffraction (Figure 4) where a linear relationship between the crystallinity and crystallite size was observed [25]. The degree of Crystallinity (Xc) of the nanocomposites was calculated using the following Equation (1).

\[ X_c = \frac{\sum A_{Gr}}{\sum A_{Gr} + \sum A_{amr}} \times 100\% \]  

The average crystallite size of nanocomposites was measured from the FWHM at 2θ = 20.5° which is 110/200 plane of electroactive (β phase) P(VDF-TrFE), using Scherrer relation [9, 13]. A highest portion of almost 53% crystallinity and crystallite size of 16 nm was found at copolymer-0.1wt % filler case. Figure 5 shows a sharp reduction in the crystallinity and crystallite size of the nanocomposite after the percolation threshold (>0.09 wt %) of reduced graphene oxide. The changes in the nanocomposite’s crystallinity by higher wt % of reduced graphene oxide fillers, was shown schematically in Figure 7. A longer and bigger conductive network of reduced graphene oxide fillers (Figure 2(d,e)) adversely affects the surface uniformity and hence causes non-homogenous dispersion of conductive flakes through the copolymer matrix which reduces the nanocomposite crystallinity (Figures 3 and 4) [9]. The process of non-uniform dispersion of increased rGO wt % into the P(VDF-TrFE) is also shown schematically in Figure 7. After a percolation network completion (near 0.1 wt % reduced graphene oxide) in the copolymer matrix along with the isotropic to nematic phase transition, due to the high agglomeration of filler sheets, the dipoles of polymer are pinned by the surface charges or defects at the interface between the matrix and the filler sheets which can reduce the crystallinity and the piezoelectric effect of the nanocomposite [29]. Highly agglomerated fillers area can reduce the electrostatic force between the copolymer matrix and the
reduced graphene oxide functional groups that lower the crystallinity of the nanocomposite (Figures 5 and 6) [27, 28]. The AC conductivity ($\sigma = G \cdot A / L$) of a prepared nanocomposite was measured at room temperature ranges from 1 to 100 kHz (Figure 8) in impedance analyzer by taking the inverse of resistance value ($G$; conductance, ohm$^{-1}$), ($A$; cross sectional area, m$^2$), and ($L$; length, m). We used two samples for each amount of filler weight % and measured their average to calculate the AC conductivity. The optical image of the as prepared sample has been shown in Figure 1. Samples with 0, 0.05, 0.1, 0.15, 0.2 wt % of reduced graphene oxide in P(VDF-TrFE) matrix corresponding volume fractions 0, 0.04, 0.09, 0.14, 0.19 vol % using the simple rule of mixture as shown in Equation (2) [30].

$$\text{Vol} \% = \frac{W \rho_{(P(VDF-TrFE)}}{\rho_{\text{rGO}}} + w(\rho_{(P(VDF-TrFE)}} - \rho_{\text{rGO}})$$

Here, $W$ is the wt %, $\rho_{(P(VDF-TrFE)}}$ is the density of P(VDF-TrFE) and $\rho_{\text{rGO}}$ is the density of reduced graphene oxide [30]. The conductivity of the polymer/conductive-filler composite originates from two mechanisms: (1) ohmic conduction, through direct contact of conductive fillers, and (2) non-ohmic conduction, through the barrier-tunneling effect between the conductive fillers separated by a polymer layer. The percolation transition can be seen as the transition from non-ohmic conduction to ohmic conduction, when the filler concentration approaches the percolation threshold [4].

$$\sigma \propto (f_{\text{filler}} - f_c)^s \text{ for } f_{\text{filler}} > f_c$$

$$\sigma \propto (f_c - f_{\text{filler}})^t \text{ for } f_{\text{filler}} < f_c$$

In Equation (1), $f_c$ is the percolation threshold, $f_{\text{filler}}$ is the wt % of reduced graphene oxide fillers, and $s$ and $t$ are the critical exponents in the insulating ($f_{\text{filler}} < f_c$) and conducting ($f_{\text{filler}} > f_c$) region, respectively. The best fits of the experimental conductivity values to the log–log plots of the power
laws give $f_c = 0.09 \text{ wt} \% \ t = 1.82$, and $s = 0.86$ (Figure 9). A sharp increase in the conductivity between 0 wt % and 0.1 wt % was found where a percolation threshold of 0.09 wt % was calculated by using the power law of equation [25]. At percolation, continuous conductive channels are formed by reduced graphene oxide fillers through the copolymer matrix while beyond percolation the number of such conductive channels affects to increase agglomeration [24]. P(VDF-TrFE) matrix works as dielectric medium between adjacent reduced graphene oxide flakes which form micro-capacitor [8, 12, 22]. With the increasing of reduced graphene oxide flakes (Figure 2(b–e)) on the P(VDF-TrFE) matrix, an increasing phenomena in the dielectric constant of the as prepared nanocomposites were observed from the frequency range of 1000 to 100,000 Hz in Figure 10. The dielectric constant was calculated by using the Equation (4).

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d}$$  

(4)

Where, $C$ is the capacitance, $A$ is the area (m$^2$), $\varepsilon_r$ is the relative dielectric constant, $\varepsilon_0$ is the dielectric permittivity of free space, $d$ is the thickness of the nanocomposites [12]. Furthermore, the linearity between the crystallinity and energy harvesting properties was also observed as the piezoelectric charge constant $d_{33}$ (pC/N), and the crystallinity of the as prepared nanocomposites increases up to 0.1 wt % fillers ratio (Table 1). The highest amount of piezoelectric charge constants gave us enhanced open circuit voltage (average $\sim 9 \text{ V}$) and short circuit current (average 0.9 $\mu$A) from copolymer-0.1wt % fillers nanocomposite at 2N applied force (Figure 11(a,b)). The energy harvesting outputs has been summarized in Table 1.

4. Conclusions

In this article, five different kinds of piezoelectric nanocomposites were prepared to study the optimum crystallinity, $Ac$ conductivity, dielectric constant by analyzing the effect of conductive fillers wt % change associated with fillers structural phase shifting. Among these nanocomposites, the copolymer with 0.1 wt % fillers has shown an enhanced crystallinity of $\sim 53$% with a piezoelectric charge constant of $-23 \text{ pC/N}$ along with the open circuit voltage of $\sim 9 \text{ V}$ and the short circuit current of 0.9 $\mu$A. It was observed that, the nano alignment of rGO flakes affect the electroactive properties of the copolymer and near to percolation threshold an improved crystallinity, piezoelectric charge constant and dielectric properties can be achieved. These copolymer-reduced graphene oxide filler nanocomposites with such high crystallinity and electrical and dielectric outputs are potential results for practical applications in flexible electronics.

Disclosure statement

No potential conflict of interest was reported by the authors.

| Nanocomposite | Degree of crystallinity | Piezoelectric charge constant ($d_{33}$ pC/N) | Output voltage and current (average) |
|---------------|-------------------------|---------------------------------------------|-------------------------------------|
| Copolymer     | 40 $\sim$ 42%           | -13                                         | 1.5 V, 0.3 $\mu$A                   |
| Copolymer – filler 0.05 wt % | 44 $\sim$ 46%         | -18                                         | 4 V, 0.5 $\mu$A                     |
| Copolymer – filler 0.1 wt %      | 50 $\sim$ 52%           | -23                                         | 9 V, 0.9 $\mu$A                     |
| Copolymer – filler 0.15 wt %     | 34 $\sim$ 36%           | -8                                          | 0.6 V, 0.04 $\mu$A                  |
| Copolymer – filler 0.2 wt %      | 30 $\sim$ 32%           | -5                                          | 0.2 V, 0.002 $\mu$A                 |

Figure 11. (a) Short circuit current. (b) Open circuit voltage from Au/copolymer-reduced graphene oxide 0.1 wt %/PET-ITO nanogenerator.

Table 1. Degree of crystallinity, piezoelectric properties, and energy harvesting outputs of five different nanocomposites.
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