PVDF/Graphene Composite Nanofibers with enhanced piezoelectric performance for development of robust nanogenerators

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Abstract

Graphene reinforced Poly(vinylidene fluoride) composite nanofibers were prepared and their morphology, crystallinity, polymorphism and electrical outputs were investigated for the first time. . Nanofibers were prepared using electrospinning technique with different graphene contents. DSC, FTIR and WAXD analyses were used to evaluate the polymorphism of PVDF crystals upon graphene addition. It was observed that addition of a small amount of graphene (0.1%wt) significantly increased the $F(\beta)$ and open-circuit voltage of nanofibers. However, further increase in graphene content decreased the electrical output of randomly oriented nanofibers. The developed PVDF/graphene nanogenerator has the ability to fully synchronize the finger movement and its generated electricity can light up a commercial LED for 30 seconds. This new type of PVDF generator has the potential to be used as a self-charging power source and could be used in powering the personal electronics.

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1. Introduction

Since the first report by Wang et. al. [1] in 2006 on the potential of ZnO nanowires for energy harvesting, many attempts have been devoted to the development of nanoscale electrical power generators and several inorganic materials have been used as potential energy harvesters. This includes nanowire and nanorods made of inorganic materials such as ZnO[1-3], 1-D ZnO nanorods on a 2-D graphene electrode[4], CdS[5], GaN [6]and ZnS[7]. These nanoscale electrical generators can power personal portable electronic devices, wireless sensing and implantable biological devices. Nevertheless, the inorganic materials are brittle in nature and have low formability which limits their application. On the other hand, polymeric electrical generators display exceptional formability and possess a lower weight which makes them ideal for application where light weight is required[8-10].

Poly(vinylidene fluoride) (PVDF) and its copolymers are the most extensively studied polymers for piezoelectric generators[11-17]. It is well-known that PVDF have five different polymorphs of β , α , γ , ϵ and δ . Among various PVDF polymorphs, considerable attention has been paid to α , β and γ phases. β -polymorph has an all-trans conformation, α -polymorph has a trans- gauche⁺-trans-gauche⁻ (tg⁺tg⁻) conformation and γ -polymorph has a conformation between α - and β -phases (tttg⁺tttg⁻)[18-22]. Out of five polymorphs of PVDF, β -polymorph demonstrates piezoelectric properties due to its all-trans conformation which enable its crystals to have unidirectional polarization[23, 24]. Meanwhile, the most thermodynamically stable polymorph is

α ; therefore, there is a great interest to change this polymorph to β form. In our earlier work, we have shown that nanofillers can change the α polymorph to β form [25-27].

Several studies in literature report the power outputs of electrical generators based on PVDF nanofibers and films. Fang et. al. [28] claimed that PVDF nanofiber-based electrical generators have higher power outputs than that of PVDF thin films. Some of the reported electrical output of PVDF generators are as follows: PVDF nanofibers (20 mV/0.3 nA)[29], single PVDF nanofiber (30 mV/3 nA)[30], PVDF film (0.4 V) [31], porous PVDF film (1.3 V/0.3 μ A)[32], PVDF mats (1 V)[33], PVDF microbelts (6 V)[34], Porous PVDF film (11 V/10 μ A)[29], PVDF nanofiber membranes (2.2 V/4.5 μ A)[28]. One thing that stands out from these reported data is that there is still opportunity for improvement in their electrical performance and that there is need to further increase the electrical outputs of these devices. In this regard electrospinning is a convenient method to prepare nanogenerator without further treatment. It has been proven that the physico-chemical properties and electrical output of the electrospun fibers strongly depend on the processing conditions[35, 36].

Recently, several research groups demonstrated the potential of graphene for improvement of electrical output in PVDF based generators. This improvement in piezoelectric performance is mainly due to the role of graphene in inducing the β polymorph in PVDF films [37-43]. Most reported values for electrical output of generators are in the order of tens of mV, however, Alamusi et al. [38] reported open circuit voltage of 4V for samples with 0.2 wt% graphene. Considering higher electrical output of PVDF nanofibers compared to PVDF films and influence of graphene on enhanced performance of PVDF films, herein we report on development of nanofiber-based PVDF/graphene electrical generator with extremely high electrical output. Our results show a two-fold increase in electrical output of PVDF nanofiber. To the best of our

knowledge, this is the first time that piezoelectric properties of PVDF nanofibers containing graphene nanoplatelets are reported.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF) ($M_w=275000$ g/mole, $M_n=107000$ g/mole) and Dimethylformamide (DMF) were purchased from Sigma Aldrich, Inc. and Graphene nanoplatelets were supplied from XG science Inc grade C.

2.2. Electrospinning of PVDF/graphene nanofibers

PVDF/DMF solutions (20 wt.%) containing different graphene contents (0%, 0.1%, 1%, 3% and 5%wt) were sonicated for 20 min followed by stirring at 60 °C over night. The electrospinning conditions were adjusted at spinning voltage, working distance and feeding rate of 20 kV, 17 cm and 1 ml/h, respectively. The sample details of electrospun PVDF/graphene nanocomposites have been listed in Table 1.

Table 1. PVDF/graphene electrospun nanocomposites

Sample code	graphene (% wt)
K0	0
K0.1	0.1
K1	1
K3	3
K5	5

2.3. Scanning electron microscope (SEM)

SEM imaging was conducted using Zeiss Supra TM 55VP SEM after sputter-coating the samples with gold. Image J software was used to estimate the mean diameters of electrospun nanofibers.

2.4. Transmission electron microscope (TEM)

A Gatan Orius SC1000 digital camera on a JEOL 2100 transmission electron microscope (TEM) operating at an accelerating voltage of 200kV was used for TEM imaging.

2.5. Fourier transfer infrared (FTIR) spectroscopy

To analyze the polymorphism of PVDF/graphene electrospun nanofiber, a Bruker 70 FTIR device was used at 64 scans from 600 cm^{-1} to 2000 cm^{-1} using a resolution of 4 cm^{-1} .

2.6. Differential scanning calorimetry (DSC)

DSC thermographs of PVDF/CNC electrospun nanocomposites were obtained through heating the samples from $25\text{ }^{\circ}\text{C}$ to 220°C with heating rate of $10^{\circ}\text{C}/\text{min}$. This was conducted on a TA Instrument Q200 differential scanning calorimeter.

2.7. Wide angle X-ray diffraction (WAXD)

X-ray patterns of PVDF/graphene nanofibers were obtained using PANalytical XRD diffractometer at 40 kV and 20 mA in the range of $2\theta = 5 - 40^{\circ}$.

2.8. Piezoelectric testing of electrospun nanocomposite fibres

To assess the electrical output of PVDF/graphene nanofiber, mats with thickness of $50\text{ }\mu$ were prepared and mats with dimension of $2 \times 2\text{ cm}^2$ were sandwiched between two metal electrodes. Then, a custom-built cyclic compression tester made of solenoid was used to mechanically impact the samples using a $2 \times 2\text{ cm}^2$ plastic hammer with adjustable frequency and load as shown in Figure1, open circuit voltage and short circuit current were measured using an oscilloscope. Voltage on capacitance was measured across a $1\mu\text{F}$ capacitor at different time intervals.

Figure 1. Schematic images of piezoelectric test device, a plastic hammer impacted the nanofiber mat sandwiched between two metal electrodes and the output voltage measured by an oscilloscope.

3. Results and Discussions

SEM images of electrospun nanofibers are presented in Figure 2 which shows a beaded morphology for PVDF nanofibers. Addition of graphene to PVDF nanofibers clearly reduced the number of beads. Decrease in bead content with increasing the graphene amount can be related to the fact that the charge density of the polymer solutions is increased in presence of graphene. Increased charge density will generates a higher elongational force on the ejected jets and therefore will result in a bead free morphology.

Figure 2. SEM images of PVDF/graphene electrospun nanofiber (a) K0: 0%, (b) K0.1: 0.1%, (c) K1: 1%, (d) K3: 3% and (e) K5: 5%. Scale bar is 10 μm . (f) TEM images of K0.1: 0.1%.

Table 2. Mean diameters of PVDF/graphene electrospun fibers with different graphene loadings

sample	K0	K0.1	K1	K3	K5
Mean diameter (nm)	165±10	107±8	106±8	80±7	229±21

This higher elongational force can also reduce the fibers diameters as demonstrated in Figure 2. The mean diameter of PVDF nanofibers have been calculated and presented in Table 2. As shown, mean diameter for PVDF nanofibers decreased significantly with addition of graphene to PVDF solution. Contrarily, for K5 sample with 5wt% graphene a significant increase in diameter observed. This phenomenon can be due to the fact that 5wt% is above the percolation threshold of graphene in the nanofibers; therefore, there is more elongational forces on the graphene compared to polymer solution which in turn leads to ejected jet stretching as if it is neat PVDF solution as shown schematically in Figure 3 and confirmed by TEM images. **Figure 3.a and 3.b presents the TEM image of sample K0.1 and K5. As can be seen from Figure 3.a diameter of K0.1 sample increases where the graphene present inside the nanofiber while rest of nanofiber has lower diameter. However, for sample K5 with 5% graphene whole the nanofiber has higher diameter as grapheme presents everywhere inside the nanofiber. Nevertheless, the TEM image of sample K5 can explain the reason for disappearing of the beads in this sample. Whole the fiber is filled with graphene and wiping instability can't occur in sample K5.** We found that this increase in nanofiber diameter for K5 sample has a significant effect on the electrical output. DSC thermograms of PVDF and PVDF/graphene nanocomposite fibers are presented in Figure 4. All nanofibers demonstrated an endothermic peak at 170 °C associated with the melting temperature of PVDF.

Figure 3. a) In low graphene content polymer solution is stretched during the electrospinning while (b) sample with high graphene content elongational force is largely applied onto the graphene network rather than onto polymer solution.

Table 3 shows the values of heat of fusion (ΔH_m) and crystallinity content (X_c) for the electrospun nanofiber calculated using equation 1.

$$X_c = \frac{\Delta H}{x_\alpha \Delta H_\alpha + x_\beta \Delta H_\beta} \quad (1)$$

where, ΔH is the melting enthalpy, x_α and x_β are the α - and β -phase content, respectively. ΔH_α and ΔH_β are the melting enthalpies of a 100% crystalline α and β -phases, respectively[44]. Values of 93.07 Jg^{-1} and 103.4 Jg^{-1} was used as a melting enthalpies of 100% crystalline α and β -phases, respectively. x_α and x_β were obtained from the FTIR measurements and equations 2 to 4:

$$A_{763} = K_\alpha^{763} \cdot X_\alpha \cdot t \quad (2)$$

$$A_{1275} = K_\beta^{1275} \cdot X_\beta \cdot t \quad (3)$$

$$A_{840} = (K_\beta^{840} \cdot X_\beta + K_\gamma^{840} \cdot X_\gamma + K_{am}^{840} (1 - X_{total}))t \quad (4)$$

where A_j is the baseline-corrected absorbance in jcm^{-1} , X_i is the mole fraction of the i phase, t is the thickness in micrometers, K_i^j is the absorption coefficient at $j \text{ cm}^{-1}$ for the i phase and X_{total} is the total crystallinity. On the other hand the thickness of the nanofiber mats was measured using absorption peak at 1070 cm^{-1} , where the absorption coefficient is independent polymorphism and can be presented as: $A_{1070} = 0.095t + 0.07$ [44]. The calculated absorption coefficients were 0.132, 0.140 0.150, 0.365 and 0259 μm^{-1} , for K_β^{840} , K_β^{1275} , K_γ^{840} , K_α^{762} and K_{am}^{840} , respectively[44].

Figure 4. DSC thermogram of PVDF/graphene electrospun nanofibers

Table 3. DSC results of electrospun nanofibers

PVDF/graphene nanocomposite	K0	K0.1	K1	K3	K5
Melting temperature (°C)	168.7	170.2	170.3	170.1	169.2
Melting enthalpy (J/g)	47.9	37.6	35.6	33.3	32.4
X_c (%)	50	41	39	36	35
$F(\beta)$ (%)	77±2	83±4	76±3	74±2	75±2

As shown in Table 3, PVDF crystallinity dropped from 50% to 41% with addition of only 0.1wt% of graphene; however, further addition of graphene gradually decreased the crystallinity to 35%. This suggests that graphene acts as a nucleating agent, as during the electrospinning process a large number of nuclei grow simultaneously in a restricted space of nanofiber. The nucleating effect of carboneous nanomaterials have been reported previously [45]. This large number of nuclei cause further crystal defects which in turn lead to the lower percent crystallinity[46].

X-ray and spectroscopy analysis were used to obtain a detailed understanding of PVDF polymorphism. WAXD pattern and FTIR spectrum of PVDF and PVDF/graphene nanofibers are presented in Figure 5 and 6. PVDF electrospun nanofiber show three characteristic peaks at $2\theta=18.5^\circ$, 20.1° and 27.0° associated to the reflections of α (020), β ((200), (110)) and α (111) polymorphs, respectively [47-49]. Interestingly it can be observed that in sample containing 0.1 wt% graphene, the distinct α peak at $2\theta=18.5^\circ$ change to β characteristic shoulder peak at 20.1° ; and α peak at 27.0° completely disappears. Nevertheless, for nanofiber samples with higher graphene content α characteristic peaks at $2\theta=18.5^\circ$ and 27.0° emerge again.

To quantitatively investigate the effects of graphene on polymorphism of PVDF nanofibers, FTIR analysis was conducted as shown in Figure 6. The FTIR spectrum of the electrospun nanofibers shows both α and β characteristic peaks at 763 cm^{-1} and 840 cm^{-1} , respectively. To calculate the amount of β polymorph in PVDF and PVDF/graphene composite nanofibers equation 2 was employed [44]:

$$F(\beta) = \frac{A_\beta}{1.26A_\alpha + A_\beta} \quad (2)$$

Figure 5. WAXD patterns of PVDF/graphene electrospun with various graphene contents: K0: 0%, K0.1: 0.1%, K1: 1%, K3: 3% and K5: 5%.

Figure 6. FTIR spectra of PVDF/graphene electrospun nanofibers

where A_{α} and A_{β} are absorption peaks of α (763 cm^{-1}) and β (840 cm^{-1}) polymorphs. It is worth to note that $F(\beta)$ increased significantly for K0.1 sample with only 0.1wt% graphene content while samples containing more than 0.1wt% graphene have the same amount of $F(\beta)$ as pristine PVDF nanofibers (Table 3). **Graphene addition induced charge accumulation at the boundary,**

and thus facilitated the arrangement of the PVDF chains in the b-phase conformation[50].

Figure 7. Swapping the negative and positive electrodes has reversed the front and the back peak position when K0.1 sample impacted with frequency of 5Hz.

To examine whether the observed signal could be related to the PVDF piezoelectric output, the reversibility test was conducted. From Figure 7 it is clear that by swapping the positive and negative electrodes, the front and back peaks are reversed. These results demonstrate orientation of PVDF dipoles along the mat thickness as recently suggested by Mandal et. al. [51].

To demonstrate the potential use of the developed PVDF/graphene nanofibers as nanogenerators, conversion of mechanical energy to electricity was examined for a finger tapping action through a press-hold-release process (Figure 8 and Video S1). We found that electrospun nanofiber generators demonstrate good synchronization of finger movements. Mechanical strain during the pressing action produces piezo-potential along the mat thickness and consequently free electrons will transfer across the positive and negative electrodes using an external circuit. These free electrons will accumulate at the electrode nanofibers interface and create a positive voltage peak. During the holding action, free electrons are balanced by piezo-potential through external circuit,

therefore no voltage peak is observed. However, during the release action, piezo-potential vanishes and accumulated free electrons are back in to the electrode and therefore negative

Figure 8. Voltage values induced upon press-hold- release process by finger in PVDF/graphene nanofibers generator.

signal is observed which is the typical behavior of nanofiber generators. To investigate the effect of graphene on the open-circuit voltage (Voc) and short circuit current (Isc) of samples, nanofiber generators were impacted by 0.2 MPa pressure and frequency of 1Hz as presented in Figure 9. It can be seen that presence of only 0.1wt% graphene in PVDF nanofibres increased open-circuit voltage and short-circuit current from 3.8 to 7.9V and 2-4.5 μ A, respectively. This could be due to the higher F(β) content of nanofiber sample containing 0.1 wt% graphene (K0.1) compared to pristine PVDF (K0). Open circuit voltage of PVDF/graphene nanofibers decreased with further increase in graphene content which can be attributed to the lower F(β) and crystallinity. However, interestingly sample K5 shows very low output voltage of 0.85V. Given that graphene is a very conductive additive, it can be assumed that 5wt% is above the percolation threshold of graphene and therefore a conductive mat is formed causing short-circuit in electrodes. Generally speaking, output voltage of nanofiber generators have a complex

relationship with several factors such as $F(\beta)$, crystallinity, nanofibers diameter and conductivity of nanofiber mat. Further research is required to separate contributing factors of individual parameters in electrical output of nanofiber-based electrical generators.

The values obtained for electrical output of PVDF/graphene nanofibers are similar to the reported voltage for PVDF/CNT (8V) [52] and P(VDF-HFP)/silver (3V) [53] nanofibers . A simple rectifying bridge can create positive signals to simply charge a capacitor. Figure 10 shows voltage on capacitance of a $1\mu\text{F}$ capacitor for K0.1 sample. It is clear that this sample is able to charge the capacitor to 6.5V. To further confirm this, a LED light was turned on for more than 30s when a $33\mu\text{F}$ capacitor was charged to 6.5V (Video S2). This demonstrates the potential application of the developed electrospun PVDF/graphene nanofibers as the portable self-powering devices.

Figure 9. (a) V_{oc} for electrospun generators and (b) comparing the V_{oc} and I_{sc} values of the dopes.

Figure 10. Voltage on Capacitance when a rectifying bridge was used to charge a 1 μ F capacitor

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4. Conclusion

In this study, effect of addition of graphene nanoplateles on crystallinity, polymorphism and electrical output of PVDF electrospun nanofiber generators were investigated. SEM images revealed that the presence of graphene up to 5wt% reduces nanofibers diameter. Based on DSC analysis, increasing the graphene content from 0.1wt% to 5wt% decrease the nanofibres crystallinity from 46% to 32%, respectively. Formation of both α and β polymorphs in samples was confirmed by FTIR and WAXD analysis and FTIR evaluation of polymorphism demonstrated that addition of 0.1wt% of graphene increased $F(\beta)$ from 77% to 83%. However,

further addition of graphene decreased the $F(\beta)$ to 75%. Significant increase in piezoelectric output of PVDF nanofibers was observed when only 0.1wt% of graphene was used. Open-circuit voltage of PVDF nanofiber was 3.8V while addition of 0.1% graphene increased this value to 7.9V. To the best of our knowledge this is the first time that the role of graphene nanoplatelets on increasing the electrical output of the PVDF nanofiber generators is reported. This study demonstrates the potential application of graphene- PVDF composite nanofibers for portable self-powering electronic devices.

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