Original Article

Investigation on the electrospun PVDF/NP-ZnO nanofibers for application in environmental energy harvesting

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\textbf{A B S T R A C T}

PVDF is one of the most widely used dielectric polymers that has four phases. Among them, only its β phase shows piezoelectric property, which is accessible through an electrospinning synthesis method. In this research, a solution of dimethylformamide (DMF) and tetrahydrofuran (THF), with different ratios, and two different polymer concentrations, as well as various ZnO percentages, were used for synthesis of PVDF/NP-ZnO nanofibers composite. The samples that led to the formation of nanofibers were characterized. The results indicate that nanofibers were appropriately formed at lower concentrations of polymer and zinc oxide with equal ratio of the two solvents. To study the effects of synthesis conditions on the morphology and diameter of the nanofibers, the samples were synthesized at different intervals and at different injection rates. The results show that at lower intervals, the injection rate should be reduced to form more uniform nanofibers without nodes and sprays. Finally, flexible piezoelectric nanogenerators were fabricated based on the best samples and were tested under vibrational mechanical forces. The results indicate a maximum output power of 32 nW/cm\textsuperscript{2}. The greater output current and voltage were resulted by using more uniform and stretched nanofibers.

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\textbf{1. Introduction}

Today, alternative energy sources are widely considered by many researchers as potential solutions to many economic and environmental challenges due to the dominance of world energy supply by fossil fuels. Among them dissipated environmental energies have been widely considered. As new sources of energy, they can be employed to supply electrical energy for various self-biased sensors, low power instrumenta

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water waves, and etc. The piezoelectric effects of materials can be used to produce electrical energy by using a suitable device designing. Among them, piezoelectric nanofibers of polyvinylidene fluoride (PVDF) have been widely employed in fabrication of nanogenerators or high sensitivity sensors and actuators, due to the particular properties such as flexibility, high porosity and high-surface area, chemical and mechanical stability, and environmentally friendly [3,4] behavior.

There are several methods that can be used to synthesis PVDF nanofibers and its nanocomposites. Among them, electrospinning, as a highly controllable method, is capable of converting PVDF into nanofibers, enhancing it with piezoelectric properties. Other methods are drawing, template synthesis, phase separation, self-assembly, and etc., which have been already used to synthesis all kinds of nanofibers [5].

Electrospinning is an easy and low cost method with industrial production capability. Schematic of the electrospinning system which is used in this study is shown in Fig. 1. The system involves a high voltage power supply, the injection pump, a syringe, and a cylindrical collector coated with aluminum substrate. Some of the parameters that affect the electrospinning process are: (1) solution properties such as viscosity, surface tension, electrical conductivity, (2) machine parameters such as injection rate, voltage and distance, and (3) environmental parameters such as solvent temperature, humidity, and velocity of air flow [6–13].

The PVDF polymer has 4 phases α, β, γ and δ, among which the β phase is oriented in such direction which showing the property of polarization. In normal mode, this polymer exists in β phase. Using an electrospinning method, in presence of a suitable electric field, PVDF polymer can be converted from α phase to β one. Many studies have been done on the synthesis of PVDF nanofibers and their applications in nanogenerator fabrication. The first time, Chang et al. [10] investigated a piezoelectric nanogenerators using PVDF nanofibers which were synthesized in a field-close electrospinning method. They obtained an 30 mV output voltage from their fabricated nanogenerators, when was actuated with an external vibrational forces. The maximum output current of their nanogenerators exceeds 4 nA. Further, Nakashima et al. [1] examined the mechanical properties of PVDF electrospun nanofibers, which was synthesized from PVDF solution with 16 to 24%wt PVDF. They disclosed that by increasing the solution concentration, smoother and thicker fibers can be achieved. They also showed that the diameter of the fibers increased linearly with the solution concentration. They mentioned that the result has been due to the increased viscosity of the solution. In 2013, Dhananjay et al. [3], studied the effect of synthesis parameters on the diameter and morphology of PVDF electrospun fibers. They observed that when the voltage increases, the mean diameter of the fiber decreases. In other published work, a 22 mV output voltage has been resulted by application of electrospun PVDF nanofibers in piezoelectric nanogenerators [14]. A PVDF-ZnO nanocomposite synthesized by electrospinning method was also applied in nanogenerator fabrication [15]. It has been indicated that the output voltage of nanogenerator increases from 351 mV to 1.1 V, when employing ZnO nano-particles in PVDF nanofibers. However, simultaneous effects of the nanoparticle additive ratios, with other effecting parameters, has not been well understood. In this paper, a composite of zinc oxide nanoparticles (NP-ZnO) and PVDF polymer is considered for nanogenerator application profiting from simultaneous properties of two piezoelectric materials, ZnO ceramic and PVDF polymer. Various percentages of ZnO nanoparticle are added to the PVDF/DMF/THF solution, which is prepared for synthesis the nanofibers by electrospinning method. Besides the effect of the electrospinning system conditions and the solution components, the effects of NP-ZnO percentage in the properties of the synthesized nanofibers, and in the amount of the output power of the fabricated nanogenerators are also investigated.

2. Experimental

Required materials including polyvinylidene fluoride (PVDF) with a molecular weight of 534,000 provided from Sigma Aldrich Co., and dimethylformamide and tetrahydrofuran solvents from Merck Inc, Zinc oxide, zinc nitrate and high purity potassium hydroxide from Sigma Aldrich Co are used for NP-ZnO synthesis.

2.1. Synthesis of NP-ZnO

In order to synthesize NP-ZnO, the solutions of 2.0 M zinc nitrate and 4.0 M potassium hydroxide were prepared in distilled water. To do this, the required amounts of each solution were calculated and added into 250 mL distilled water. Then, the solution was placed on a magnetic stirrer for 15 min. When a uniform solution was formed, KOH was slowly added to the solution while still was on the stirrer while its temperature was remained at the room temperature. After a while, a gel-like solution was formed. The gel solution was filtered to completely separate the remaining liquid from the gel. To do it, the gel was poured into distilled water, where washed and filtered. After three times of washing and filtering, the gel was placed in a furnace at 500 °C for 3 h to form a yellow powder. To determine the size and shape of the nanoparticles, the powder was analyzed using SEM.
Table 1 – Conditions for synthesis of nanofiber samples using electrospinning system.

<table>
<thead>
<tr>
<th>Field intensity (kV/cm)</th>
<th>Distance (cm)</th>
<th>Flow rate (mL/h)</th>
<th>DMF:THF ratio</th>
<th>ZnO concentration (wt%)</th>
<th>PVDF concentration (wt%)</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>10</td>
<td>0.5</td>
<td>1:1</td>
<td>7</td>
<td>15</td>
<td>A</td>
</tr>
<tr>
<td>1.1</td>
<td>10</td>
<td>1</td>
<td>1:1</td>
<td>7</td>
<td>15</td>
<td>B</td>
</tr>
<tr>
<td>0.733</td>
<td>15</td>
<td>1</td>
<td>1:1</td>
<td>7</td>
<td>15</td>
<td>C</td>
</tr>
<tr>
<td>1.2</td>
<td>10</td>
<td>1</td>
<td>3:1</td>
<td>7</td>
<td>15</td>
<td>D</td>
</tr>
<tr>
<td>1.12</td>
<td>10</td>
<td>0.5</td>
<td>3:1</td>
<td>7</td>
<td>15</td>
<td>E</td>
</tr>
<tr>
<td>1.4</td>
<td>10</td>
<td>1</td>
<td>1:1</td>
<td>12</td>
<td>15</td>
<td>F</td>
</tr>
<tr>
<td>1.85</td>
<td>10</td>
<td>1</td>
<td>3:1</td>
<td>12</td>
<td>15</td>
<td>G</td>
</tr>
<tr>
<td>2.35</td>
<td>10</td>
<td>1</td>
<td>3:1</td>
<td>18</td>
<td>15</td>
<td>H</td>
</tr>
<tr>
<td>2.3</td>
<td>10</td>
<td>0.5</td>
<td>3:1</td>
<td>18</td>
<td>15</td>
<td>I</td>
</tr>
<tr>
<td>1.75</td>
<td>10</td>
<td>1</td>
<td>3:1</td>
<td>7</td>
<td>18</td>
<td>J</td>
</tr>
<tr>
<td>1.2</td>
<td>10</td>
<td>0.5</td>
<td>3:1</td>
<td>7</td>
<td>18</td>
<td>K</td>
</tr>
<tr>
<td>2.6</td>
<td>10</td>
<td>0.5</td>
<td>1:1</td>
<td>12</td>
<td>18</td>
<td>L</td>
</tr>
<tr>
<td>1.75</td>
<td>10</td>
<td>1</td>
<td>3:1</td>
<td>12</td>
<td>18</td>
<td>M</td>
</tr>
<tr>
<td>1.7</td>
<td>10</td>
<td>0.5</td>
<td>3:1</td>
<td>18</td>
<td>18</td>
<td>N</td>
</tr>
</tbody>
</table>

2.2. Synthesis of PVDF/NP-ZnO

To synthesize nanofiber samples, different compositions for the solution were used. First, according to Table 1, the solvents were mixed with two different proportions for DMF:THF, as 1:1 and 3:1, and then the PVDF polymer was added to the solvents with two concentrations of 15 and 18%wt. Subsequently, NP-ZnO with three weight percentages; 7, 12 and 18, were added to the solution where was placed on the stirrer for 24 h. To remove the bubbles, the solution was placed in an ultrasonic bath for 10 min. Finally, a clear and uniform solution was obtained and was poured in the syringe of the electrospinning machine. Electrospinning conditions consisted of two different distances from needle tip to collector, 10 and 15 cm, and two injection rates of 0.5 and 1 mL/h. Samples were synthesized at ambient temperature with 18 gage needle. The selected distances are in the usual electrospinning range. Lower distance ranges is considered as field-close electrospinning method [16]. In this type of electrospinning, in order to keep the diameter of the nanofibers in a range of 100 nm, and do not get thicker, two rates of the lowest possible injection rates were chosen [17]. With the chosen conditions, it was possible to synthesize 15 samples of nanofibers. The latter corresponding conditions are mentioned in Table 1. The combinations of other possible conditions, which are not included in the table, were also considered for the synthesis of nanofibers, but because of the non-continuous and spray-form films, they were removed from the list of the samples. It should be noted that after considering other conditions, the electrospinning voltages were considered so that the solution can be ejected from the syringe toward the collector, due to the enough generated electrostatic force by the applied electric field.

3. Results and discussion

3.1. Results of ZnO synthesis

The morphology of ZnO nanoparticles was studied using a scanning electron microscope (SEM), the result is depicted in Fig. 2. As shown, zinc oxide nano-particles are well formed and the particles size approximately is within the nanometer range. To determine the distribution of the particles size, the image obtained from the SEM was investigated using Image J software. It is shown in Fig. 3. The graph shows that the average zinc oxide particle is between 50 and 100 nm, and about 60% of the formed particles are less than 100 nm in size.
3.2. Results of PVDF/NP-ZnO synthesis

As was mentioned in the experimental work, the synthesized zinc oxide nanoparticles, with various percentages, were added to the prepared solution for synthesis of PVDF nanofibers. In the synthesis steps using an electrospinning device, it was observed that with increasing the DMF ratio, which augments the surface tension strength of the solution, it was necessary to increase the applied voltage to produce a stable jet of the solution toward the collector. In Fig. 4, a PVDF/NP-ZnO film is shown which was detached from the aluminum substrate, indicating the formation of a continuous and stable layer. SEM analysis was performed only on samples of the stable films to study the morphology and the diameter of nanofibers.

3.2.1. SEM analysis of PVDF/NP/ZnO films

SEM images from electrospun PVDF/NP-ZnO samples are shown in Fig. 5. In this figure, the presence of zinc oxide nanoparticles is observed on PVDF fibers. Examining SEM images show that only a handful of samples have made good nanofibers among synthesized specimens. As it is seen in samples B, F, G and H, there is a spray-form with nano-fissures, which indicates that the applied electrospinning conditions does not match with their solvent specifications. Since the samples I, J, K, L, M, N and O showed complete spraying and did not produce the stable films. The images of these specimens are not presented.

Discussing samples of the case of 10 cm distance between syringe and the collector. Comparing to the sample A, in the case of sample B the injection rate increases, more spraying forms and nodes were produced. It should be indicated that in such conditions, the solution did not have enough time to be stretched and formed the fiber. It means that the injected jet from the tip of the needle reached the collector before it gets dried. However, in sample A, due to the fact that less volume flow rate of the solution exits from the tip of the needle, the solution can be dried up before reaching the collector and forms nanofibers on the substrate. The mentioned problem for sample B is resolved by increasing the needle distance to the collector. The latter is the case of sample C, as shown in Fig. 5C, where, at a higher distance, the output jet found enough time to dry before reaching the collector.

In sample D, all conditions are the same as sample B, except the ratio of the two solvents that has been changed. In this case, increasing of DMF part in the solution, which has a lower boiling point compare to THF, the drying conditions of the solution are improved prior reaching to the collector. Thus the nanofibers are formed more appropriately. Under these conditions, with the reduction of the injection rate, which is used for the synthesis of sample E, spraying form does not occur, but the produced nanofibers are non-uniform. In samples F and G, where the proportion of NP-ZnO in the solution are increased, a large amount of spraying and nodes are formed. Increasing the DMF ratio in the solvent, case of sample G, the morphological state of the fiber has been degraded again and more nodes and sprays are occurred. These conditions have not been corrected by reducing the injection rate, which is the case of samples I, K, L and O (see Table 1), without any form of nanofibers. Comparing the SEM images of the samples shows that the using higher ZnO content in the solution, the fiber condition in terms of nodes and spraying form is more degraded. Thus adding ZnO percentage, more than 7%, completely eliminates the proper electrospinning conditions to form the nanofibers.

It is also observed that increasing the polymer content in the solution, even in the low zinc oxide weight ratio, which is the case of J and K samples, electrospinning was not performed. In such cases further reduction in the weight percent of NP-ZnO may improve the formation of the nanofibers.

From the nanofiber synthesis results, it is also concluded that with augmenting distance between the needle and collector and with increasing the injection rate, the applied voltage of the electrospinning should be also increased to provide enough electrostatic forces for creating the jet of the solution.

3.2.2. Diameter distribution in PVDF/NP-ZnO nanofiber samples

PVDF/NP-ZnO nano-fibers that formed stable films were investigated in terms of diameters by Image J software. Broad distribution of ZnO nanoparticles mean diameter is seen in Fig. 6. Such a broad distribution can be resulted because of increasing the time of the sintering of the solution. These causes to grow up the particles with different sizes.

According to this figure, samples A and C have the fiber diameter in range of 200 nm to one microns. However most of the fibers are located in the upper range. In sample D, most fibers have a diameter of less than 600 nm, and there are plenty of fibers in diameter below 200 nm. In sample E, the diameter of the fibers is increased, about 50% of the fibers have diameters between 400 and 800 nm, and near 30% of the fibers have a diameter greater than 1 micron. Investigating the diameter distributions in samples shows that the presence of ZnO significantly reduces the diameter of the fibers. The reason is due to an increase in the conductivity of the solution in presence of the larger amounts of ZnO. However, it is seen that the diameter reduction has been associated with nodes and droplets, which can be linked to a fiber diameter of less than 100 nm. The latter is equal to the diameter of the ZnO nanoparticles that does not allow the particles to well sit on or in the fibers.

In the samples with fiber diameter larger than the diameter of nanoparticles, such as the sample E, nanoparticles are placed on or in the fibers. But in samples G, H, I and J, with an average
Fig. 5 – SEM images of electrospun PVDF/NP-ZnO samples.

3.2.3. XRD results of PVDF/NP-ZnO

XRD analysis was used to determine the formation of beta-phase in the polymer and the presence of ZnO nanoparticles in the composite. As seen in Fig. 7, XRD chart shows the formation of the beta phase (marked with green at $2\theta \approx 20$ degree), which is responsible for PVDF piezoelectric property. Also, the presence of ZnO, as indicated by the red lines in the XRD
Fig. 6 – Diameter distribution of PVDF/NP-ZnO nano-fibers.

chart, is well compatible with the literature [18]. Aluminum peaks (which are marked in blue) also refer to the aluminum substrates that it was not detached before the analysis [19].

3.3. PVDF/NP-ZnO characterization

3.3.1. Instantaneous output current and voltages

PVDF/NP-ZnO films from A, C, D, E and F nanofiber samples, which were deposited on Al (as bottom contact) substrates, were cut into 1cm × 1cm sheets and coated with Al, as the upper metallic contact. In this way, five piezoelectric nanogenerators were fabricated. Fig. 8 shows the schematic of the prepared nanogenerators.

Performance of the fabricated nanogenerators was examined by applying vibrational mechanical forces at two frequencies of 4 and 8 Hz with a constant magnitude of 1.5 N. The peak to peak values of the output voltage and current are mentioned in Table 2. Comparing the measured outputs shows that, with increasing frequency, voltage and current flow increased in some samples.

But, in general, it can be said that the instantaneous output is not very sensitive to the frequency range used in the applied forces. In the output of the samples given in Table 2, the sample 5, which has thinner nanofibers, is more sensitive to the applied frequency. The reason for this may be attributed to the presence of more ZnO in the sample, because Np-ZnO is harder comparing to the PVDF polymer. The latter fact causes a slightly increasing in the hardness of the entire sample.

However, due to the fact that the nanofibers are very thin as seen in this sample and a lot of spraying form also were produced that decreased the quality of the film, the sample 5 shows less output current and voltage. Also, the outputs of the nanogenerator based on the sample D, which uses a larger proportion of DMF in its synthesis procedure, has very thinner nanofibers, is more sensible to the applied frequency. The latter is believed to be due to an increase in hardness of the sample.

Among the fabricated nanogenerators, sample 1, which is based on the sample A of the synthesized nanofibers, provides better output current and voltage. However for this sample, it is seen that, as the frequency increases, the amplitude of the current and voltage decreases. The reason believed to be due to the large diameter of the nanofibers, which augments the mass of the sample, a little bit more than the other samples.

The voltage and current instantaneous curve of the sample 1 is plotted at two mentioned frequencies, in Fig. 9.

3.3.2. Calculation of the effective output power

At this step, to calculate the effective power produced by the nanogenerators, the piezoelectric nanogenerators’ root mean squares (rms) of the voltage and current were measured simultaneously over a constant load, about 50 kΩ, at the applied forces with frequencies of 4 and 8 Hz. Then, by multiplying the maximum value of the output currents and voltages, the maximum output powers are calculated. The

Fig. 7 – XRD analysis of PVDF and PVDF/NP-ZnO nanofibers films.

Fig. 8 – Schematic of PVDF/NP-ZnO nanogenerators.
Table 2 – The peak to peak values of output current and voltage measured on PVDF/NP-ZnO nanogenerators.

<table>
<thead>
<tr>
<th>Current at 8 Hz (µA)</th>
<th>Current at 4 Hz (µA)</th>
<th>Voltage at 8 Hz (mv)</th>
<th>Voltage at 4 Hz (mv)</th>
<th>Number of NPs in 4900 µm² of nanofiber</th>
<th>Nano fiber film</th>
<th>Sample nano generator</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>0.04</td>
<td>60</td>
<td>80</td>
<td>450</td>
<td>A</td>
<td>1</td>
</tr>
<tr>
<td>0.02</td>
<td>0.015</td>
<td>80</td>
<td>80</td>
<td>450</td>
<td>C</td>
<td>2</td>
</tr>
<tr>
<td>0.03</td>
<td>0.02</td>
<td>70</td>
<td>60</td>
<td>460</td>
<td>D</td>
<td>3</td>
</tr>
<tr>
<td>0.02</td>
<td>0.025</td>
<td>60</td>
<td>50</td>
<td>480</td>
<td>E</td>
<td>4</td>
</tr>
<tr>
<td>0.0231</td>
<td>0.0138</td>
<td>70</td>
<td>50</td>
<td>850</td>
<td>F</td>
<td>5</td>
</tr>
</tbody>
</table>

Fig. 9 – Outputs of fabricated nanogenerator based on sample 1, (a) voltage at 4 Hz, (b) voltage at 8 Hz, (c) current at 4 Hz and (d) current at 8 Hz.

Table 3 – The Effective output power of PVDF/NP-ZnO nanogenerators.

<table>
<thead>
<tr>
<th>Power at 8 Hz (nw/cm²)</th>
<th>Power at 4 Hz (nw/cm²)</th>
<th>Nano fiber film</th>
<th>Sample nano generator</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>20</td>
<td>A</td>
<td>1</td>
</tr>
<tr>
<td>28</td>
<td>15</td>
<td>C</td>
<td>2</td>
</tr>
<tr>
<td>21</td>
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<td>D</td>
<td>3</td>
</tr>
<tr>
<td>11.1</td>
<td>6.4</td>
<td>E</td>
<td>4</td>
</tr>
<tr>
<td>1.05</td>
<td>0.34</td>
<td>F</td>
<td>5</td>
</tr>
</tbody>
</table>

results are presented in Table 3. Knowing that the amount of obtained power depends on the value of the considered load, if its effect can be considered equal in all the samples, it can be said that increasing the amount of zinc oxide at the synthesis procedure, the case of the nanogenerator of sample 5, causes a reduction on the output power, which is believed to be due to the poor quality of the synthesized nanofiber film.

Among the fabricated nanogenerators, sample 1 produced the highest power that can be attributed to the uniformity and elongation of its fibers, compare to the other samples. The rms outputs of the current and voltage of sample 1 are plotted in Fig. 10, at two applied frequencies. These values, which were measured at the same sampling rate and in interval of 60s, clearly demonstrate the positive effect of frequency increasing on the obtained output for all samples. Of course, the mentioned enhancement depends to the softness and hardness rate of the sample and maybe corrected in a certain frequency range, and so, at this point, it is not possible to make a general conclusion.
4. Conclusion

In this paper, composite nanofibers of PVDF/NP-ZnO were synthesized with electrospinning method for application in piezoelectric nanogenerators. The effects of zinc oxide nanoparticles on diameter and quality of the nanofibers, as well as on the power output of the nanogenerators, are investigated at different electrospinning conditions. It is seen that increasing the injection rate augments the required field intensity. Also, in order to prevent the spraying of films and the possibility of forming uniform nanofibers, with increasing the injection rate, either the distance of the needle to the collector should be increased, or the portion of the solvent with the higher boiling point should be augmented in the solution. It is also observed that with increasing NP-ZnO in the PVDF solution, the electrostatic conditions destroyed. In the latter case, while nano-fibers get thinner, a lot of spraying-form are also occurred.

The following results are obtained by examining the outputs of PVDF/NP-ZnO nanogenerators:

1. As the frequency augments, the rms output voltage and current increases for all the nanogenerators, but in instantaneous measurements, this increase is observed only for harder samples, such as samples with higher levels of zinc oxide.
2. Distorting the electrospinning conditions increases the amount of nodes and sprays in the samples, thereby reducing the output power of the nanogenerators.
3. Nanofiber samples that have higher quality, uniform morphology and diameter, produces more output power.

Conflicts of interest

The authors declare no conflicts of interest.

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