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Effect of Source Solution Components on Quality of Electrospun PVDF Nanofibers for Nanogenerator Application

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High surface area flexible thin films of Polyvinylidene Difluoride (PVDF) nanofibers are vastly used because of low cost, simple, safety and environmentally friendly production methods. PVDF nanofibers are inherently piezoelectric when produced by high voltage electrospinning method. In this paper, PVDF nanofibers are synthesis in a electrospinning apparatus, using a solution that contains PVDF dissolved in two solvents, THF (Tetrahydroforan) and DMF (N,N-Di-Methyl Formamid), which DMF has a higher boiling point than THF. The effects of THF to DMF ratio in the solution, and also, PVDF concentration on the morphology and diameter of the synthesised nanofibers are studied. Field emission scanning electron microscopy analysis of the nanofiber thin films indicates that by adding THF in the source suspension, smoother and more uniform nanofibers with lower diameter are resulted. However, by further increasing THF ratio, the cone-jet mode is formed on the tip of the needle, rapidly dried, before reaching the collector substrate. Results of the further experiments indicate that decreasing of PVDF concentration in the deposition source solves the latter problem. On the other hand, by decreasing the THF ratio to DMF, the solution cannot completely be dried, before collecting by the substrate. The best and uniform nanofibers with the diameter of 200 to 300 nm are obtained from a ratio of 3:1 For THF:DMF and 10 % PVDF concentration. Fabricated nanogenerator, based on the best mentioned sample, shows an output power of 0.56 μW/m² when actuated by a vibration mechanical force with the frequency of 8 Hz.

Keywords: PVDF, Nanofiber, Electrospinning, Nanogenerator, THF, DMF.

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1. INTRODUCTION

Polymeric materials have interesting applications in today researches because of their favorable and superior properties such as flexibility, environmental friendly, low cost, and high possible mass productions. Among various application field of polymeric materials, wireless self-bias systems, that extract their supply energy from environment, are recently developed by replacing the base material in the energy harvester devices using suitable polymers [1].

Polyvinylidene difluoride (PVDF) is a polymer that can show piezoelectric properties when synthesis by suitable methods in high voltage conditions. α phase PVDF typically is not a piezoelectric material. PVDF must be converted to β phase in order to behave as piezoelectric materials. So, PVDF nanofibers, that are synthesis using a high voltage electrospinning method, mostly are in β phase and inherently synthesis with piezoelectric property [2]. Piezoelectric PVDF nanofibers as light weight porous thin film are vastly applied in different devices such as pressure sensors, mechanical actuators, energy harvesting devices, artificial muscles and etc [3-6].

As schematically shown in Fig. 1, electrospinning apparatus prepares a high voltage between the needle tip of syringe and the collector, which direct the charged solution toward the substrate by electrostatic forces. If the solution, process and ambient parameters are well adjusted, the solution will be solidified on moving substrate in form of the ordered nanofibers thin film [7, 8].

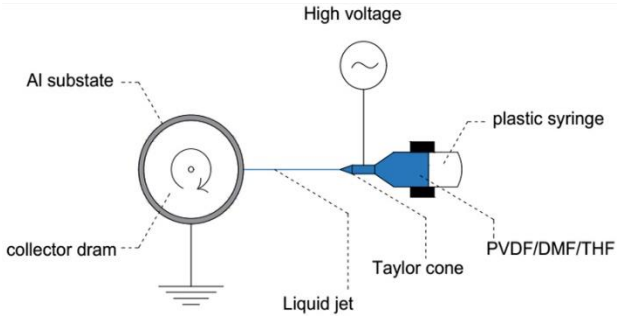

Fig. 1 – Schematic diagram of the basic electrospinning setup

For successfully production of nanofibers, one should precisely determine the effective parameters, step by step, to find the best synthesis procedure. In this regards, lots of work have been done since 2000 when Reneker [9], for the first time, reported the synthesis of nanofibers by electrospinning method. Among them, the crystallinity and morphology of the fibers were studied in various temperatures [2]. It was found that the average diameter of the PVDF nanofibers decreases with increasing ambient temperature. However, they found that the fraction of β phase increases to a maximal value at the temperature 25 °C, and then a slight decrease is happened with more temperature rising. In recent years, most of researches focus on effect of other additives on synthesis nanofibers. The most additives that have been used are CNT [10], ZnO [11] for improving the physical, chemical, mechanical and electrical properties of the nanofibers. An introduction of electrospinning, the history of electrospinning,

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and basic electrospinning setups related theories can be found in the published work of Zhenyu Li and Ce Wang [8] where they documented the electrospinning methods and the parameters that influence the nanofiber fabrication.

However the charged solution jet instability issue is very important for a successful formation of nanofibers. The fluid typically used in electrospinning may not solidify sufficiently on route to the collector to form the ordered nanofibers [9-10, and 12]. However, fluid charging occurs due to high applied electric field which affect also the diameter of electrospun fibers [13]. In this work, PVDF nanofibers are synthesis by electrospinning method. The effects of solution's compositions and their ratios on morphology and on the diameter of the deposited nanofibers are studied through scanning electron microscopy (SEM). X-ray diffraction (XRD) analysis of the thin films and Current and voltage measurement of the fabricated nanogenerator are also presented to show the piezoelectric properties of the synthesis material.

2. EXPERIMENTAL

PVDF powder with molecular weight of 534000 was purchased from sigma Aldrich, solution of N, N-dimethylformamide and Tetrahydrofuran from Merck Chem Company. All the materials were used without further purification.

For preparing the source solution, first, DMF and THF were mixed with the ratios of 1:1, 3:1 and 1:3, respectively, and then, PVDF powder was added to the mentioned solutions with different weight of 10, 15 and 20 % wt. The latter solutions were stirred for 24 hours, using a magnetic stirrer, until the powder get completely solved and a homogeneous solution results. Information about the solution ratios and concentration of the polymer, for each sample, are listed in table 1. Other DMF:THF ratios and PVDF weight percent, that are not included in the set of the samples, the membrane was not formed on the substrate for vast of the applied voltage, and so excluded from the table.

The distance between syringe pump and the dram (L) was 15 cm and the solution flow rate was about 1 mL/h, for all the samples. All the processes were done in room temperature. Depending to the other considered conditions for each sample, applied voltages were chosen which varied from 9 to 16 kV. The voltage condition for each sample is also added to Table 1.

Form and morphology of the samples were studied using a precise FESEM instrument. XRD analysis was used to analysis the crystallinity property of the materials. Also, a study is done based on the calculated average diameter of the nanofibers for each sample. Finally, by placing an Al broad contact over the best nanofiber sample, a nanogenerator is fabricated and characterized.

Table 1 – Source solution ratios and applied voltages of fabricated PVDF nanofiber thin films

Sample	DMF/THF ratio	PVDF % wt	Applied Voltage (kV)
A	1:3	10 %	16
B	1:3	15 %	15
C	1:1	15 %	13
D	1:1	20 %	11
E	3:1	10 %	9
F	3:1	20 %	11

3. RESULTS AND DISCUSSION

In first step of the electrospinning synthesis method, to set the best conditions for each solution, different applied voltages were examined. This parameter should be adjusted corresponding to viscosity and surface tension of the solution for various considered ratios. Different voltages were applied with mentioned injection rate and distance between the dram and syringe pump. To see if the voltage is suitable or not, Taylor cone on the needle tip and the form of the jet toward the collector are verified. Voltage should be adjusted due to the change in the surface tension and viscosity as a result of varying the concentration and ratio of the different solvents that are used. If the applied voltage is lower than that should be, the Taylor cone will not form, and the liquid will be leaked from the needle tip. Contrary, if the voltage is higher than the suitable one, the conical jet is not stable and will be removed from the needle tip.

The considered solution for preparing the samples with 20 % wt. of PVDF and the solution ratio of 1:3 could not be formed in Taylor cone, so it did not prepare the needed jet under applying a wide range of voltages. It is believed that the mentioned fact is due to the very low boiling point of the Taylor cone on the tip of the needle. Thus when the percentage of THF in solution is high, electrospinning of PVDF nanofiber is impossible and the solvent could not break the molecular chain of the polymer, and so, a gel-like solution is produced. To solve the mentioned problem, in further step, in case of the samples A and B, the PVDF weight percentage was reduced to 15 % and 10 % to see if the nanofiber could be formed or not. It is observed that the decreasing of PVDF percentage in high THF ratio solution results a stable jet, and so, the thin nanofibers is formed. The SEM results for samples A and B are shown in Figures 2a and 2b. The suitable voltage for 15 % PVDF in solution ratio of 1:3 was obtained about 15 kV. For 10 % PVDF with the same solution ratio, the best functioned voltage was 16 kV. It is seen that with decreasing the PVDF weight percent to 10 %, the nanofiber are smoother, with lower diameters, also less beads are observed over the formed nanofiber. It is expected that if the PVDF weight percent decreased again, the thinner nanofibers will be performed.

Distribution of the nanofiber diameter for samples A and B are calculated and presented in figures 3a and 3b. For sample A, the most of the nanofibers have a diameter between 200 to 400 nm and this distribution is uniform. The abundance of the diameters in sample B is between 300 to 600 nm. This sample is less uniform comparing to sample A.

In the case of samples C and D, where the solution ratio is 1:1, the suitable applied voltage were found about 13 and 11 kV, for the PVDF percentage of 15

and 20 % wt, respectively. Figures 2c and 2d show the SEM image of the samples C and D.

It is seen that when the PVDF concentration increases, the thicker nanofibers are formed. However, the beads are also formed on the fibers with increasing the concentration of the polymer. The latter results indicates that the applied electric field could not completely overcome the surface tension of the solution and so the beads are formed. Presentation of the broken thin fibers in all the images is believed to be due to the non-uniform spinning of the collector dram. Because that no fibers are formed in the case of 10 % wt PVDF, it seems that the best concentration for DMF:THF ratios of 1:1 is between 15 to 20 %. Investigating the best form of nanofibers could be made by choosing the other concentration in this range.

Distribution of the diameter for sample C is calculated and shown in Figure 3c. For this sample, the most of

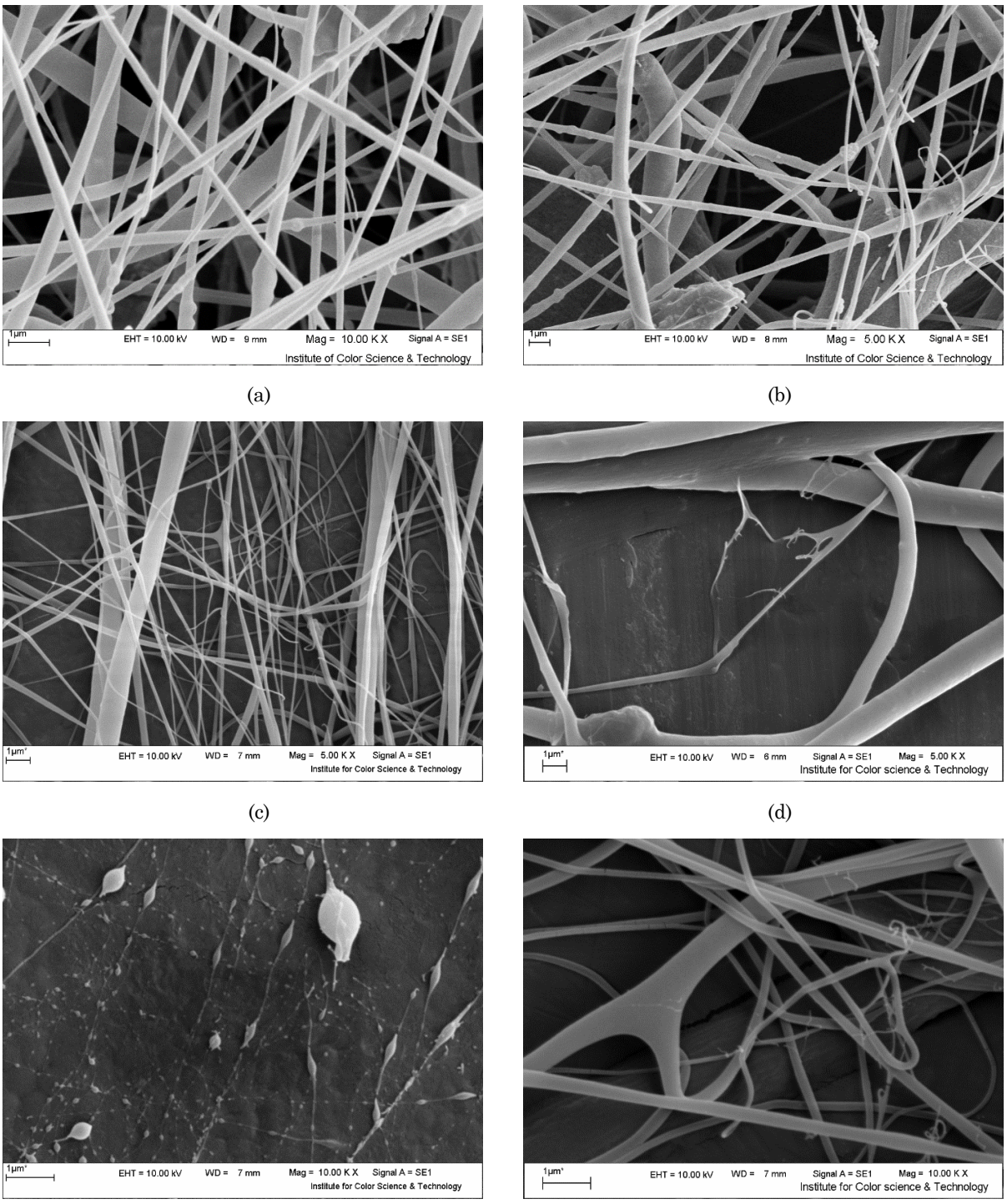


Fig. 2 – SEM Images of electrospinning samples with THF:DMF ratio and PVDF concentration of: a) 1:3, 15 % wt., b) 1:3, 20 % wt., c) 1:1, 10 % wt., d) 1:1, 15 % wt., e) 3:1, 10 % wt. and f) 3:1, 20 % wt.

the nanofibers have a diameter between 150 to 300 nm that indicate the thinnest nanofibers can be produced by the conditions that is used to synthesis sample C. However the very thick fibers are also existed in this sample.

In the SEM image of samples E (Figure 2e), it is seen that the fibers are not formed and only solution droplet is generated. This is due to the low concentration of the polymer. Since for the concentration of 15% also no fibers were formed, it is concluded that in the case of low concentration of the THF, PVDF concentration should be more increased. In SEM results of sample F, the smooth fibers with no beads are formed (Figure 2f).

Distribution of the diameter for sample F are calculated and plotted in Figures 3a and 3b. For this sample, the most of the nanofibers have a diameter of 200 nm but the less abundance thicker fibers also produced that indicates the diameter distribution in this film is not uniform.

It should be reminded that the reported tests were done in a constant distance and solution flow rate. So, it is possible that the results change if the two mentioned conditions vary. Also, the molecular weight of PVDF was about 534000 that will affected the results if it changes. However, from the obtained results, it is seen that whenever the THF ratio increases, the fibers get thinner and smoother, and more, the solution behaves better in lower concentration of PVDF.

The abundance of the nanofiber diameters for the good samples are compared in Figure 4.

Based on the obtained results, sample A was chosen for nanogenerator fabrication by placing an Al broad contact over the thin film, as the upper contact. The fabricated nanogenerator is schematically shown in Figure 5. To show the piezoelectric properties of this sample, an XRD analysis is done of sample A, which the corresponding pattern is plotted in figure 6. The XRD result suggests a multi crystalline nanofiber with a maximum peak around 20 ° of 2θ (θ phase) that results the piezoelectric properties of the material. The peak at 18 ° of 2θ corresponds to θ phase of PVDF nanofibers. The three peaks at the left side of the curves correspond to crystalline Al which was used as substrate.

The performance of fabricated nanogenerator was studied by applying a vibrational force with two different frequency of 4 and 8 Hz. The instantaneous output short circuit current and open circuit voltage, at 4 and 8 Hz, are plotted in Figure 6 (a-d). It is seen that increasing the applied frequency leads to higher current and voltage. To calculate the output power of the nanogenerator, the root mean square of current (I_{rms}) and voltage (V_{rms}) in presence of a high resistive load is measured. As the sampling rate for the latter measurement was lower than the work frequency, the resulted *rms* values are sometimes lower that the actual values. By multiplying the maximum values of current and voltage for the mentioned curves, the output power was obtained.

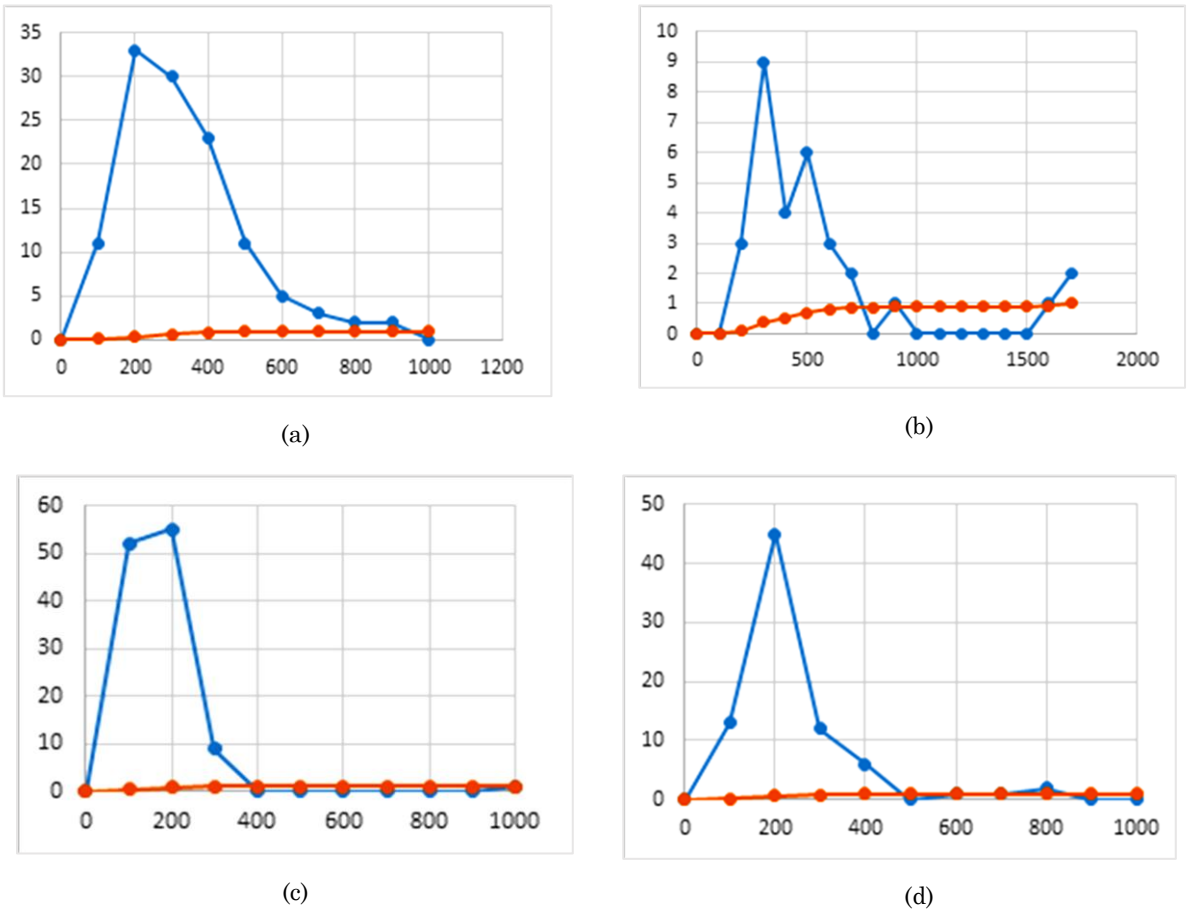


Fig. 3 – Diameter distribution of electrospinning samples with THF:DMF ratio and PVDF concentration of: a) 1:3, 15 % wt, b) 1:3, 20 % wt, c) 1:1, 10 % wt, d) 1:1, 15 % wt, e) 3:1 10 % wt and f) 3:1, 20 % wt

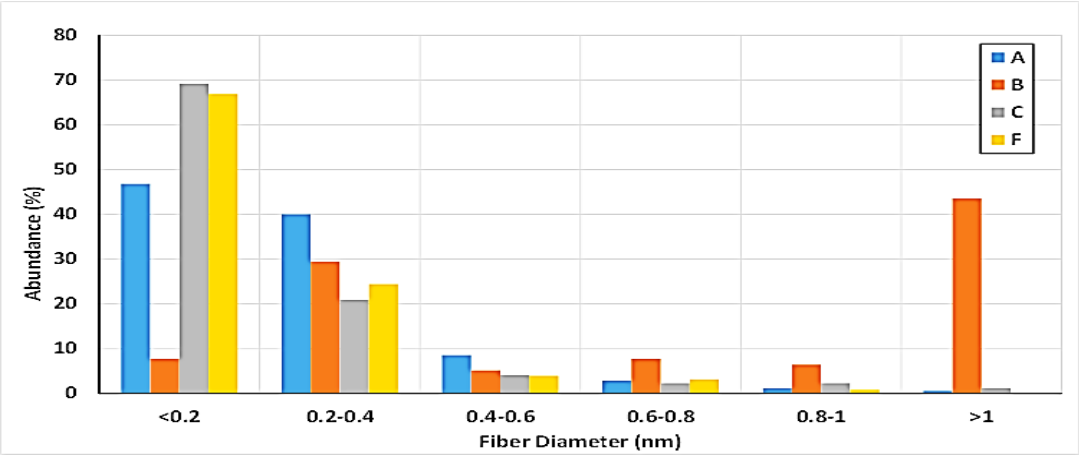


Fig. 4 – Comparing the abundance of nanofibers Diameter for the electrospinning samples with different THF:DMF ratio and PVDF concentration

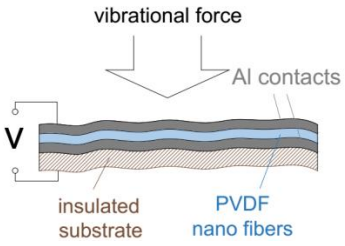


Fig. 5 – Scheme of piezoelectric nanogenerator based on PVDF nanofiblers

Therefore, the fabricated nanogenrator, when are actuated with 4 and 8 Hz vibrational force, can produces a power of 0.12 and 0.56 μW/m², respectively.

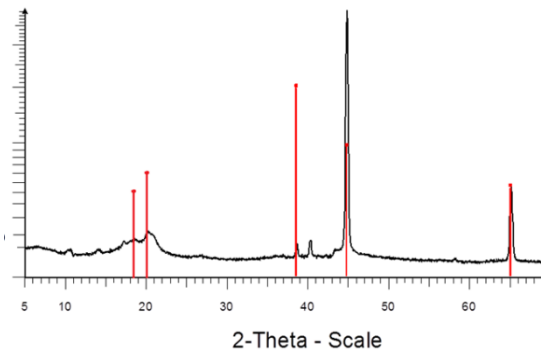


Fig. 6 – XRD pattern for PVDF nanofibers of the sample with THF:DMF ratio 1:3 and PVDF concentration of 10 % wt.

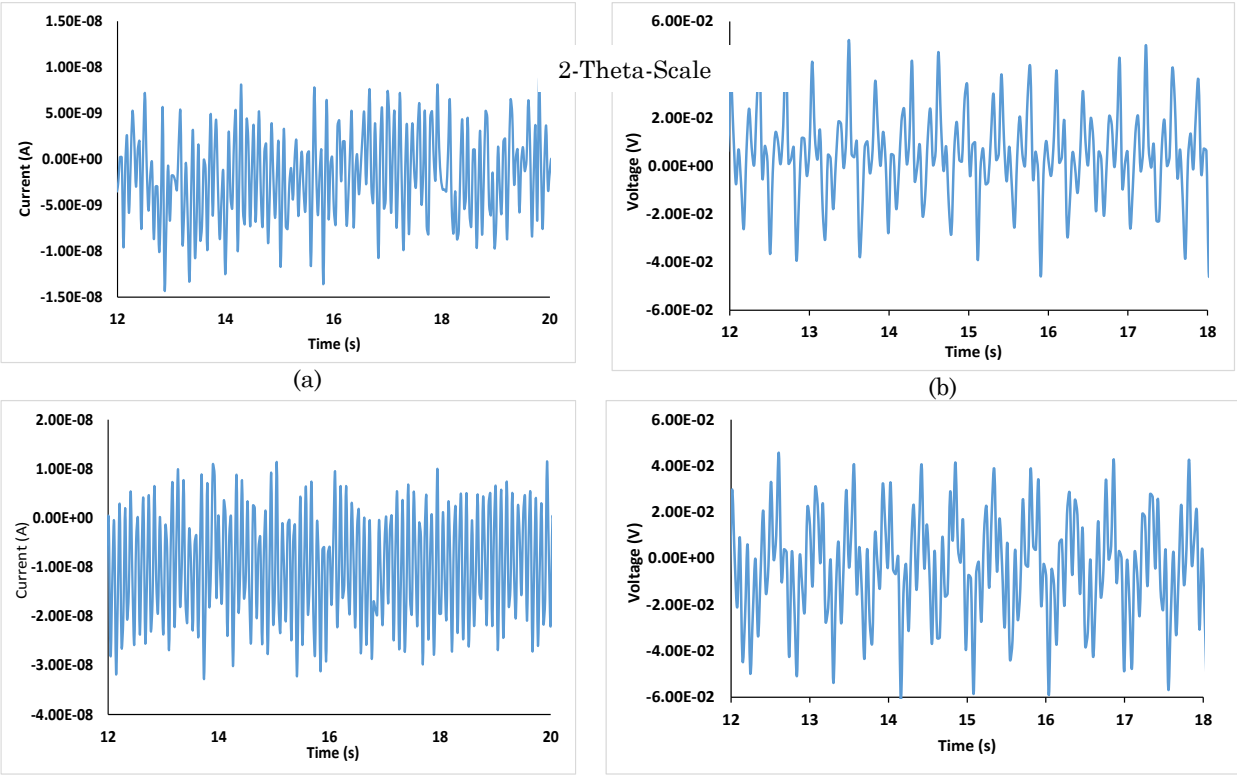
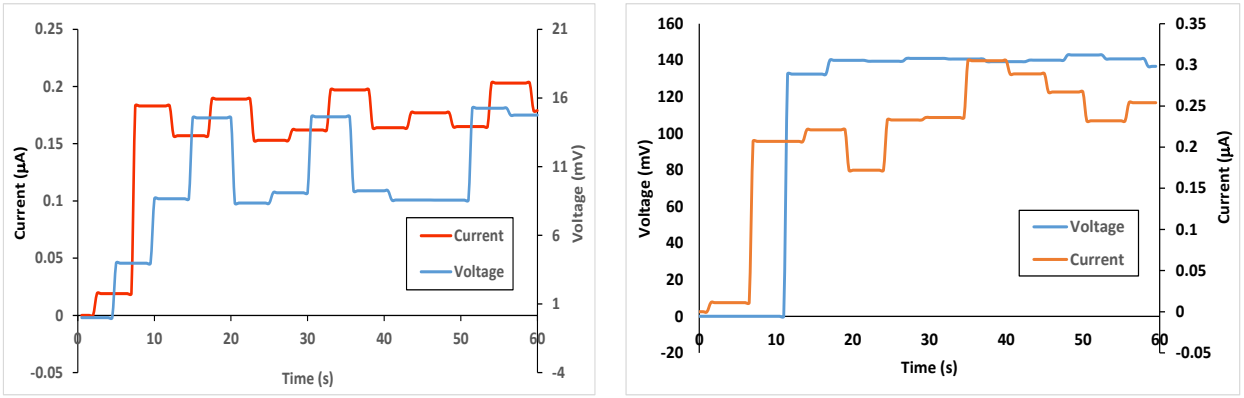


Fig. 7 – Outputs of the nanogenerator based on PVDF nanofibers when actuated with 4, 8 Hz vibrational force a) 4 Hz, current, b) 4 Hz, voltage, c) 8 Hz, current, d) 8 Hz, voltage



(a) (b)

Fig. 8 – I_{rms} of the output current and voltage measured in a) 4 Hz and b) 8 Hz applied vibrational force for the fabricated nanogenerator based on PVDF nanofibers

4. CONCLUSION

PVDF nanofibers were synthesized using an electrospinning method to apply as piezoelectric material for fabrication of an energy harvesting device. For dissolving the PVDF powders, two solvents, named THF and DMF, were mixed together with different ratios. The suitable applied voltages were found by examining the Taylor cone and the solution jet outward the syringe pump. It was found that by increasing of THF ratio, the cone-jet on the tip of the needle rapidly dried, before reaching the collector substrate. Decreasing of PVDF concentration in the solution is suggested to over the mentioned problem. It is concluded that: 1. the lower boiling point of THF, comparing to DMF, gives more time for the jet to reach the collector, when the PVDF concentration is enough low. 2. THF could not well dissolve a high concentration of PVDF, so a gel-like solution are resulted that could not produce the thin film of nanofibers. 3. Finally, the best and uniform nanofibers with the diameter of 200 to 300 nm are obtained from a ratio of 3:1 For THF:DMF and 10 % PVDF concentration.

In XRD result, existing of the crystalline θ phase proves the possibility of using the nanofibers as piezoelectric material. Characterizing the fabricated nanogenerator based on sample A, and actuating it with 4 and 8 Hz vibrational forces, results a power of 0.12 and 0.56 μW/m^2, respectively, as the output of the device.

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