



## **Fabrication and structural study of piezoelectric PVDF composite nanofibers by electrospinning technique**

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### **Abstract**

This research focused on the preparation of composite nanofiber material prepared from poly(vinylidene fluoride) (PVDF) and carbon black (CB) for nanogenerator application, using electrospinning based process. Firstly, the PVDF/CB composites were prepared with different content of carbon black varied from 0.1, 0.3, 0.5 and 0.7% by weight. The condition of electrospinning process for PVDF/CB composite, such as applied voltage and polymer concentrations were then varied while flow rate of feed and distance from the collector were kept constant. The Fourier Transform Infrareds Spectrometer (FTIR) analysis showed that the applied voltage affects strongly on the  $\beta$  phase ratio of composite fiber which increases with increasing applied voltage. Moreover, the morphology analysis from Scanning Electron Microscopy (SEM) show that the best condition for electrospinning process are 10 kilovolt of voltage, 1.00 milliliter/hour of feed flow rate and 15 centimeter of distance from collector. The optimal  $\beta$  phase ratio (0.81) was obtained when PVDF/CB composite was doped by 0.1% w/w of carbon black but this value is insignificantly lower than pure PVDF nanofiber (0.83). In addition, the result shows that if carbon black exceeds 0.1% w/w, the  $\beta$  phase ratio inversely decreases. PVDF nanocomposite fibers have good fibrous structure, smooth, orderly morphology, regular dispersion and with increasing voltage. In case of 0.1% w/w carbon black content, nanofiber size includes between 200-700 nanometers. This preparation process can be an alternative method for preparation of composite nanofiber material which could produce electrical energy from vibration and it can be the knowledge for research's electronic devices.

**Keywords:** Electrospinning, Composite nanofiber, Poly(vinylidene fluoride), Carbon black, Beta phase

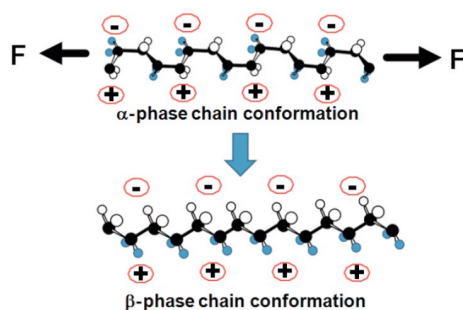
### **Introduction**

Being able to convert mechanical stress to electricity and vice-versa, piezoelectric material was introduced since 40 years ago but receives high attention only less than 20 years from the smart material communities because of its potential to be used as transducer, sensor and actuator. As this kind of solid can develop a voltage when mechanically deformed, it could be also used as energy generating material. With recent power shortage problem, development of power harvesting material becomes a challenging topic in many research fields because of its potential to overcome the limitation of traditional power supplies such as regular batteries. Piezoelectric materials have many advantages to reach this objective because they have unlimited lifetime, cost-effective and simple. Traditionally, a perovskite ceramic piezoelectric such as lead zirconate titanate (PZT) that shows remarkable piezoelectric effect was intensively used as sensor in many domains such as aerospace, consumer electronics, automotive, biomedical and electric industry [1-3]. However, this piezoelectric crystalline solid commonly used unfortunately suffers from some physical drawback because of its low mechanical properties and low flexibility for forming process.

Within the last decades, electroactive polymers (EAPs) such as nylon-11 [4], polylactic acid (PLA) [5] and poly(vinylidene fluoride) (PVDF) [6] have attracted many interests due to its excellent mechanical properties, chemical stability and electrical properties. Among them, PVDF and its copolymer have the most outstanding electrical properties, therefore promising for many applications in the domain of sensor, batteries, chemical welfare protection, biomedical and electronic [7]. PVDF has been found to have a strong pyro-, ferro- and especially piezoelectric behavior [8] with piezoelectric coefficient ten times higher than that of other polymers. Moreover, as

one of semicrystalline thermoplastic polymers, PVDF is very flexible to be formed to any shape and resists to high mechanical stress which allow it to be applied as piezoelectric energy generator. Well known to be polymorphism, PVDF consists of four distinct conformations:  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ . These crystalline phases possess different chain orientation and thus, different *internal polarization* which is the most important key concept for PVDF piezoelectric property. The most thermodynamically stable PVDF phase at room temperature is non-polar  $\alpha$  phase with random orientation of each polymer chain in macro-scale, so that all dipole moment cancel each other and the overall net dipole moment becomes zero. Furthermore, dipolar polarization and interfacial polarization can be achieved when very high voltage electric field is applied to the non-electroactive phase during *poling* process and the electroactive  $\beta$ ,  $\gamma$  and  $\delta$ -phase could be consequently occurred. Applied electric field induces the rotation of dipole moment and forces them to be aligned to electric field. In this way, the overall dipole polarization is not zero anymore, when each chain dipole moment is perpendicular to the main polymer chain [9]. Among them,  $\beta$ -phase has the highest dipolar moment per unit cell ( $8 \times 10^{-30}$  cm) compared to  $\gamma$  and  $\delta$ -phase [10-11].

Since  $\beta$  conformation is the most electroactive phase of PVDF, the development of polar  $\beta$ -phase within polymeric structure becomes the basic criteria for the increasing application of this electroactive polymer [12]. As previously mentioned, electrical *poling* process of PVDF thin film and its mechanical stretching during the manufacturing process can effectively allow the formation of  $\beta$ -phase [13-14] (Figure 1).



**Figure 1: Conversion of  $\alpha$  conformation to  $\beta$  conformation by mechanical stretching**  
( $\circ$  = Hydrogen atom,  $\bullet$  = fluoride atom and  $\bullet$  = carbon atom) [15]

In the other hand, Yee et al. [16] announced another method for  $\beta$ -phase induction by electrospinning fabrication method. In this specific process, the viscous polymer solution is injected to the collector, undergoing the uniaxial stretching when subjected to the high-voltage electrostatic field [17]. Compared to traditional strong electrical poling, electrospinning process combines electrical poling and mechanical stretching altogether, thus can effectively align the fiber along to certain orientation. This method shows unique advantages by producing the paralleled polymeric fiber with high  $\beta$ -phase ratio without additional poling process by transforming non-polar  $\alpha$  phase to the polar  $\beta$  phase [16].

Furthermore, it has been also demonstrated that the addition of small heterogeneous fillers can raise the interfacial polarization by nucleation mechanism from specific dipole-surface charge interaction between filler and slightly positive charged  $\text{CH}_2$  group [18]. This inclusion of various small particle fillers into polymer matrix can efficiently enhance the ratio of  $\beta$ -phase. Hereafter many alternative ways to obtain the desired electroactive  $\beta$ -phase were developed by doping PVDF with numerous filler such as  $\text{BaTiO}_3$  [19], clays minerals [20], metal particles [21], ceramic filler [22], quaternary phosphorus salt functionalized graphene [23], ferrite nanoparticle [24], palladium [25], gold [26], and carbon nanotube [27]. It has been demonstrated that the addition of these heterogeneous fillers can raise the interfacial polarization by nucleation mechanism from specific dipole-surface charge interaction between filler and slightly positive charged  $\text{CH}_2$  group [18]. All of these researches mainly focus on the direct addition of particular filler to PVDF film, more rarely relies on the incorporation of nanofiller to electrospun PVDF fiber. Zhang et al. [28] and Liu et al [29] demonstrated that the addition of modified carbon nanotubes (CNTs) assisted the growth of crystalline  $\beta$  phase in PVDF composite fiber. The latter study reported that the addition of MWCNTs to electrospun PVDF fiber can increase the crystallinity of  $\beta$  phase, thus enhancing piezoelectricity properties which were investigated by X-ray diffractometer and ANSYS FEA commercial stimulation software.

Nanocomposites fabricated from PVDF and carbon, have the potential to be used as smart materials, because of the combination of the piezoelectric properties of PVDF and the conductive properties of carbon. Among these carbon derived filler, carbon black is one of the most promising filler for PVDF, because of its low price, high electrical properties and high surface area. Furthermore, it was reported that carbon black nanoparticle can induce

the network self-assembly in polymer-carbon black composite [30]. In this present study, the formation of  $\beta$  phase in PVDF assisted by the addition of carbon black particle was investigated. The electrospinning parameters such as polymer concentration, carbon black content, solvent and applied voltage were thoroughly studied in detail while the injection rate and tip-to-collector distance were kept constant, with respect of  $\beta$  phase ratio and morphology of electrospun PVDF composite nanofibers. The influence of electrospinning process parameters to  $\beta$ -phase fraction was also discussed and finally, the microstructure morphology of PVDF-CB composite nanofiber was studied by scanning electron microscopy.

## Materials and methods

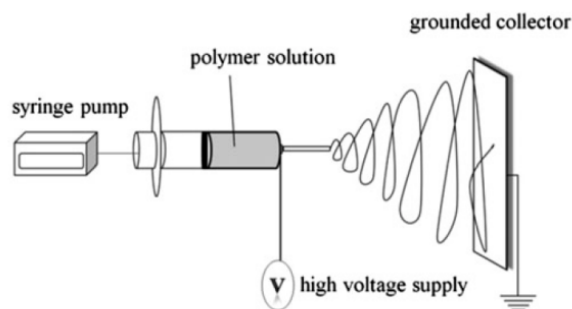
### Materials

Poly(vinylidene fluoride) (PVDF; MW=543,000) was purchased from Sigma Aldrich, Carbon Black N220 (CB) was purchased from Nanorubberchem (Thailand), Dimethylformamide (DMF; content > 99.9%) and Acetone ((CH<sub>3</sub>)<sub>2</sub>CO) were purchased from Roongsub Chemical (Thailand). All chemicals were used without any further purification.

### Methods

#### Electrospinning process

The electrospinning process consists of a high-voltage power source, syringe containing polymer solution with needle, syringe pump and a grounded collection device (Figure 2).



**Figure 2: Schematic representation of the electrospinning process [31]**

The electrospinning solutions with different concentrations of PVDF were prepared by dissolving PVDF pellets and carbon black into a mixture solvent of DMF/Acetone (4/6 w/w) at room temperature for 24 h. The polymer concentrations were varied at 10 wt% and 19 wt% because of solubility limitation and the carbon contents were varied at 0.1 wt%, 0.3 wt%, 0.5 wt% and 0.7 wt%. Electrospinning processes were conducted at room temperature while the applied voltages were varied at 5 kV, 7 kV, 10 kV, 13 kV and 15 kV. The volume of PVDF solution was kept constant at 5 mL which was all introduced to fill the syringe incorporated with the needle (Number 24G×1, 0.55×25 mm of diameter). The syringe was then placed in the automated pump using feeding machine to 1 mL/h to ejaculate the solution out of the syringe with the distance tip-to-collector fixed at 15 cm. All electrospun PVDF nanofibers were then dried in the vacuum oven at 80 °C for 24 h to remove the residual solvent and preserved in desiccator.

#### Nanofibers characterization

All PVDF-CB composite nanofibers were characterized by Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR) (Thermo Scientific, Model, NICOLET is5) and scanning electron microscopy (SEM) (JEOL Model JSM-6610 LV). The  $\beta$ -phase content ( $F(\beta)$ ) in PVDF-CB composite nanofiber was calculated from corresponding infrared spectra using Beer-Lambert law cited in equation 1, first described by Gregorio et al. [32].

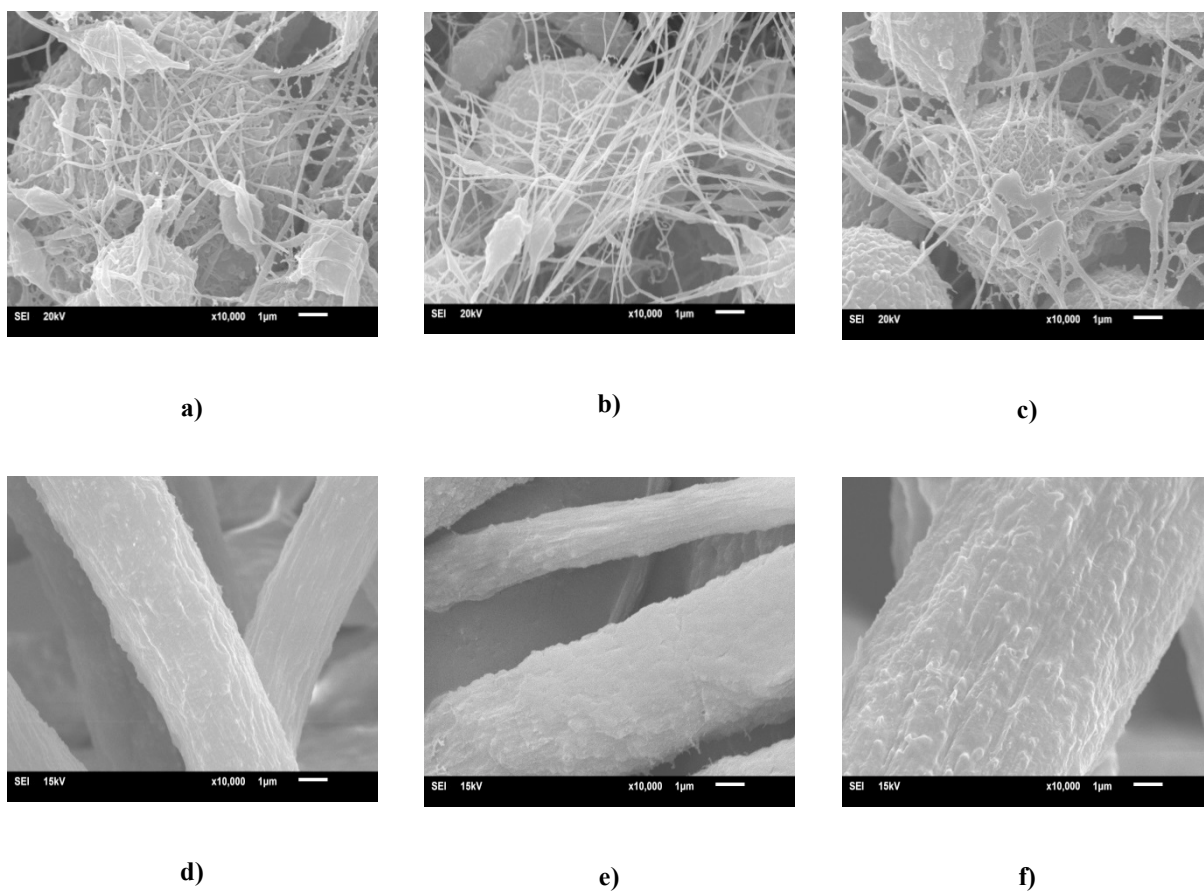
$$F(\beta) = \frac{A_{764}}{\frac{K_{\beta}}{K_{\alpha}} A_{764} + A_{840}} \quad (1)$$

Where  $A_{\alpha}$  and  $A_{\beta}$  are the absorbance at  $764 \text{ cm}^{-1}$  and  $840 \text{ cm}^{-1}$ , respectively and  $K_{\beta}$  ( $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ ) and  $K_{\alpha}$  ( $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ ) are the absorption coefficients at the respective wavenumber [33]. This equation is widely used for the calculation of relative fraction of  $\beta$ -phase ( $F(\beta)$ ) for the system containing PVDF and filler [34-36]. It is noteworthy that this calculation provides the *relative*  $\beta$ -phase ratio to  $\alpha$ -phase.

## Results and discussion

PVDF-CB composite nanofibers were fabricated using needle-based electrospinning method under different parameters such as polymer concentration, carbon black content and applied voltage. The obtained results and discussions are described as following.

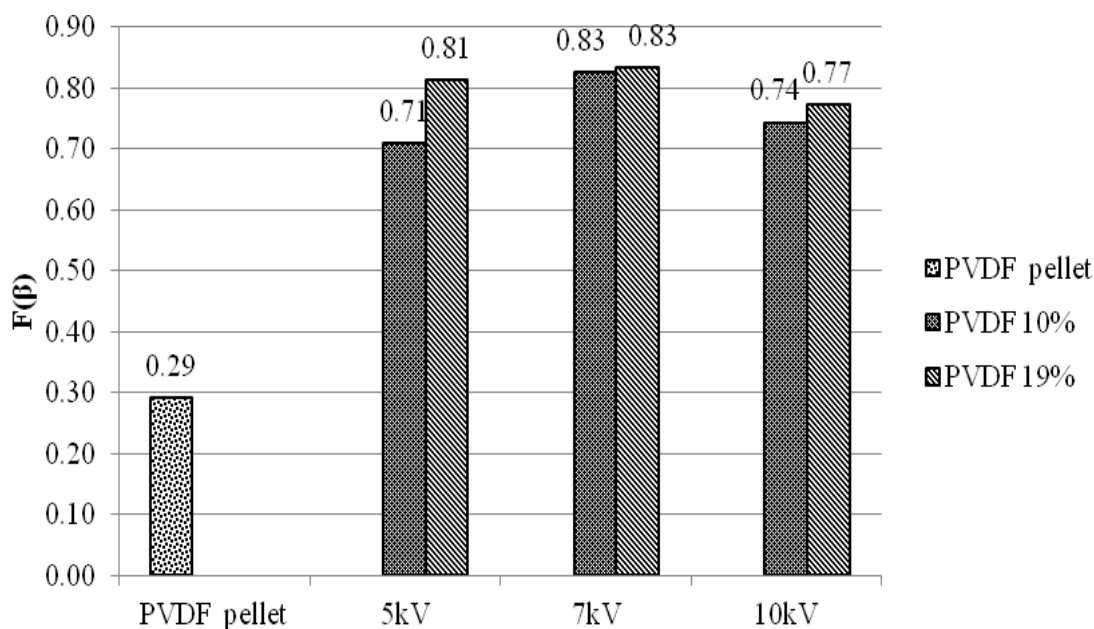
### Effect of polymer concentration and applied voltage for pure PVDF nanofibers



**Figure 3: Typical SEM image of pure PVDF nanofibers at concentration of 10 wt% with a) 5 kV b) 7 kV c) 10 kV and at concentration of 19 wt% with d) 5 kV e) 7 kV f) 10 kV.**

The ratio of  $\beta$  phase for pure PVDF composites were investigated by FTIR spectra and relatively calculated by using above equation (equation 1). Figure 3 and Figure 4 show the influence of polymer concentration and applied electrospun voltage on the  $\beta$  phase ratio of different concentration of pure PVDF nanofibers and on the morphology of the obtained nanofibers. When the concentration of PVDF is only 10 wt%, non-uniform morphology of PVDF fibers are clearly detected in presence of large droplet and small bead in between and the fiber diameter are 50-100 nm (Figure 3 a – c).

The size of PVDF fibers obviously increase to 1-10  $\mu\text{m}$  and PVDF droplets disappear with increasing polymer concentration to 19 wt% (Figure 3 d-f). Apparently the bead morphology and density are affected by polymer concentration. When the polymer concentration increases from 10 wt% to 19 wt%, the bead density decreases and completely dissolves to form the larger PVDF fibers. The influence of polymer concentration on the morphology and the fiber diameter were largely investigated [34-35]. It was explained that the entanglement of polymer macromolecular chains in the solution seems to be responsible. In fact, the polymer concentration must be high enough to overcome the entanglement concentration ( $C_e$ ), thus the bead and droplet structure are formed in majority when polymer concentration is too low and the fibrous structure could be attained, only when polymer concentration is 2-2.5 times of  $C_e$ . The polymer jet is susceptible to Rayleigh instability [37] and always tends to form a droplet. Effectively, with the increasing polymer concentration, the chain entanglements in the polymer solutions assist to stabilize the initial polymer jet, preventing the jet breakup into beads or droplets. The solvent evaporation which follows, eventually stabilizes the jet and helps the continuous fibers to form [36]. Moreover, with the increasing of PVDF concentration and applied voltage, the mean diameters also increase and the more coarse fibers are observed (Figure 3 d – e). In the other hand, polymer concentration directly corresponds to the solution viscosity and the lower viscosity, from the one side, promotes the generation of smaller fibers. However, from another side, low polymer chain entanglements leads to the formation of beaded fibers as presented in the Figure 3a-c).



**Figure 4: The effect of PVDF concentration on the  $\beta$  phase ratio**

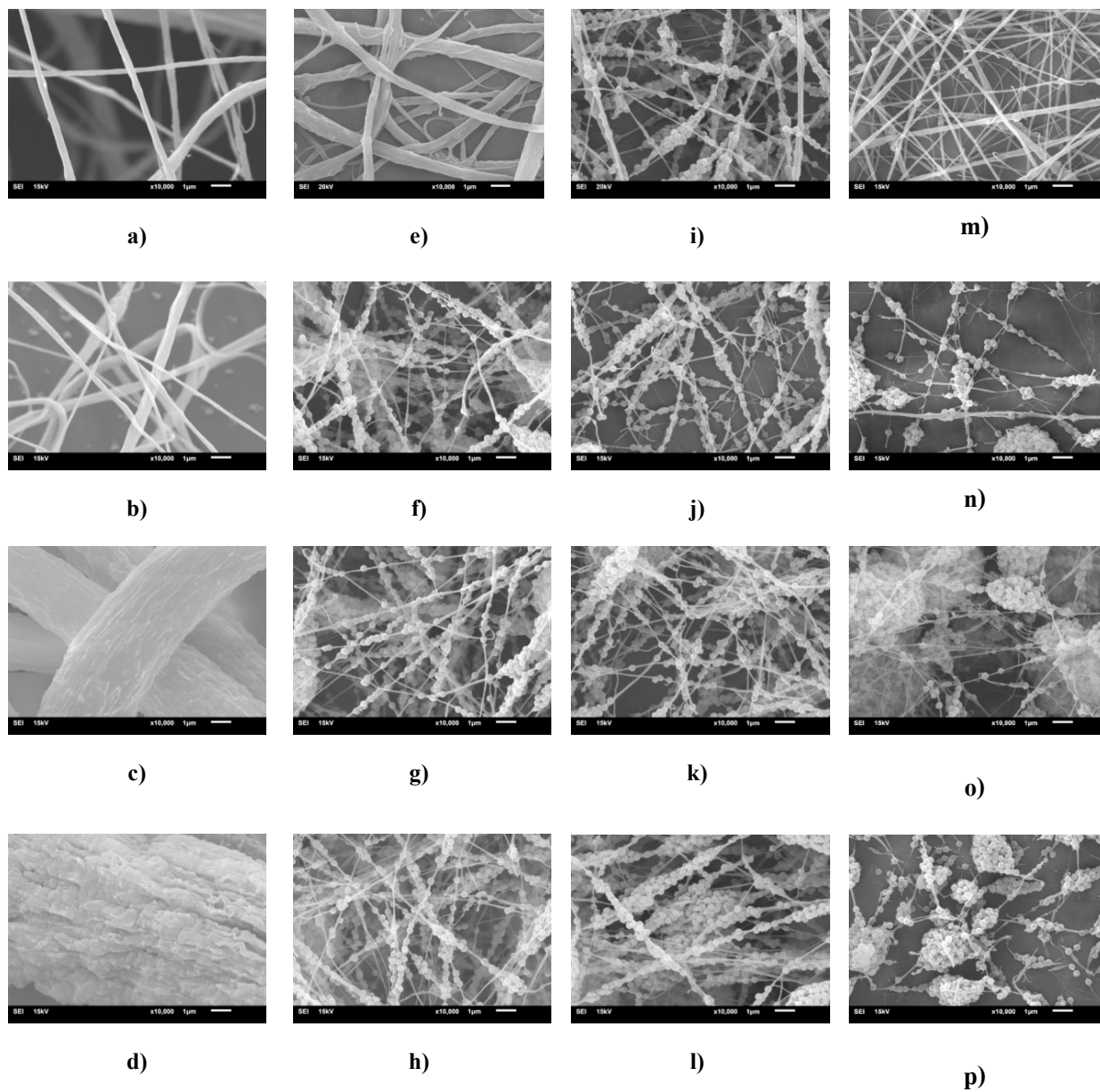
Figure 4 evidently shows the effect of polymer concentration and applied electrospun voltage on the  $\beta$  phase ratio of PVDF fibers. The  $\beta$  phase ratio of non electrospun pure PVDF is actually very low (0.29) compared with electrospun PVDF fibers in which the  $\beta$  phase ratio vary between 0.71-0.83. The formation mechanism of  $\beta$  orientation has been previously studied by many research groups [38-42]. The formation of  $\beta$  crystal structure could be explained by the stretching of PVDF chain orientated along the fiber length [28] when a charged polymer

jet is ejected from the tip. The polymer jet solution is held by the surface tension when the surface charges are induced by applied electric field. This stretching is similar to the drawing process and facilitates the conversion of  $\alpha$  orientation to  $\beta$  orientation, entraining the enhancement of  $\beta$  phase ratio. When comparing between 10 wt% and 19 wt% of PVDF solution, the  $\beta$  phase ratio increases when polymer concentration increases. This effect of polymer concentration on increasing of  $\beta$  phase ratio is nevertheless contradictory with the result obtained by Shao et al [43]. In this previous paper,  $\beta$  phase content tends to decline at very high polymer concentration (from 20 to 26 wt%). This effect could be explained by the stronger macromolecular chain entanglement which prevents the stretching to be easily performed. However, studied polymer concentration in this research is lower than 20 wt%, such effect must be absent. Moreover, the applied electric field is the driving force for fiber formation during electrospinning and affects also the  $\beta$  phase ratio. Increasing electric field means the higher electrostatic force for the polymer stretching, results to higher  $\beta$  phase ratio when applied electric voltage increases from 5 kV to 7 kV (Figure 4) for both concentration. In the other hand,  $\beta$  phase ratio tends to decline when electrical voltage is superior to 7 kV regardless polymer concentrations. The similar trend of decreasing of  $\beta$  phase ratio after attaining the optimal value was also observed by Shao et al [43]. When the polymer concentration is lower than 18 wt%, electrospinning process becomes discontinuous because of an unsteady solution flow rate. The formation of PVDF fibers with non-uniform diameter is mainly formed [28]. According to higher  $\beta$  phase ratio, desired viscosity and more uniform fiber morphology, the concentration of 19 wt% was considered for further preparation of PVDF-CB composite nanofiber.

### **Effect of carbon black content and applied voltage for PVDF composite nanofibers**

The morphology of PVDF-CB composite nanofiber and the distribution of carbon black particles in PVDF matrix were thoroughly investigated by SEM analysis. The carbon content and applied voltage clearly affect the morphology of electrospun PVDF composite. As shown in the Figure 5, when carbon content is low at 0.1 wt%, the coarse fibrous structures were obtained with similar morphology as pure PVDF electrospun fiber (Figure 3 d-f) when the same polymer concentration was used (19 wt%). When the carbon content increases from 0.1 wt% to 0.7 wt%, the bead density on the fibers dramatically increases as well. Most of composite fiber prepared from higher carbon content than 0.1 wt% represents very high number of beads incorporated to the formed fiber, except when the applied voltage is low to be 5 kV (Figure 6 e, i and m). These beads could be formed by carbon black particle mixed with PVDF and this non uniform morphology could be mainly attributed to the bad distribution of carbon black particle in polymer matrix, resulted from low interfacial adhesion between carbon black particle and PVDF chains matrix. This interfacial adhesion plays an important role in homogeneity of polymer/particle filler composite and could be improved by surface modification of filler particle.

The effect of polymer carbon black mixture viscosity seems to be contradictory with the result obtained with the pure polymer solution where lower polymer solution (so lower viscosity) leads to the formation of smaller size fiber in presence of many beads on. Herein, the influence of mixture viscosity directly correlated to the carbon content provokes the inverse effect (Figure 5). Aside from carbon black content, the applied voltage is also one of the most important factors affecting the density of beading and uniformity of fiber. The applied voltage has also similar effects with the decreasing the fibrous structure of composite fiber caused by enhancement of bead. Especially with very high carbon content (0.7 wt %) and high applied voltage (10 kV and 13 kV) (Figure 5 o and p), the density of beads becomes so high that the fibers structure almost all collapse. As shown previously (Figure 3), the applied voltage must be strong enough to produce the electric field which overcomes and breaks the surface tension of the solution. When too high voltage is applied, the unstable polymer mixture could be produced, the jet hereafter behaves erratically.



**Figure 5: Typical SEM image of PVDF-CB composite nanofiber structure: 0.1 wt% of carbon black at a) 5 kV b) 7 kV c) 10 kV d) 13 kV, 0.3 wt% of carbon black at e) 5 kV f) 7 kV g) 10 kV h) 13 kV, 0.5 wt% of carbon black at i) 5 kV j) 7 kV k) 10 kV l) 13 kV and 0.7 wt% of carbon black at m) 5 kV n) 7 kV o) 10 kV p) 13 kV .**

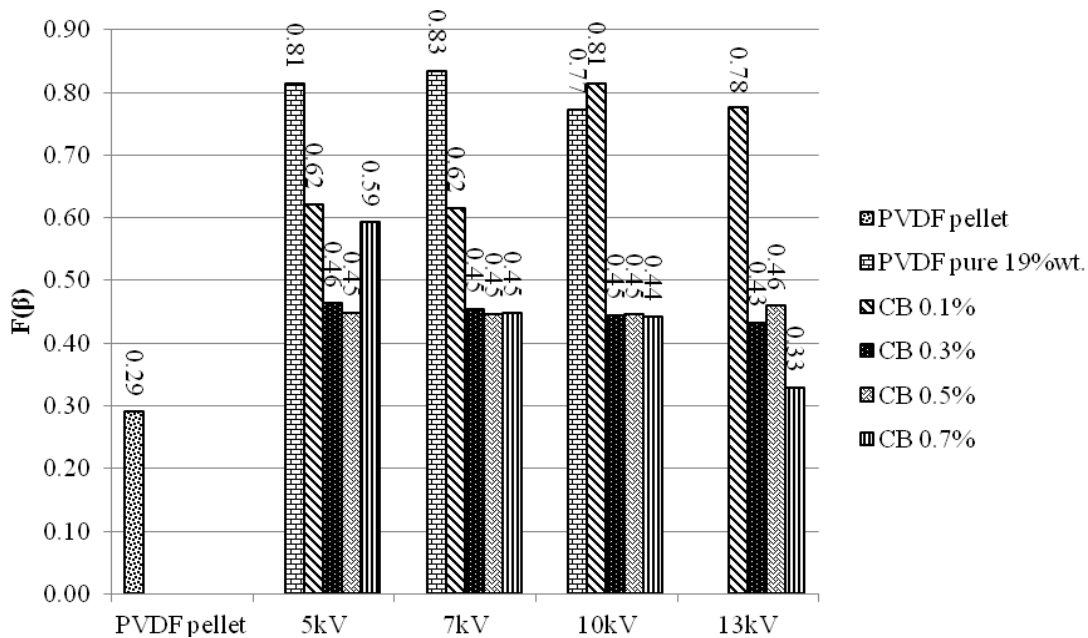


Figure 6: Effect of carbon black content and applied voltages on  $\beta$  phase ratio of PVDF-CB composite nanofiber.

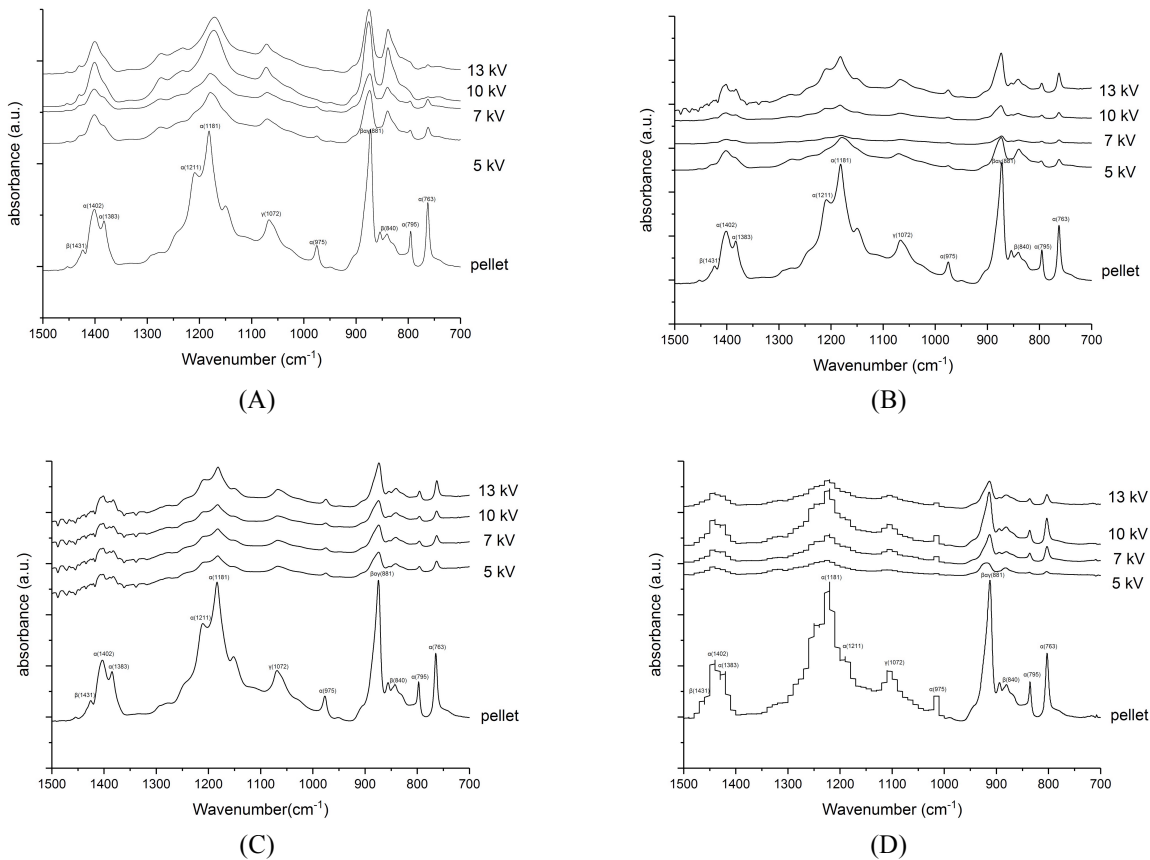


Figure 7: FT-IR absorbance spectrum of PVDF-CB in carbon black percentages by weight of 0.1(a), 0.3(b), 0.5(c) and 0.7(d)



The addition of particulate filler such as carbon black was expected to straighten PVDF chain, forming  $\beta$  conformation instead of the coiled  $\alpha$  phase. The kinetic of PVDF crystallization could be modified by the induction of nuclei provoked by the added filler and the electrostatic interaction between functional groups on the carbon with  $\text{CF}_2$  dipole could be increased, similar to the results obtained from Lim et al. [15]. Figure 6 inversely shows the effect of carbon black content on the  $\beta$ -phase ratio of PVDF-CB composite nanofibers. The addition of high carbon black content to PVDF apparently has the negative effect on  $\beta$ -phase ratio, especially when the carbon content is more than 0.1 wt%.

FTIR analysis (Figure 7) confirms that, for 0.3 wt%, 0.5 wt% and 0.7 wt% carbon content, still considerable amounts of  $\alpha$  phase (represented by the absorption band at  $763\text{ cm}^{-1}$ ) remained in the PVDF electrospun fibers ( $\beta$ -phase ratios are less than 50%). The inverse result is observed when carbon content is low at 0.1 wt%, where  $\beta$ -phase ratios are higher (Figure 7a) and reach the optimum at 0.81 with 10 kV of applied voltage. Characteristic absorption band of  $\beta$ -phase at  $840\text{ cm}^{-1}$  strongly increases in intensity, while characteristic absorption band of  $\beta$ -phase at  $763\text{ cm}^{-1}$  is evidently flatten (Figure 7a). This  $\beta$ -phase ratio is comparable and only slightly lower than that obtained in absence of carbon black with the same condition. This contrast could be ascribed by the irregular distribution of carbon black in polymer matrix as shown by SEM image (Figure 5). Moreover the too high amount of carbon black particle and the formed carbon black aggregate could prevent the formation of PVDF nuclei and forbid the polymer to elongate the same direction resulting the lower and unsatisfied  $\beta$ -phase ratio, as the FTIR spectra shows also the absence of evident chemical interaction between carbon black surface and PVDF matrix.

## Conclusion

This research was conducted on the preparation of composite nanofiber material prepared from poly(vinylidene fluoride) and carbon black for nanogenerator application. The preparation of nanocomposite materials between poly(vinylidene fluoride) and carbon black using electrospinning process can increase the  $\beta$  phase ratio only at low carbon black content. Moreover, the optimum polymer concentration for the preparation of composite nanofiber was 19% w/w of poly(vinylidene fluoride), representing the best  $\beta$  phase ratio (0.83). Thus the polymer concentration directly correlates to the solution viscosity, lower viscosity, from the one side, promotes the generation of smaller fibers but in case lower concentration of polymer solution, it was led to the formation of beaded fibers. Finally, the synthesis of nanocomposite materials between poly(vinylidene fluoride) and carbon black by using 0.1% w/w of carbon black was the optimum condition, the  $\beta$  phase ratio was 0.81. In addition, when carbon black content exceeds 0.1% w/w leads to the formation of smaller size fiber in presence of many beads, the  $\beta$  phase ratio inversely decreases.

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## References

- [1] Jaffe, B.; Cook Jr, W. R.; Jaffe, H. in: Piezoelectric ceramics. Academic Press, London, UK, **1971**.
- [2] Safari, A.; Akdogan, E. K. in: Piezoelectric and Acoustic Materials for Transducers Applications, Springer, New York, **2008**.
- [3] Ye, Z. Handbook of advanced, Dielectric, Piezoelectric and Ferroelectric Materials: Synthesis, Properties and Application, CRC Press, North America, **2008**.
- [4] Mathur, S.C.; Scheinbeim, J. I.; Newman, B. A. Dielectric studies of dipolar relaxation processes in nylon 11. *Journal of Applied Physics* **1984**, *56*, 2419-25.
- [5] Huang, L.; Zhuang, X.; Hu, J.; Lang, L.; Zhang, P.; Wang, Y.; Chen, X.; Wei, Y.; Ying, X. Synthesis and characterization of electroactive and biodegradable ABA block copolymer of polylactide and aniline pentamer. *Biomacromolecules* **2008**, *9*, 850-8.
- [6] Lovinger, A. J. Ferroelectric polymer. *Science* **1983**, *220*, 1115-21.
- [7] Lovinger, A.J. Poly(vinylidene fluoride). In: Bassett, E. (Ed.). Developments in Crystalline Polymers-I. Applied Science Publishers/Cambridge University Press. **1982**, 197-273.
- [8] Persano, L.; Dagdeviren, C.; Su, Y.; Zhang, Y.; Girardo, S.; Pisignano, D.; Huang, Y.; Rogers, J. A. High performance piezoelectric devices based on aligned arrays of nanofibers of poly(vinylidene fluoride-co-trifluoroethylene). *Nat. Commun.* **2013**, *4*, 1633.

- [9] Martins, P.; Lopes, A. C.; Lanceros-Mendez, S. Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications *Progress in Polymer Science* **2013**, *39*, 683.
- [10] Martins, P.; Nunes, J. S.; Hungerford, G.; Miranda, D.; Ferreira, A.; Sencades, V.; Lanceros-Mendez, S. *Journal of Physical Chemistry C*. **2012**, *116*, 1570-4.
- [11] Ribeiro, C.; Sencades, V.; Gomez Ribelles, J. I.; Lanceros-Mendez, S. Facile Formation of  $\beta$  Poly(vinylidene fluoride) Films using the Short Time Annealing Process *Soft Mater.* **2010**, *8*, 274-87.
- [12] Pan, H.; Na, B.; Lv, R.; Li, C.; Zhu, J.; Yu, Z. Z. Polar phase formation in poly(vinylidene fluoride) induced by melt annealing. *Journal of Polymer Science Part B: Polymer Physics*. **2012**, *50*, 1433-7.
- [13] Holmes-Siedle, A.G., Wilson, P.D., Verrall, A.P. (1984). PVDF: an electronically-active polymer for industry. *Materials&Design*, *4* (6), 910-918.
- [14] Sato, T., Ishikawa, H., Ikeda, O. (1982). Multilayered deformable mirror using PVDF films. *Applied Optics*, *29*, 363-366.
- [15] Lim, J.Y., Kim, S., Seo, Y. (2015) *Enhancement of  $\beta$ -phase in PVDF by electrinsinning*. Paper presented at the AIP conference proceeding, published by the American Institute of Physics.
- [16] Yee, W.A., Kotaki, M., Liu, Y., Lu, X. (2007). Morphology, polymorphism behavior and molecular orientation of electrospun poly(vinylidene fluoride) fibers. *Polymer*, *48*, 512-521.
- [17] Theron, A., Zussmann, A., Yarin, A.L. (2001). Electrostatic field-assisted alignment of electrospun nanofibers. *Nanotechnology*, *12*, 384-390.
- [18] Wu, Y.; Hsu, S. L.; Honeker, C.; Bravet, D. J.; Williams, D. S. The role of surface charge of nucleation agents on the crystallization behavior of poly(vinylidene fluoride). *Journal of Physical Chemistry B* **2012**, *116*, 7379-88.
- [19] Ye, H.; Shao, W.; Zhen, L. Crystallization kinetics and phase transformation of poly(vinylidene fluoride) films incorporated with functionalized BaTiO<sub>3</sub> nanoparticles. *Journal of Applied Polymer Science*. **2013**, *129*, 2940-9.
- [20] Shah, D.; Maiti, P.; Gunn, E.; Schmidt, D. F.; Jiang, D. D.; Batt, C. A.; Giannelis, E. R. Crystallization kinetics of poly(vinylidene fluoride)/MMT, SiO<sub>2</sub>, CaCO<sub>3</sub>, or PTFE nanocomposite by differential scanning calorimeter. *Advanced Materials*. **2004**, *16*, 1173-7.
- [21] Li, Y. J.; Xu, M.; Feng, J. Q.; Dang, Z.M. Dielectric characteristics of polyvinylidene fluoride-polyaniline percolative composites up to microwave frequencies. *Appl. Phys. Lett.* **2006**, *89*, 7, 07290.
- [22] Mendes, S. F.; Costa, C. M.; Caparros, C.; Sencadas, V.; Lanceros-Mendez, S. Fabrication Method Study of ZnO Nanocoated Cellulose Film and Its Piezoelectric Property. *J. Mater. Sci.* **2012**, *47*, 1378-1388.
- [23] Wang, J.; Wu, J.; Xu, W.; Zhang, Q.; Fu, Q. Simultaneous Reduction and Functionalization of Graphene Oxide by 4-Hydrazinobenzenesulfonic Acid for Polymer Nanocomposites. *Compos. Sci. Technol.* **2014**, *91*, 1-7.
- [24] Martin, P.; Moya, X.; Phillips, L. C.; Kar-Narayan, S.; Mathur, N. D.; Lanceros-Mendez, S. Elastic aging from coexistence and transformations of ferroelectric and antiferroelectric states in PZT. *Journal of Physics D*. **2011**, *44*, 1-4.
- [25] Mandal, D.; Kim, K. J.; Lee, J. S. Simple synthesis of palladium nanoparticles,  $\beta$ -phase formation, and the control of chain and dipole orientations in palladium-doped poly(vinylidene fluoride) thin films. *Langmuir* **2012**, *28*, 10310-7.
- [26] Wang, W.; Zhang, S.; Srisombat, L. O.; Lee, T. R. Predicting mechanical properties of polyvinylidene fluoride/carbon nanotube composites by molecular simulation. *Macromolecular Materials and Engineering* **2011**, *296*, 178-84.
- [27] Jiang, S. L.; Yu, U.; Xie, J. J.; Wang, L. P.; Zeng, Y. K.; Fu, M. Positive temperature coefficient properties of multiwall carbon nanotubes/poly(vinylidene fluoride) nanocomposites. *J. Appl. Polym. Sci.* **2010**, *116*, 838-842.
- [28] Zhang, Y.J., Zhao, Z.D., Yu, W.X. (2010). Preparation and characterizations of PVDF/MWCNT nanocomposites. *Polymer Materials Science and Engineering*, *26*, 141-144.
- [29] Liu, Z.H., Pan, C.T., Lin, L.W., Lai, H.W. (2013). Piezoelectric properties of PVDF/MWCNT nanofiber using near-field electrospinning. *Sensors and Actuator A*, *193*, 13-24.
- [30] Konishi, Y., Cakmak, M. (2006). Nanoparticle induced network self-assembly in polymer-carbon black composites. *Polymer*, *47*, 5371-5391.
- [31] Yee-Shuan Lee and Treena Livingston Arinze. Electrospun Nanofibrous Materials for Neural Tissue Engineering. *Department of Biomedical Engineering, New Jersey Institute of Technology, Newark, NJ 07102, USA*, 2011.
- [32] Gregorio Jr, R., Cestari, M. (1994). Effect of Crystallization Temperature on the Crystalline Phase Content and Morphology of Poly(Vinylidene Fluoride). *Journal of Polymer Science: Part B: Polymer Physics*, *32*, 859.
- [33] Richards, C.D., Anderson, M.J., Bahr, D.F., Richards, R.F. (2004). Efficiency of energy conversion for devices

- containing a piezoelectric components. *Journal of Micromechanics and Microengineering*, 14, 717-721.
- [34] Lim, J.Y., Kim, J., Kim, S., Kwak, S., Lee, Y., Seo, Y. (2015). Nonisothermal crystallization behaviors of nanocomposites of poly(vinylidene fluoride) and multiwalled carbon nanotubes. *Polymer*, 62, 11.
- [35] M. Chowdhury and G. Stylios. Effect of Experimental Parameters on the Morphology of Electrospun Nylon 6. *Fibres. Int. J. Basic Appl. Sci.*, 2010, 10, 116.
- [36] B. Veleirinho, M. F. Rei and J. Lopes-DA-Silva. Solvent and concentration effects on the properties of electrospun poly (ethylene terephthalate) nanofiber mats. *J. Polym. Sci., Part B: Polym. Phys.*, 2008, 46, 460.
- [37] Mokhtari, F., Latifi, M., Shamshiraz, M. (2016) Electrospinning/electrospray of polyvinylidene fluoride (PVDF): piezoelectric nanofibers. *The journal of The textile Institute*, 107, 1037-1055.
- [38] Enomoto, S., Kawai, Y., & Sugita, M. (1968). Infrared spectrum of poly(vinylidene fluoride). *Journal of Polymer Science: Part A-2*, 6, 861–869.
- [39] J. Fang, X. Wang and T. Lin. Electrical power generator from randomly oriented electrospun poly(vinylidene fluoride) nanofibre membranes. *J. Mater. Chem.*, 2011, 21, 11088.
- [40] E. S. Cozza, O. Monticelli, E. Marsano and P. Cebe. On the electrospinning of PVDF: Influence of the experimental conditions on the nanofiber properties. *Polym.Int.*, 2013, 62, 41.
- [41] L. Yu and P. Cebe. Crystal polymorphism in electrospun composite nanofibers of poly(vinylidene fluoride) with nanoclay. *Polymer*, 2009, 50, 2133.
- [42] Z. Liu, C. Pan, L. Lin and H. Lai. Piezoelectric properties of PVDF/MWCNT nanofiber using near-field electrospinning. *Sens. Actuators, A*, 2013, 193, 13.
- [43] Shao, H., Fang, J., Wang, H., Lin, Tong. (2015). Effect of electrospinning parameters and polymer concentrations on mechanical-to-electrical energy conversion of randomly-oriented electrospun poly(vinylidene fluoride) nanofibers mats. *RSC Advances*, 5, 14345-14350.