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Effect of Graphite Dopant in Polyvinylidene Flouride (PVDF) Electrospun Composites

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ABSTRACT

Polyvinylidene Fluoride (PVDF) is a high purity thermoplastic fluoropolymer that has huge potential, has been employed in numerous electronics, space, and aeronautics industries. The beta-phase of PVDF is the most beneficial due to its superior piezoelectric and pyroelectric properties, which are essential for high-performance applications. Thus, the research on attaining the beta-phase has been critical. PVDF crystallinity could be enhanced by varying processing methods and parameters, including electrospinning. Various researchers have reported on the electrospinning PVDF as a successful route to get beta-phase. The morphology, crystalline phases, and electrical conductivity of PVDF fiber are significantly influenced by electrospinning parameters. In this work, the effect of graphite loading in PVDF is one of the parameters examined. The objective of this work is to investigate the impact of graphite dopant loading on the electrical conductivity of electrospun PVDF composite. The most straightforward and affordable way to create PVDF fibers is by electrospinning. PVDF was first dissolved using N, N-Dimethylformamide (DMF) before mixing with graphite (0.25 wt%, 0.50 wt%, 0.75 wt%, and 1.0 wt%). Each solution was then electrospinned to produce conductive composite fiber. The parameters were fixed at 25 kV voltage; 1.5 ml/h flow rate; and 12 cm tip-to-collector distance. The morphology, electrical conductivity, and crystalline phases of electrospun PVDF fibers were examined using scanning electron microscope (SEM), four-point probe and X-ray diffraction (XRD) machine. As the graphite concentration rises, SEM micrograph showed that more beads were developed along with fiber sizes increment. Short electrospinning times result in insufficient electrospun mat thickness, which affects peak shift, according to XRD examination of all fibers. According to the results of the four-point probe examination, the conductivity rises dramatically and the resistance decreases as the graphite concentration increases.

Keywords: *Electrospinning, Polyvinylidene flouride, Graphite, Conductive composites fibers*

1. INTRODUCTION

Polyvinylidene Flouride (PVDF) is a semi-crytalline polymer that exhibits excellent piezoelectric, pyroelectric, ferroelectric and dielectric properties [1]. The high electric dipole moments of PVDF monomers ($5\text{-}8\times10^{-30}$ cm) have sparked extensive study into their potential use in sensors, actuators, and nanogenerators. High piezoelectric response is caused by the higher electronegativity of fluorine (F) atoms compared to carbon © and hydrogen (H) [2].

The term piezoelectricity refers to the study of the piezoelectric properties of PVDF, which involve a material's ability to convert internal elastic energy into dielectric energy when subjected to an external load. [3]. The piezoelectric properties of PVDF make them versatile polymer, besides being easy processing and incorporated with other functional materials to enhance their performance. PVDF is a vinylidene monomer (CH_2CF_2) homopolymer that has the highest flexural modulus of any fluoropolymer. This is because larger CF_2 groups crystallize with adjacent smaller CH_2 groups on adjacent chains [4]. PVDF is a semicrystalline polymer with a chain that is stretched in a zigzag pattern. Crystallinity is anything between 35 to 70 percent depending on the sample [5]. PVDF is combined with a variety of other compounds to enhance the performance characteristics of the applications that it will ultimately be used for, whether they be processing applications or end-use applications. PVDF resin may be broken down by strong bases, amines, esters, and ketones, thus it must be handled with care. Depending on the specifics of the situation, the result might range anywhere from swelling to complete dissolution in particular solvents.

However, their piezoelectricity mainly depends on their crystalline phase, which includes five polymorphs of α, β, γ, δ and ε. The α phase is thermodynamically stable and easy to find, however it is considered non-ferroelectric. PVDF intermolecular interactions are connected by short-range Van-der-Walls forces that have low potential barrier for chain molecules rotation, which result in easy conversion between different phases [6]. The main attributes for PVDF piezoelectric properties are β phase and γ phase, where β phase shows largest electric dipole moment among all crystalline phases.

Various efforts were done by previous researchers to increase the yield of β phase in PVDF, namely by modifying its nano structures with different piezoelectric materials, conductive and non-conductive fillers as a dopant, at different dopant concentrations, using varying methodology. Among the established methods, stretching and poling are claimed as effective ways in producing phase to increase the piezoelectric properties in PVDF. In fact, electrospinning, which operates under strong electric field and stretching force induced β phase formation and dipoles arrangement, promoting high percentage of crystallinity (49%) and high degree of β phase (76.2%) [7]. Numerous studies showed PVDF fibers by electrospinning are biocompatible, flexible, lightweight, ultrafine with tunable thickness, and able to produce high phase content. It is known as the simplest and most efficient technique in producing nanofibers, with the ability to vary its yield by adjusting the conditions of the material, its viscosity or conductivity, as well as processing variables such as the voltage that is supplied, the spinning distance, the flow rate, and the temperature [8-9]. The electrospinning method is particularly adaptable, allowing for the processing of a wide range of polymers into polymeric nanofibers as well as the co-processing of polymer mixtures and combinations of polymers and low molecular weight non-volatile compounds. Blends of polymers and low molecular weight non-volatile compounds are manageable in the electrospinning procedure [10].

Introducing filler into PVDF during electrospinning also increases the chance of getting its β phase. Adding graphite may increase the conductivity of the yield PVDF composite, besides supporting the arrangement of β PVDF structures. Graphite is known to effectively improve the electrical properties of polymer. Graphite is a remarkable example of a rare substance where its structure, which is visible on scales from nanometers to millimeters, endows it with exceptional qualities that make it useful in a wide variety of contexts. Graphite's unusual set of qualities can be traced back to the anisotropy of its bonds. Graphite exhibits bond anisotropy due to the presence of both strong covalent connections inside the graphite plane and weak Van-der-Walls -type bonding between graphite planes [11]. In comparison with other carbon families, graphite is still relevant and attractive as it possesses lowest cost of all, despite of having good mechanical, thermal and electrical properties [12]. Thus in this study, graphite is used as a filler in electrospun PVDF composite.

2. METHODOLOGY

2.1. Materials

The solvent used to dissolve PVDF fiber and the graphite is Dimethylformamide (DMF). The PVDF and graphite come in powder form, which was supplied by Sigma- Aldrich. The molecular weight of PVDF is 534,000 g/mol. The electrical properties for the graphite is 1.50 W/(m·K) for the thermal conductivity and for electrical conductivity is 3×10-3 μΩ^{-1}·cm^{-1}.

2.2. Methods

PVDF powder is dissolved in DMF solution to produce 15wt% PVDF concentration, followed by the addition of graphite powders at varying concentrations of 0 %, 0.2 5%, 0.50 %, 0.75 % and 1.00 % to create a polymer fiber composite solution. The mixture is mixed by magnetic stirrer for 2 hours until it is homogeneous and transparent before undergoing sonification for 1 hour to improve homogeneity. Figure 1 shows the the experimental flow chart.

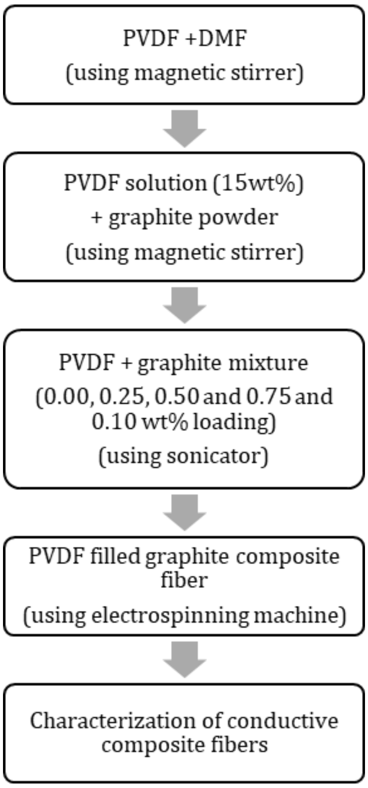

Figure 1. Flow chart of PVDF filled graphite electrospun fiber.

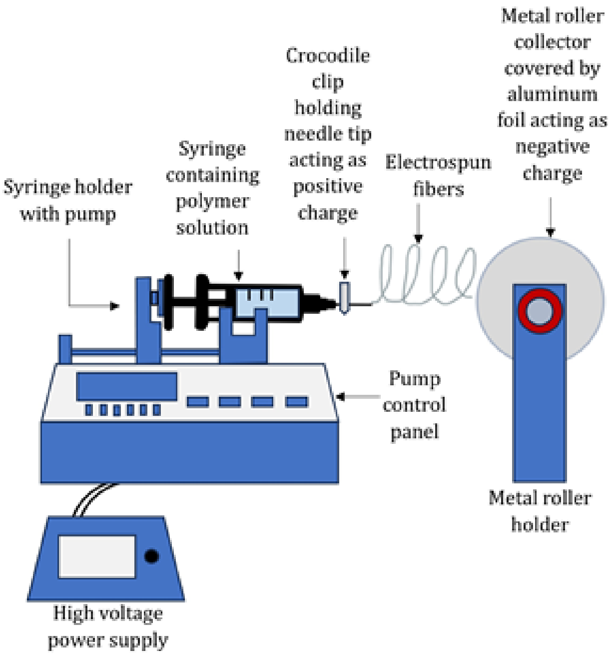

Figure 2. Electrospinning process set-up.

Electrospinning is a successful process for collecting PVDF fibers after the solution is prepared. The prepared PVDF and graphite mixture is filled into a 10ml syringe with an inner diameter of 0.8mm, which is placed horizontally at the syringe pump on the injection holder. The electrospinning process is carried out at 1.5ml/h flow rate, 25kV voltage and 12mm tips to collector distance. The syringe is prepared by scraping and polishing the needle, and a crocodile clip is attached to conduct current from the power supply. This activates the pump machine, allowing PVDF to flow out of the needle's tip. The fiber is collected using a metal roller covered in aluminium foil, oriented at right angles to the syringe's nozzle (Figure 2).

2.3. Characterization

The morphology of PVDF fibers was examined with a Hitachi TM3000 scanning electron microscope (SEM). The samples were produced to be l cm × 1 cm in size. The phase of PVDF fibers was determined using X-Ray Diffraction (XRD) analysis with the XRD-600 model from Shimadzu, Tokyo, Japan. The scan rate was 0.02% and the range of 2θ scans was 5° to 50°. PVDF fibers' electrical conductivity was measured using a four-point probe. Keithley 6221 AC/DC source and Keithley 2182A nanovoltmeter were used in the study. The samples were measured with 100V of voltage present.

3. RESULTS AND DISCUSSION

3.1. Morphological Analysis

Figure 3 displays SEM images of PVDF composite electrospun fibers with varying graphite percentages. All fibers displayed braided fibers with variable diameters.

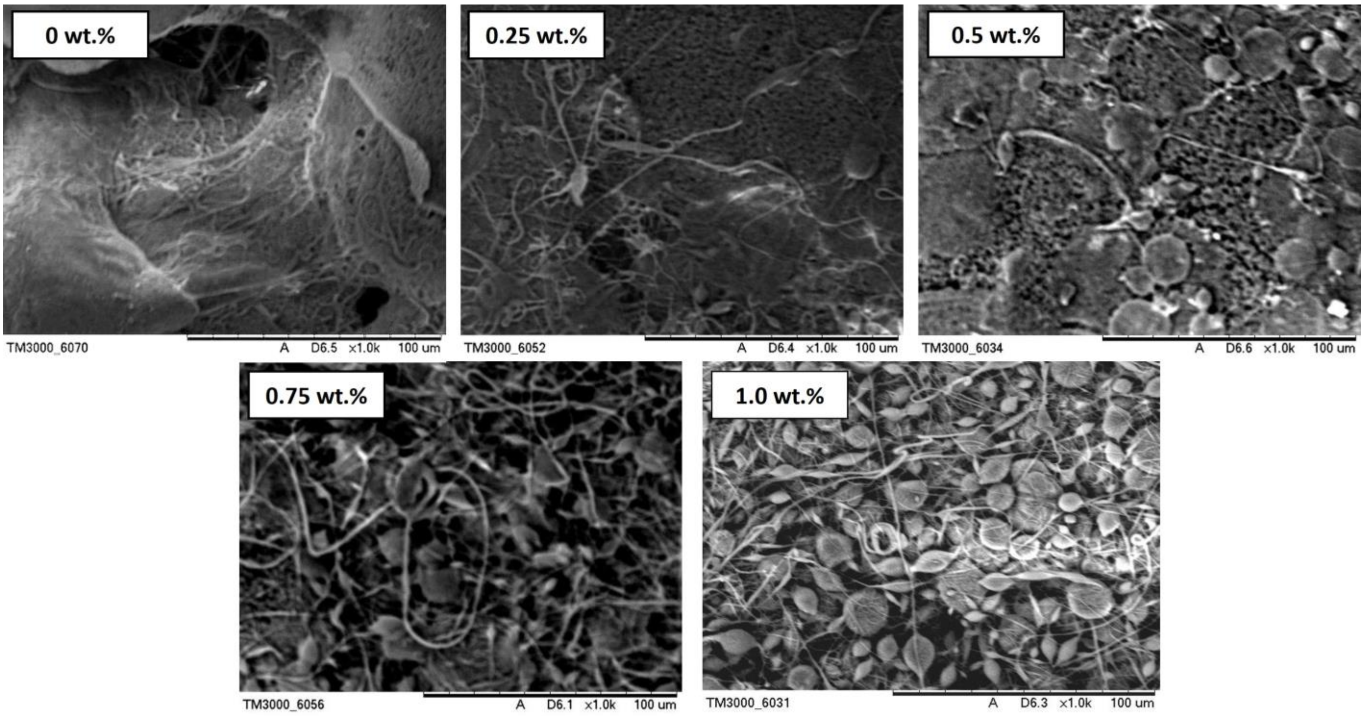

Figure 3. SEM image of PVDF composite electrospun fibers with different percentages of graphite content.

Including graphite in PVDF solutions leads to the development of beads, which are popular due to clustering or agglomeration of graphite particles, poor dispersion, and potential modifications in rheological characteristics. Changes in solution properties can interfere with fiber formation and result in beads. Additionally, there may be inherent incompatibility between graphite and PVDF due to their differing physical properties, which can hinder the electrospinning process and encourage beads formation.

The sample containing 0 wt.% graphite of electrospun PVDF composite fiber exhibited the least amount of bead formation in comparison to the other samples. The electrospun PVDF composite fibers in samples containing 0.25 wt.%, 0.50 wt.%, and 0.75 wt.% exhibit beaded fibers. As the filler ratio is increased, the smooth nanofiber morphology of the classical fiber undergoes a gradual transformation to polymer aggregates that are visible as beads. The shape of these beads varies depending on the concentration of the filler used. When the concentration of filler is increased, the concentration of polymer beads increased and tend to form a more spherical structure [13]. This finding was also similarly discussed by previous researchers where, as the viscosity of the solution increased, for this case, the increasing graphite loading has increased viscosity of PVDF solution; the beads size and the average distance between beads are larger, while the fiber shape becomes more spindle-like than spherical as we could observed at 1.0 wt% graphite loading in Figure 3 [8].

3.2. Phase Determination

Figure 4 shows the XRD plots with various graphite content percentages that were illustrated by XRD patterns seen from 0° to 50°. Among the other samples, sample 0.75 wt.% exhibits the highest diffraction peak at 22.69°, followed by samples 0.50 wt.% at 22.68°, 0.25 wt.% at 21.73°, 0 wt.% at 22.63°, and sample 1.0 wt.% at 22.49° (Table 1).

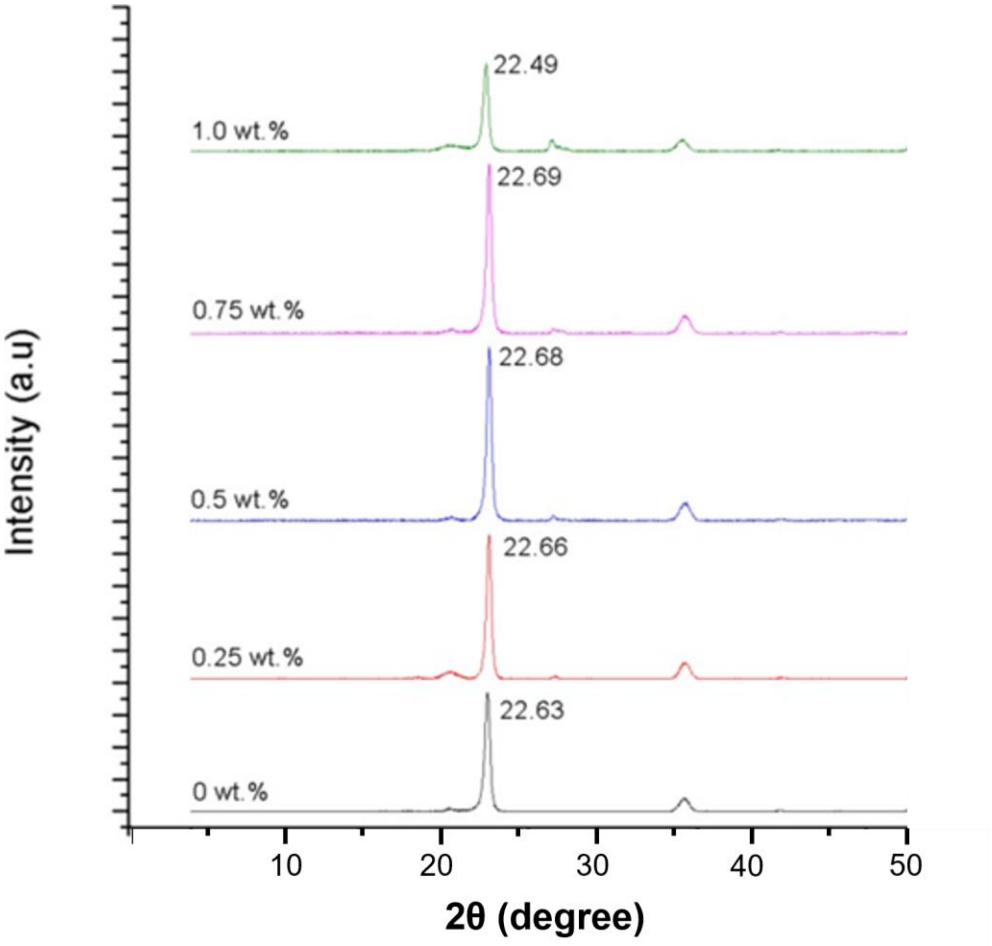

Figure 4. XRD plots of PVDF composite electrospun fibers with different percentages of graphite content.

The percentage of graphite content effect towards crystalline structure of electrospun fibers was also observed by XRD. According to Figure 4, the highest percentage of graphite content (1.00 wt%) shifted the peak closer to the desirable β-phase crystal peak at around 2θ = 20.8°. This phenomenon was also discovered by Manojit and Parasharam [6] where they have stated that the addition of carbon-based filler has increased the piezoelectricity of the PVDF, which in this case the XRD peak of 1.00 wt% graphite is closest to the β-phase structure. Similar findings on the effect of carbon as a filler may help to align the electrospun fiber formation, thus enhancing the β-phase formation was also reported by Sanskruti et al. [8].

Meanwhile, the peak of samples 0, 0.25, 0.50 and 0.75 wt.% shifted further from desirable β-phase samples. This phenomenon can be attributed to the fact that orientation of nanofibers.

Table 1 XRD peaks location of PVDF composite electrospun fibers with different percentages of graphite content

Graphite loading (wt%)	Peak positions 2θ(°)
0.00	22.63
0.25	22.66
0.50	22.68
0.75	22.69
1.00	22.49

It is because of a combination of two element tendency to the orientation of fiber. The orientation of the fibers can affect the XRD pattern by causing preferred crystallographic orientations and altering the diffraction peak positions.

3.3. Electrical Properties

Figure 5 displays the average resistance of five samples with varying graphite percentages as measured by a four-point probe. Observation indicates that samples without graphite has the highest average resistance of 3.3115 Ω. As the percentage of graphite loading increased, the resistance of samples decreased. The sample containing the highest graphite, 1.00 wt% demonstrates the lowest resistance of 2.5514 Ω. With the increment of graphite content, the average conductance of samples has increased as exhibited in Figure 6.

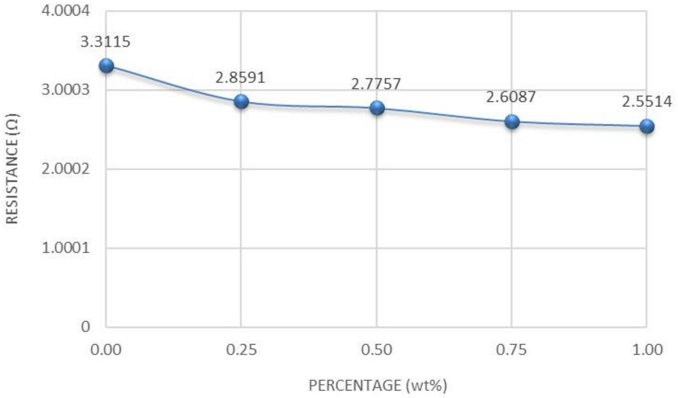

Figure 5. Average electrical resistance of PVDF composite electrospun fibers with different percentages of graphite content.

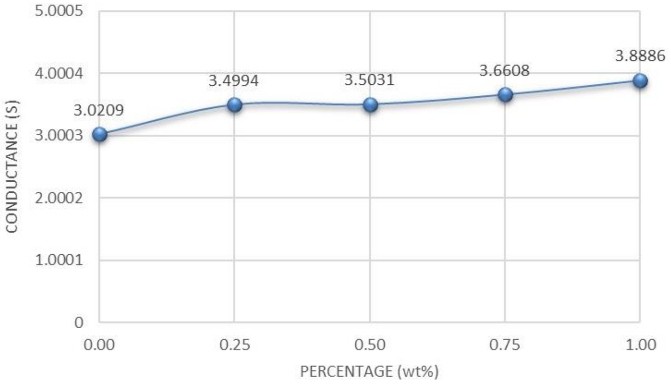

Figure 6. Average electrical conductance of PVDF composite electrospun fibers with different percentages of graphite content.

The average of five samples with varying graphite percentages as measured by a four-point probe to measure their conductance. It can be observed that samples with 0 wt% of graphite have the lowest average conductance of 3.0209 Siemens. The value of conductance has gradually increased as the graphite loading increased in fiber, which went up to 3.8886 Siemens at 1.00 wt% of graphite. Graphite is known as one of the fillers used conventionally to increase the electrical conductivity of yield products. The improved electrical conductivity also signed of good dispersion of graphite in polymer [12]. The increment of conductance as the percentages of graphite increased is also supported by XRD findings where the nearest peak to β-phase is found in the highest graphite percentage loading. Similar findings were also discussed by previous researchers where they reported that apart from enhancing mechanical and thermal properties, carbon materials are able to increase conductivity, which made them unique and favourable in increasing the piezoelectricity of PVDF [8]. Table 2 summarizes the resistivity and conductivity data of the PVDF filled graphite electrospun fiber yield samples.

Table 2 Average resistance and conductance of PVDF composite electrospun fibers with different percentages of graphite content

Graphite Loading (wt%)	Average resistance (Ω)	Average conductance (S)
0.00	3.3115	3.0209
0.25	2.8591	3.4994
0.50	2.7757	3.5031
0.75	2.6087	3.6608
1.00	2.5514	3.8886

4. CONCLUSION

The study examined the impact of graphite addition on the morphology, crystalline phases, and electrical characteristics of electrospun PVDF composite fibers. The morphology was determined using Scanning Electron Microscope analysis, and the beaded appearance of the fibers was attributed to filler, inadequate stirring process, and insufficient time. The percentage of graphite content also affected the thickness of the fibers, with higher graphite content causing more bead formation. XRD analysis revealed that the PVDF fiber peaks did not appear at the expected position of 20.1°-20.8°, but instead were located at 22.49° to 22.69°. This issue was due to the insufficient thickness of the electrospun PVDF fibers. The superior electrical properties of electrospun PVDF fiber were attributed to the properties of the β-phase of PVDF. The sample with the highest graphite content of 1.00 wt.% showed the highest β-phase properties and conductivity, while the sample with 0 wt.% graphite has the lowest electrical properties. The results showed a significant increase in average conductance as graphite content increased, while the average resistance decreased. Based on the overall findings of this study, electrospinning parameters are crucial for formation of β-phase, fiber size and distributions of beads. The addition of graphite fibers has an enhance the conductivity of PVDF conductive composite fibers.

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REFERENCES

[1] F. Mokhtari, M. Salehi, F. Zamani, F. Hajiani, F. Zeighami, and M. Latifi, "Advances in electrospinning: The production and application of nanofibres and nanofibrous structures," *Textile Progress*, vol. 48, no. 3, pp. 119-219, 2016.

[2] A. S. Motamedi, H. Mirzadeh, F. Hajiesmaeilbaigi, S. Bagheri-Khoulenjani, and M. A. Shokrgozar, "Effect of electrospinning parameters on morphological properties of PVDF nanofibrous scaffolds," *Progress in Biomaterials*, vol. 6, pp. 113–123, 2017.

[3] G. Kalimuldina, N. Turdakyn, I. Abay, A. Medeubayev, A. Nurpeissova, D. Adair, and Z. Bakenov, "A Review of Piezoelectric PVDF Film by Electrospinning and Its Applications," Sensors, vol. 20 (18), pp. 5214, 2020.

[4] S. Ebnesajjad, "Introduction to Fluoropolymers Materials, Technology, and Applications (Second Edition), *William Andrew,* 2020.

[5] I. S. Chronakis, "Micro-/nano-fibers by electrospinning technology: Processing, properties and applications," *Micromanufacturing Engineering and Technology*, pp. 513-548, 2010.

[6] M. Pusty, and P. M. Shirage, "Insights and perspectives on graphene-PVDF based nanocomposite materials for harvesting mechanical energy," *Journal of Alloys and Compounds*, vol., 904, 2022.

[7] L. Lu, W. Ding, J. Liu, and B. Yang, "Flexible PVDF based piezoelectric nanogenerators," *Nano Energy*, vol. 78, (12), 105251, 2020.

[8] S. S. Dani, B. Sundaray, S. K Nayak, and S. Mohanty, "Electrospun PVDF and composite nanofiber: Current status and future prescription towards hybrid Piezoelectric nanogenerators," *Materials Today Communications*, vol. 38, 107661, 2024.

[9] Y. Liu, K. Li, M. M. Mohideen, and S. Ramakrishna, "Formation of fibrous structure and influential factors in melt electrospinning," in *Melt Electrospinning,* 2019.

[10] E. Kabir, M. Khatun, L. Nasrin, M.J. Raihan, and M. Rahman, "Pure β-phase formation in polyvinylidene fluoride (PVDF)-carbon nanotube composites," *Journal of Physics D: Applied Physics*, vol. 50, 163002, 2017.

[11] B. Timothy, "Graphite: Properties and Characteristics," *Comprehensive Nuclear Materials*, vol. 2, pp. 285-305, 2012.

[12] S. Gantayat, G. Prusty, D.R. Rout, and S. K Swain, "Expanded graphite as a filler for epoxy matrix composites to improve their thermal, mechanical and electrical properties," *New Carbon Materials*, vol. 30 (5), pp. 432-437, 2015.

[13] Y. J. Huang, C. L. Huang, R. Y Lai, C. H. Zhuang, W. H. Chiu, and K. M. Lee, "Microstructure and biological properties of electrospun in situ polymerization of polycaprolactone-graft-polyacrylic acid nanofibers and its composite nanofiber dressings," *Polymers*, vol. 13 (23), 4246, 2021.