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# IMPACT OF DIMETHYLFORMAMIDE/ACETONE RATIOS AND STIRRING TIME ON MORPHOLOGY AND ELECTRICAL PROPERTIES OF ELECTROSPUN PVDF FIBERS

This study examines the impact of Dimethylformamide, DMF/Acetone ratio (60/40, 70/30 and 100/0) and stirring time (16 hours and 24 hours) on Polyvinylidene Fluoride electrospun fibers. Total of six samples were prepared at 12% solution concentration were electrospun at 20 kV, 10 cm tip-to-collector distance, and 1 mL/h flow rate. Morphological analysis showed that a 70/30 ratio produced finer fibers with fewer beads than 60/40 ratio, while prolonged stirring increased fiber diameter. Electrical analysis confirmed the lowest resistance and highest conductivity for these fibers. The 70/30 ratio and 16-hour stirring time technique optimized fiber structure and electrical performance for advanced applications.

*Keywords:* DMF; Acetone; PVDF; fiber; electrospinning

## 1. Introduction

Polymeric materials play a leading role in fibers development due to their excellent processability, low cost, and abundance, and the utmost important is their chemistry-structure processing-performance could be tailored according to our desired features which in this paper, the nanofibers are required to be around 0.01 to 0.1 μm in diameter for microfiltration purposes [1].

Electrospinning also exhibits the benefits of producing PVDF fiber structures and applied high voltage or high stretching ratio of the polymer solution's jet in benefits crystallization in the β phase [2].

Polyvinylidene fluoride (PVDF) is a thermoplastic fluoropolymer which is constituted of 5 distinct crystalline structures which are β, α, δ, γ and ε phases. The most important and useful characteristic of PVDF is the β-phases due to the existence of piezoelectric effect at this phase [3]. However, PVDF is thermodynamically unstable and pure PVDF exist in the form of α-phase which exert no piezoelectric effect. PVDF is not inherently conductive due to its original properties as thermoplastic, hence it is crucial to increase the electrical conductivity to use in the application of sensors, actuators transducer and in biomedical application. Research on how to attain this β-phase has been ongoing for decades, which is in the all trans (TTTT) crystal form conformation, where all the dipoles are aligned parallel to the chain axis in one direction. Additionally, the solution parameters like concentration, molecular weight, solvent, viscosity and additional filler and processing parameters like voltage applied, flow rate, tip to collector distance, collector types, and needle diameter are crucial in determining the yield of electrospun fiber structures, and by properly manipulating these parameters, fibers with desired morphology and structures may be attainable [4].

This study investigates the influence of solution parameters which are solvent ratio on the properties of PVDF fibers and stirring time. This study is significant because it highlighted exploring and improving solutions and electrospinning parameters effects on fiber formation and characterization that have not been fully utilized in other research. Key characterization includes morphology analysis via SEM to determine fibers diameter, consistency of thickness, and amount of beading in fibers and electrical properties analysis to determine PVDF's semicrystalline structure capability in resistivities and conductivities.

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## 2. Experiment

### 2.1. Materials

N-Dimethylformamide (DMF, vapor pressure 2.7 mmHg at 20°C) supplied from Supelco, Acetone (M = 58.08 g/mol) supplied from HmbG Chemical and Polyvinylidene fluoride (PVDF, average Mw = 534000 g/mol) purchased from Sigma-Aldrich. All the materials/chemicals were used as received.

### 2.2. Material preparation

PVDF was dissolved in DMF and acetone at 12 wt.% using DMF/acetone ratios of 60/40, 70/30, and 100% DMF. The solutions were stirred at 250 rpm and 50°C for 16 or 24 hours, respectively as shown in TABLE 1.

TABLE 1

Solution composition and stirring parameter for each sample

| **Sample name** | **Sample 1** | **Sample 2** | **Sample 3** |
|---|---|---|---|
| Composition (DMF/Acetone) | 60/40 | 70/30 | 100/0 |
| Stirring time, h | 24 | 24 | 24 |
| **Sample name** | **Sample 4** | **Sample 5** | **Sample 6** |
| Composition (DMF/Acetone) | 60/40 | 70/30 | 100/0 |
| Stirring time, h | 16 | 16 | 16 |

Prior to electrospinning, the prepared solution was loaded into a 10 mL Terumo™ plastic syringe fitted with a 21G Terumo™ stainless steel needle featuring a 90° blunt end and an inner diameter of 0.8 mm, as illustrated in Fig. 1. During the electrospinning process, a negative DC high voltage of 20 kV was applied to the solution through the needle using a high-voltage power supply by Gamma High Voltage Research, Inc. The solution was dispensed at a constant feed rate of 1 mL/h using a syringe pump, while the distance between the needle tip and the collector was maintained at 10 cm. The electrospun PVDF fibers were collected on a custom-built rotating drum collector, 20 cm in diameter covered with aluminum foil. The resulting PVDF fiber mat exhibited a uniform thickness of approximately 0.08 mm, as measured by a micrometer caliper.

### 2.3. Morphology test procedure

The morphology of PVDF fibers was analyzed using a JEOL JSM 6460LA scanning electron microscope (SEM). Samples measuring 10 mm × 10 mm were prepared and mounted on a sample holder using double-sided tape. A thin platinum layer was applied to the samples using a sputter coater to enhance conductivity. The SEM analysis was conducted at an accelerating voltage of 10 kV. Morphological analysis of the resulting images was performed using ImageJ software.

### 2.4. Electrical properties test procedure

The electrical resistivities and conductivities of electrospun PVDF fiber were measured by using Four-Point Probe (FPP). The conductivity was tested by Keithley 6220 AC/DC source and Keithley 2182A nanovoltmeter. The samples were measured in the present of 100 V as constant voltage and pulse level set to 0.02 Amps. Keithley software is used to calculate and record data.

## 3. Result and discussion

### 3.1. Morphology analysis

Fig. 2 shows the SEM result of Sample 1, Sample 2, Sample 4 and Sample 5 that show the fibrous characteristics as electrospun fibers while Sample 3 and Sample 6 shows porous fibers.

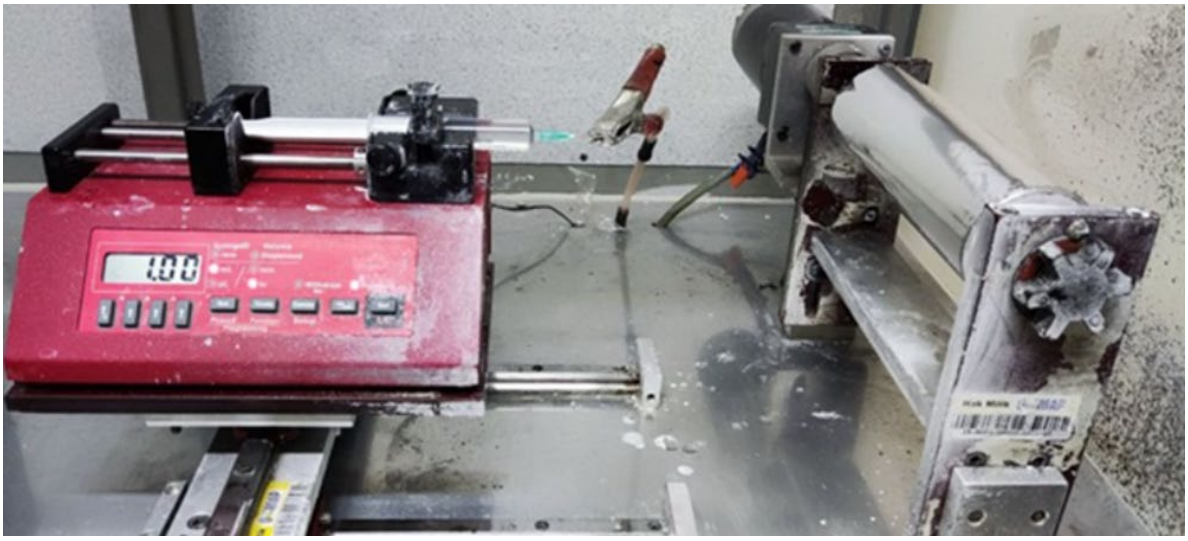
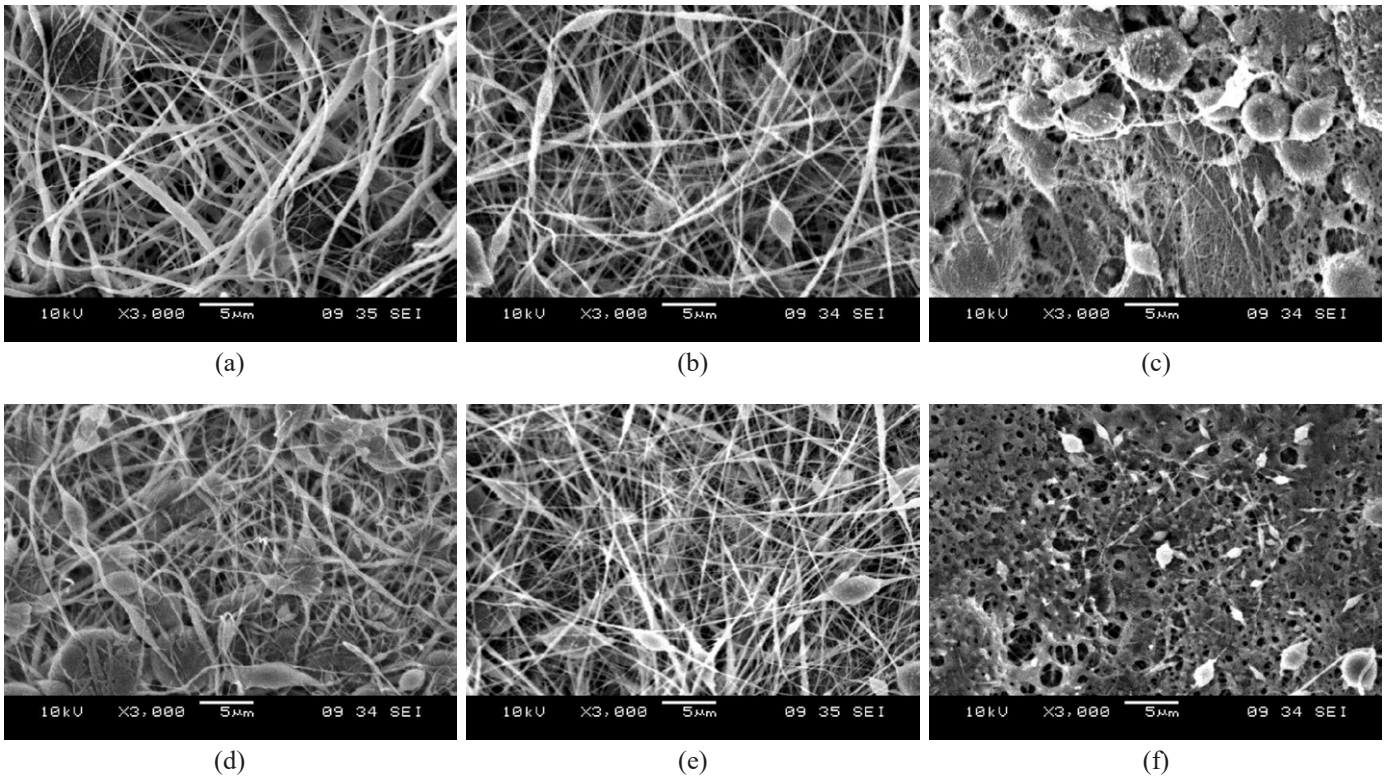


Fig. 1. Electrospinning process setup consists of syringe pump and rotating drum

These results were also supported by a researcher Abdullah where the 70/30 ratio produced the smallest average parameter due to optimum acetone percentage [5]. This also proves that adding acetone into solution helps reduce beads greatly when we compare the Sample 4 to Sample 6 result in TABLE 2. According to the same researcher, adding volatile solvents which in this experiment, acetone evaporates the solvent entirely during the electrospinning process making the solution more susceptible to create fibrous result [5]. Sample 3 and Sample 6 on other hand formed a multiple layer of PVDF deposits instead of fibers due to lack of acetone as volatile solvent. According to He, the solvent does not fully evaporate as it moves from the syringe tip to the collector, causing beads to form and making it harder to produce PVDF fibers [6]. The addition and the amount of acetone to a DMF solution plays a crucial role in controlling viscosity, which directly affects fiber formation during the electrospinning process as the DMF/acetone ratio significantly influences fiber diameter. Sample 1, with 60/40 ratio produced fibers with an average diameter of 0.866 µm, substantially thicker than Sample 2's average of 0.383 µm, a notable 77.34% difference proving the volume of acetone effects the morphology characteristic of fibers due to more stable rate of evaporation process. Additionally, a higher acetone content may cause jet instability or early breakup because of low surface tension, contributing to thicker fibers. The stirring duration also impacts fiber thickness, particularly at a 60/40 DMF/acetone ratio in Sample 1 and Sample 4, where extending the stirring time from 16 to 24 hours increased fiber diameter from 0.574 µm to 0.866 µm. This increase is attributed to prolonged stirring, which allows more time for polymer chains to interact and entangle, resulting in thicker fibers. Furthermore, a 70/30 DMF/acetone ratio proved ideal for producing finer fibers, as seen in Sample 2 with average fibers 0.383 µm and Sample 5, 0.360 µm exhibited only a slight decrease, 6.19% compared to thicker fibers in Sample 1 and Sample 4, which increased by 40.56%, highlighting the ratio's impact on refining fiber diameter stability.

Bead formation in electrospun fibers is caused by Rayleigh instability due to improper balance between viscosity and electrical forces leads the jet to break into beads instead of forming continuous fibers. [7]. These beads are usually seen as defects because they reduce the fiber's surface area, which can lower performance in applications like filtration and sensing. Sample 1, Sample 2, Sample 3 and Sample 4 exhibit bead formation within the fibers, which compromises the quality of the resulting fibers. From Fig. 2, the average large bead size in Sample 1 is larger, with 75.81 µm$^2$ or 34.25% increase and 14.00 µm$^2$ or 11.48% increase from average small bead compared to Sample 2 with average large bead and small bead 53.64 µm$^2$ and 12.48 µm$^2$ respectively. When stirring time parameter changed to 16 hours, Sample 4 exhibit worst average large bead formation with size of 97.43 µm$^2$ compared to Sample 1 where the average beads size is 24.96% increase proving prolong stirring time is necessary to dissolve more completely in the solvent, reducing undissolved aggregates or inconsistencies in the solution in exchange for thicker fibers. Sample 3 in other hand have the best average small bead and large bead formation with 36.42 µm$^2$ and 7.72 µm$^2$ respectively, proven by statement by Abdullah where adding solvent will reduce the beads area, but the ratio needs to be controlled where in this project, 70/30 ratio remains a superior solution parameter [5]. Unlike the 60/40 DMF/acetone ratio,




(a) (b) (c)

(d) (e) (f)

Fig. 2. SEM result in X3000 magnification for Sample 1 (a), Sample 2 (b), Sample 3 (c), Sample 4 (d), Sample 5 (e) and Sample 6 (f)

Sample 2 exhibits larger average beads compared to Sample 5. This difference is attributed to shorter polymer chains in Sample 2, which reduce the degree of chain entanglement, leading to instabilities in the electrospinning jet and the formation of larger beads. As shown in Figs. 3 and 4, Sample 4 displays the poorest bead distribution, characterized by the highest number of large beads and the presence of bead agglomeration. In contrast, Sample 5 demonstrates the best bead distribution, with the lowest number of large beads among all the samples, further proving 70/30 ratio is the ideal DMF/acetone ratio for PVDF fiber morphology properties.

### 3.2. Four-point probe analysis

Fig. 5 shows the average resistance and average conductance respectively for each sample. According to He (2021), due to PVDF's semicrystalline structure, it possesses multiple

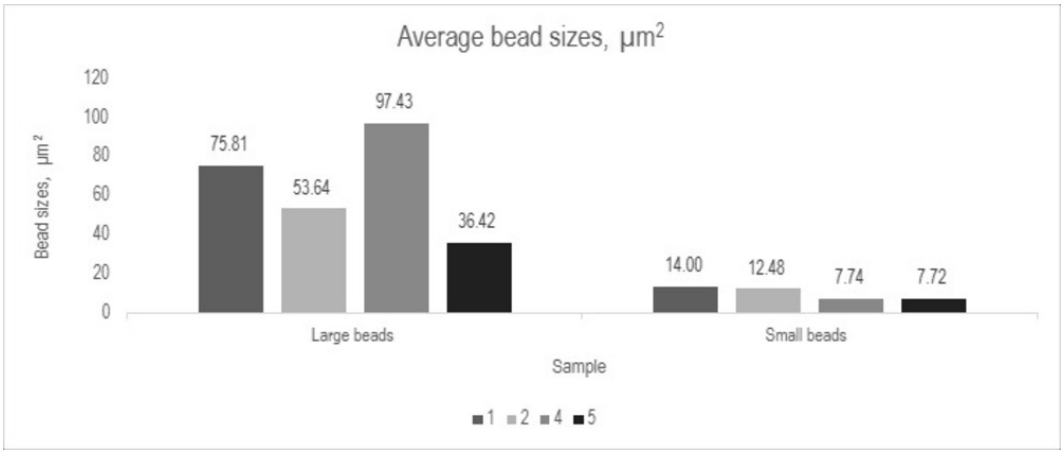



Fig. 3. Average bead sizes for Sample 1, Sample 2, Sample 4 and Sample 5 respectively presented in bar chart. Large beads categorized for beads larger than 35 µm$^2$ while small beads are smaller than 35 µm$^2$

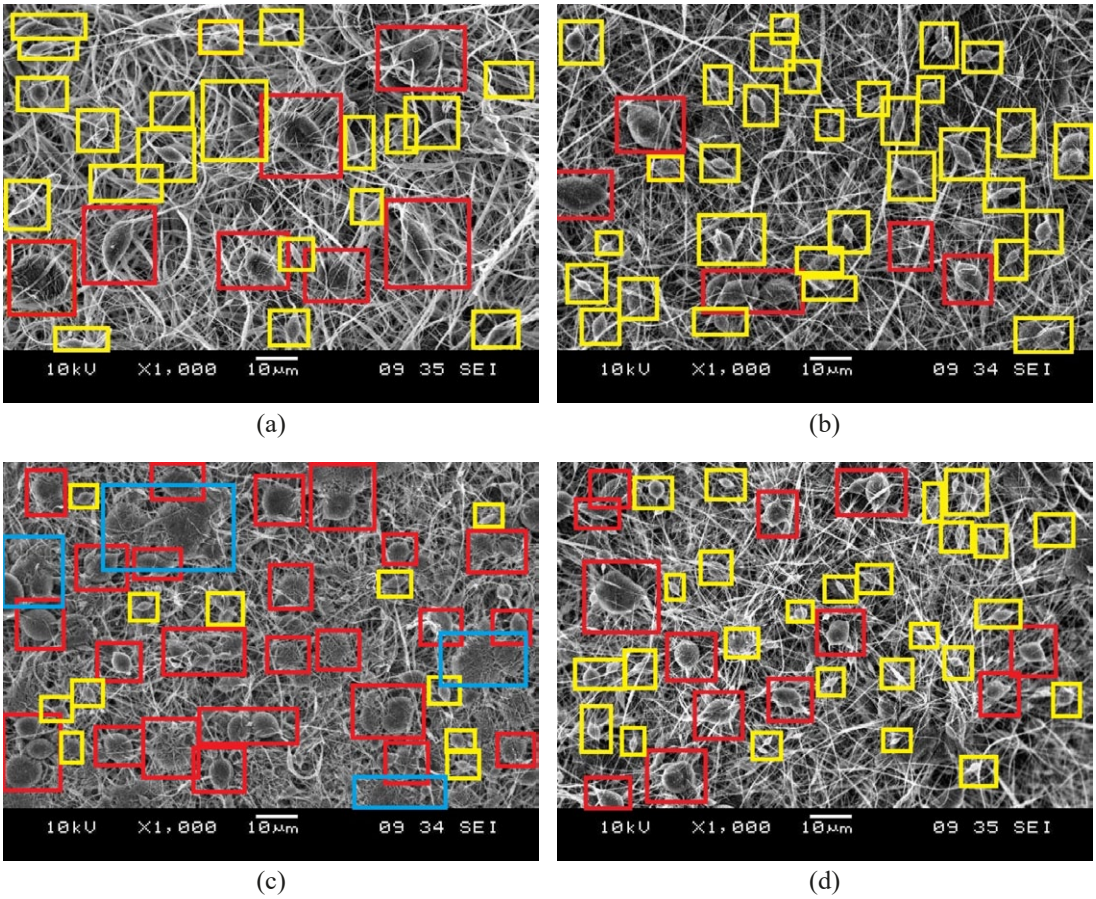
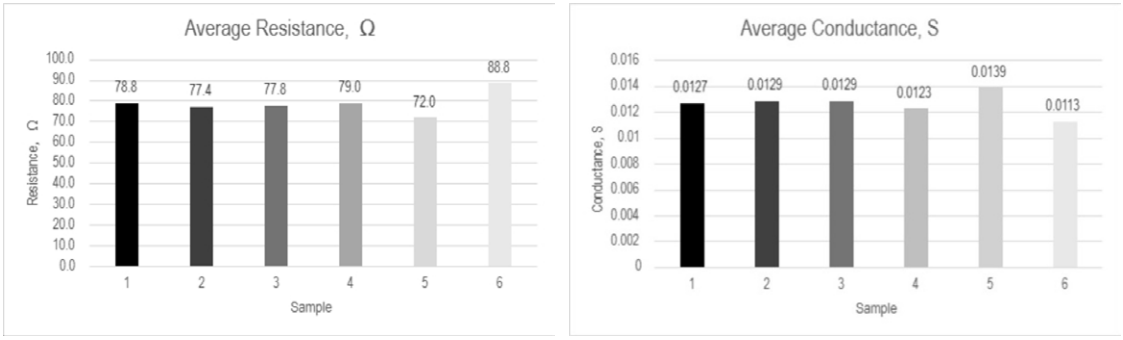



Fig. 4. SEM result in ×1000 magnification for Sample 1 (a), Sample 2 (b), Sample 4 (c) and Sample 5 (d) highlighting large beads (red), small beads (yellow) and bead agglomeration (blue)




(a) (b)

Fig. 5. Average resistance and average conductance of Sample 1, Sample 2, Sample 3, Sample 4, Sample 5 and Sample 6 presented in bar chart

distinct polymorphic phases namely α, β, γ, δ, and ε determined by the crystallization conditions as β phase demonstrates superior piezoelectric properties due to its high dipole moment per unit cell. Additionally, the electrospinning process caused the flow of the polymer under an electric field induces the orientation of the polymer chain and polarizes the fibers [6]. Futher study from the same researcher, the fiber structure enhances the piezoelectric potential of PVDF compared to films due to its geometry. When stress is applied along a specific axis, reducing the fiber diameter limits strain in the perpendicular direction, concentrating deformation along the stress axis. This geometric constraint improves dipole alignment in that direction, which is crucial for maximizing piezoelectric response, as proper dipole orientation directly affects the material's ability to generate electrical charge under mechanical stress [8]. Sample 5 with 70/30 DMF/acetone ratio shown to have lowest resistance and high conductance which are 72.0 Ω and 0.0139 S and followed by Sample 2 with same DMF/acetone ratio, 77.4 Ω and 0.0129 S. This result can be reflected in morphology result where Sample 5 having smallest and most consistent fibers diameter while having the lowest bead sizes and numbers among these sample determined the highest quality sample. Other than fibers quality, the DMF composition also play a major role in PVDF electrical properties as suggested by Abdullah where different ratio of DMF/acetone ratio affect fiber resistance and conductance value further proving 70/30 is best ratio for PVDF fiber production [5] Sample 6 in other hand is classified as worst electrical properties among all sample with 88.8 Ω and 0.0113 S because it failed to form a fibrous layer, which would result in the lowest resistance because of dense, non-porous films with lower surface area, limiting the pathways for charge carriers.

## 4. Conclusion

In conclusion, the DMF/acetone solvent ratio significantly influences PVDF fiber morphology and electrical properties. Morphological analysis showed that adding acetone will produce fiber formation and controlling acetone improved fiber formation as Sample 1 with 60/40 DMF/acetone ratio (0.866 µm diameter) and Sample 2 with 70/30 DMF/acetone ratio (0.383 µm) differing by 77.34%. Stirring time also affected fiber thickness for example in Sample 1 and Sample 4 where extending stirring time from 16h to 24 h causing increased fiber diameter from 0.574 µm to 0.866 µm due to polymer chain entanglement. The 70/30 ratio proved optimal, where Sample 5 yields the finest fibers (0.360 µm). Bead size was likewise influenced from 40% acetone content and prolong stirring time, as Sample 1 having the largest average beads (75.81 $\mu m^2$ large, 14.00 $\mu m^2$ small). Sample 5 has the best beads distribution, due to better solvent interactions from better acetone content, 30% and optimum stirring time, 16 hours. Electrically, Sample 5 showed the lowest resistance (72.0 Ω) and highest conductance (0.0139 S) correlating with their refined morphology. Thus, the 70/30 DMF/acetone ratio with 16-hour stirring is optimal for producing high-quality PVDF fibers, highlighting the critical role of solvent and processing parameters.

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