

The Preparation and Characterization of Electro Spun Poly Vinylidene Fluoride Fibers

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Abstract- Polyvinylidene fluoride (PVDF) is widely used in scientific research and manufacturing due to its unique properties. In the past decade, many PVDF polymorphic polymers have been prepared by classic electrospinning with various solvents, and the products have been extensively studied and documented. Different solvents have been noticed being greatly influential on the properties of those prepared PVDF fibers. Therefore, we used ACE and DMF solvents to prepare three different PVDF materials, analyzed the micromorphology of PVDF materials prepared using different solvents by SEM, and used XRD and FTIR vibration bands to identify the α , β and γ phases in the structure.

Index Terms— Polyvinylidene fluoride, electrospinning.

I. INTRODUCTION

In recent years electrospinning (ES) is known as a typical flexible method to prepare polymer-based fibers^[1]. The versatile applications for fibers electrospun include water-oil filtration^[2], pollutants absorption and catalysis^{[3][4]}, drug control release^[5], wound dressings^[6], parts of artificial organs^[7], fabricated supercapacitors^[8], etc. While there are several novel ES techniques (Co-axial, emulsion, melt)^{[9][10][11]} that could form products hard to create via classical solution ES process, using benign solvents for polymer and charges the liquid with a consistent high voltage is still expected as a convenient and simple way to produce non-woven fabric inside the lab.

Polyvinylidene fluoride (PVDF) nanofiber material has been proven to be an economical composite material which has the characteristics of general resin and fluororesin, additional to good high temperature resistance, chemical corrosion resistance, oxidation resistance, radiation resistance, and weather resistance, it also has special properties such as piezoelectricity, dielectricity, and thermoelectricity. PVDF is tolerant to many common organic solvents due to its high degree of fluorination. The most commonly used organic solvents for preparing PVDF electrospinning solutions include DMF and ACE, as well as mixtures of DMF and ACE in different proportions. In addition, since the discovery of piezoelectricity in PVDF, at least five different allomorphs have been constructed depending on the molecular chain conformation: α (TGTG', form II), β (TTTT, form I), γ (T3GT3G', form III), δ , and ϵ ^[12]. The diverse performance of PVDF is closely related to its complex and changeable crystal structure, and these various crystal forms can be transformed into each other under certain conditions. Among these crystal forms α , β , and γ form are generally concerned. The α phase is the one commonly obtained directly from PVDF, the β phase presents outstanding electrical characteristics including piezo-, pyro- and ferroelectric properties, while γ -PVDF is the only viable PVDF form for high-challenging environments. Based on this, this experiment selected DMF and ACE as solvents to prepare different PVDF membrane materials through electrospinning, and explored their performance differences through characterization.

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II. EXPERIMENTAL

Materials

PVDF powder ($M_w = 100000 \text{ gmol}^{-1}$) were purchased from Shanghai Macklin Biochemical Co., Ltd. Acetone (ACE) and N, N-dimethylformamide (DMF) were purchased from Tianjin Zhiyuan Chemical Co., Ltd. All chemicals were used as received.

Electrospinning

20% (w/w) PVDF powder were dissolved in ACE, DMF, and ACE-DMF mixture at 1:1 solvent ratio. After that the solution were all loaded into 10 mL plastic syringes with 2mm steel syringe needle as the spinneret and then placed on a syringe pump with a feed rate of $0.5 \text{ mL} \cdot \text{h}^{-1}$. A high-voltage supplier was connected to the syringe needle and a stainless cylindrical collector was used to collect the products. The applied voltage and the tip-to-collector distance were 20kV and 16 cm, adjusted and fixed during the experiment.

Characterization of material

Electrospun PVDF fibers were scanned using scanning electron microscopy (SEM, Thermo scientific Apreo 2C) to detect the surface morphology, with fiber diameter measured using image analysis software (ImageJ). Nanofiber samples were sputtered with platinum before analysis.

X-ray diffraction (XRD) of PVDF fibers were provided on a diffractometer (Persee XD-6), under a 0.154 nm wavelength and scan step speed $4^\circ \cdot \text{min}^{-1}$ X-ray (Cu). The accelerating voltage had been set to 36 kV, the tube current was 20 mA, and the power was 2 kw for characterization. Samples were scanned in the 2θ range of 5° to 80° . Fourier transform infrared of the fibers were measured on a Fourier transform infrared spectrometer (Nicoletis 50FTIR). Dried nanofiber membrane was put into a cleaned agate mortar, with KBr powder added and grinded together until the complete membrane structure cannot be discerned by the human eye. Used the same tableting method to press the mixture into translucent discs. The collection range was set to $4,000 \sim 400 \text{ cm}^{-1}$, the resolution was 4 cm^{-1} , and the scans were performed 20 times for each sample.

III. RESULTS AND DISCUSSION

Microscopic morphology

The obtained SEM micrographs of the samples are shown in **Figure 1**. The images show that the size distribution of electrospun fibers using DMF and a mixed solution of ACE and DMF as solvents is uniform, while the single fibers with ACE as solvent are incomplete and appear to be in an adhesion state and can be further investigated under high-resolution SEM of 5000 and 10,000 times. It also can be seen that the fiber diameter increases from ACE, DMF to their mixture and the fiber size is also the most average in the mixed solution. The fiber surface of the fiber spun by the mixture of ACE and DMF is smooth and the fiber microstructure is relatively three-dimensional, ensuring a high compatibility and uniformity of the processed fiber material. SEM results show that the overall surface of the PVDF fiber membrane produced by electrospinning using a mixed solution of ACE and DMF as the solvent has a better morphology and is suitable for further modification.

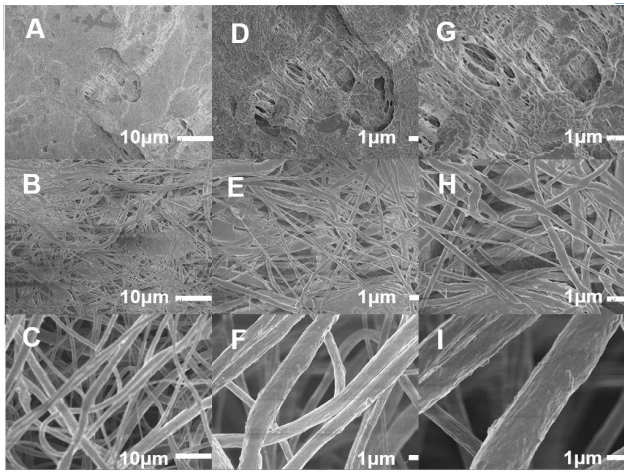


Figure 1. SEM images of PVDF nanofibers with measured fiber diameters: (A),(D),(G): PVDF in ACE, (B),(E),(H): PVDF in DMF, (C),(F),(I): PVDF in ACE: DMF 1:1 mixture.

Physical characterization

XRD characterization of PVDF fibers spun using different solvents is shown in Figure 2. It can be seen that the sample fiber using ACE as the solvent has two strong peaks at 18.4 and 20.2° and a weak peak at 26.8°, corresponding to the 020, 110 reflections of the monoclinic α phase crystal and the 110/200 reflection of the orthorhombic β phase^[13]. The sample fiber with DMF as solvent only has a strong diffraction peak at 20.2°, indicating that β phase is dominant in the structure, which may be due to the large mechanical elongation and strong electric field during the electrospinning process so that the PVDF nanofibers prepared by electrospinning all tend to be in β phase^[14]. XRD of the mixed solvent-based membrane shows a medium peak at 18.7° and a strong peak at 20.2°, which are the diffraction peaks on the (020) and (110/101) planes of the monoclinic γ phase crystal, and the trace of the 110/200 reflection peak of the orthorhombic β phase, indicating that the crystalline phases are mainly β phase and γ phase^[15]. Previously, there were some reports describing the formation of γ phase by electrospinning^[16].

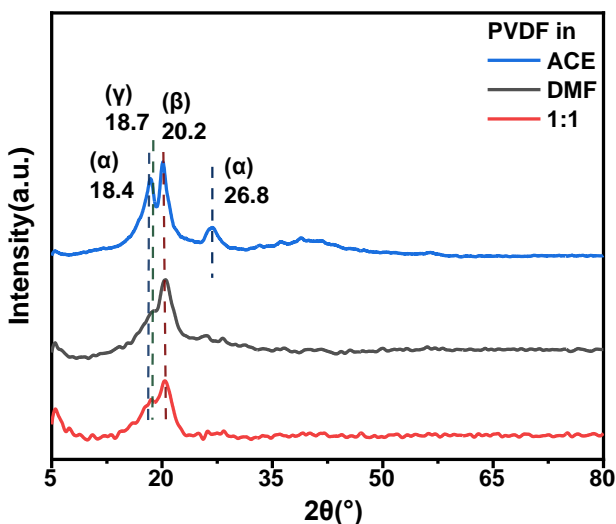


Figure 2. XRD patterns of PVDF nanofibers electrospun within different solvents.

Figure 3 shows the FTIR spectrum of electrospun PVDF fibers that highly consistent with the XRD results. Depending on the solvent, there are vibration peaks of different intensities of O-H and N-H at 3463 cm^{-1} , a common C-H vibration peak at 3019 cm^{-1} , and a weak peak at 2375 cm^{-1} that can be attributed to CO_2 in the air and the N=C peak of DMF^[17]. Similarly, the presence of ACE and DMF leads to the appearance of a weak C=O peak at 1762

cm^{-1} attributed to ACE and the O-H peak at 1612 cm^{-1} attributed to DMF^{[18][19]}.

In addition, the CF_2 characteristic peaks of PVDF are concentrated at 1500 to 400 cm^{-1} . All materials represent a strong β phase, which can be seen from the peaks at 1403, 1183, 840, and 485 cm^{-1} shared by the three materials^[20]. The PVDF membranes obtained by electrospinning with ACE and DMF as solvents alone also have traces of the α phase, because the materials obtained by dissolving in ACE have strong peaks (α phase characteristics) at 758 and 613 cm^{-1} , while the DMF group has weaker peaks of the same characteristics; the common characteristics of the mixed solution spinning membrane and DMF are a clear γ phase-specific peak at 1285 cm^{-1} , and some characteristic bands of the β phase can be identified at 517 cm^{-1} , while the α phase characteristic peak becomes weaker^[21]. In general, the crystalline phase of the membranes obtained by ACE solvent spinning is mainly β phase, but also shows strong α phase signals, while the other two groups of membranes with better morphology are mainly β phase, and also have some characteristic bands of the γ phase.

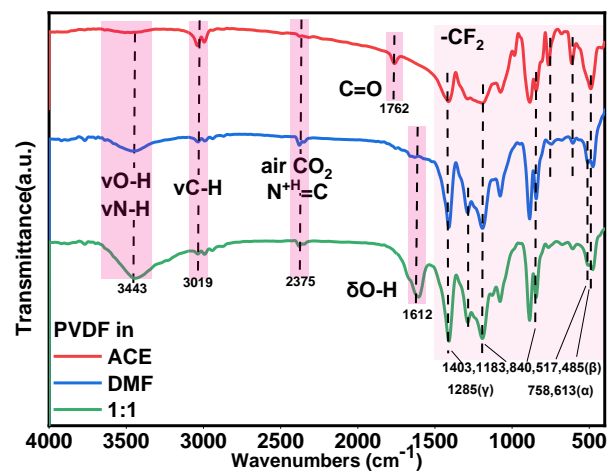


Figure 3. FT-IR results of different PVDF nanofibers.

IV. CONCLUSION

This experiment used three different commonly used PVDF electrospinning solvents to prepare PVDF electrospinning samples, and compared and summarized the SEM, XRD, and FT-IR vibration bands of the samples reported in the literature and actually obtained. By comparing the microscopic morphology of different samples and the characteristic peaks of different bands, it can be found that the sample fibers obtained by electrospinning PVDF using a solvent mixed in a certain proportion have a more suitable β phase and γ phase as a composite material matrix instead of a strong α phase, and have more uniform microscopic morphology characteristics, thereby verifying the feasibility of the comprehensive procedure for preparing materials using a 1:1 mixed solvent of ACE and DMF, providing a simple method for preparing high-performance PVDF polymers.

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