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PREPARATION OF PVDF NANOFIBERS BY OPTIMIZING SOLVENT PROPERTIES: IMPROVED SOLVENT VISCOSITY AND EVAPORATION RATE

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ABSTRACT

PVDF nanofibers have been intensively investigated in wearable energy harvesting because of their flexibility and piezoelectric properties. In this study, we prepared PVDF nanofibers by the electrospinning method. Different solvents like DMF and DMF/acetone with the ratio of 6/4, 5/5, and 4/6 were selected to adjust the solvent properties. SEM, FTIR, and DSC characterizations were used to characterize the morphology, structure, and β phase content of PVDF nanofibers. The results demonstrate that the electrospun PVDF nanofibers produced by using DMF/acetone have predominantly a fibre structure and increased β phase compared to electrospun samples using DMF alone as solvent. PVDF nanofibers fabricated by using DMF/acetone with a ratio of 4/6 exhibit the maximum content of β phase and the highest value of piezoelectric coefficient (d_{33}).

KEYWORDS

PVDF nanofibers, electrospinning, piezoelectric property, β phase.

INTRODUCTION

Smart wearable devices have received increasing attention due to the development of portable electronic devices such as cell phones, smart wristbands, etc. Traditional ceramic-based materials have higher piezoelectric properties than organic materials. Piezoelectric coefficient (d_{33}) of $PbZr_xTi_{1-x}O_3$(PZT) is 300-1000 pC/N [1,2]. They are not, however, suitable for use in wearable devices because of their poor flexibility and toxicity. The flexibility, low density, and high strength of organic polymers make them attractive materials for making wearable energy harvesting devices.

Poly (vinylidene fluoride) (PVDF, (-CH2-CF2-)n) is a piezoelectric polymer material with good piezoelectric properties compared to the other polymers. The PVDF crystalline structure consists of five crystalline phases of α-, β-, γ-, δ-, and ε- [3]. The piezoelectric properties of PVDF are associated with its electroactive phases (β and γ phase). The electrospinning method is widely used to prepare piezoelectric PVDF materials because the electroactive phase of PVDF is increased by this method in comparison to other methods.

Ribeiro et al. [4] investigated the influence of voltage on the morphology of PVDF nanofibers. In the Szewczyk et al.'s study [5], PVDF nanofibers with different electroactive phases were obtained at different relative humidity and in addition, they investigated the effect of the electroactive phase on d33. Gee et al. [6] compared the influence of voltage and solution parameters on electrospinning PVDF nanofibers, they concluded that the solution parameters statistically had the largest contribution to electroactive phase formation. However, these studies did not quantitatively analyze the β and γ phases

in electroactive phase or discuss their influence on the piezoelectric properties of PVDF.

In this study, the influence of solvents on the electroactive phase and morphology of electrospun PVDF samples were investigated by using four different solvents (DMF, DMF/acetone at the volume ratio of 6/4, 5/5, 4/6). Three different crystalline phases in PVDF, α, β, and γ, were quantitative analyzed by DSC and FTIR, and the effect of the β phase and γ phase on d33 was quantitatively studied.

MATERIALS AND METHODS

PVDF in pellet (Mw=220,000, Arkema Kynar 705, France) was used as the polymer. N, N-Dimethylformamide (DMF, CARLO ERBA, Mw=73.1 g/mol, assay≥99.9%), and acetone (CARLO ERBA, Mw=58.01 g/mol, assay≥99.8%) were used as the solvents.

The electrospinning machine (CAT000002, Electrospraying Instrument Kit Instruction Manual, Spraybase®, AVECATS, Kildare, Ireland) was used to prepare PVDF nanofibers. The PVDF solutions with different DMF/acetone volume ratios (1:0, 6:4, 5:5, 4:6) were loaded into a 10 mL syringe and connected for injection to a 20-gauge needle. The parameters during the electrospinning process were fixed as fellow: feed rate of 1 ml. h^{-1}, tip-to-collector distance (TCD) was 20 cm, and the applied voltage was 20 kV. The nanofiber samples were collected on a metal plate wrapped in aluminum foil.

Characterizations

The polymer solutions' viscosities were measured using Rheomat RM 100 Rheometer (Lamy Rheology, France) with the shear rate ranged from 0.38-1420 s^{-1} (25℃).

Differential Scanning Calorimetry (DSC 6000, PerkinElmer, USA) was used to characterize PVDF samples' crystallinity. These samples were heated up from 10℃ to 200℃ at a rate of 10℃/min, and then cooled from 200℃ to 10℃ at a rate of 30℃/min in a nitrogen atmosphere.

Fourier-transform infrared spectroscopy (FTIR, Nexus-560 spectroscopic, Nicolet, Madison, USA) analysis was performed under 64 scans with a resolution of 4 cm^{-1}, and the wavenumber ranged from 400 to 1600 cm^{-1}.

Scanning Electron Microscopy (SEM, Phenom ProX, ThermoFischer Scientific, US) was used to characterize the morphology of PVDF nanofibers. 100 nanofibers of each sample were randomly selected, and their diameter were determined by Image J (National Institutes of Health, MD, USA. Then calculate the average diameter of these 100 nanofibers.

Piezoelectric coefficients (d_{33}) of the PVDF nanofibrous membranes were measured by using d_{33} meter (model YE2730A, Sinoceramics, China) under a force of 0.25 N and a frequency of 110 Hz. Five samples were measured and the average d_{33} was obtained.

RESULTS AND DISCUSSION

Figure 1 (A) shows the SEM images of electrospun PVDF samples prepared from different solvents.

The structure of the electrospun PVDF sample is mainly a microsphere structure when the solvent is DMF. Nanofibrous structure is started to forme when acetone is added to DMF and by increasing the content of acetone, beads structure in PVDF samples decreased. Electrospun PVDF samples are mainly nanofiber structures without beads when acetone is up to 60% (in mix-solvent). Meanwhile, the nanofibers' diameter decreases, and their diameter distribution becomes more homogeneous when the acetone content increases. Variations in structures of the nanofibers are linked to the volatility of the solvent. While the solvent cannot fully evaporate between the needle tip and the collector, more microspheres and beads are formed [7]. DMF is a non-volatile solvent and acetone has a higher volatility. Therefore, The DMF is not entirely evaporated during electrospinning process, causing a microsphere or beads structure. The volatilization rate of solvent is increased by adding acetone and so,

the sufficient volatilization of the solvent is beneficial to the stretching effect of the electric field on the nanofibers and reduces the average diameters of the fibers.

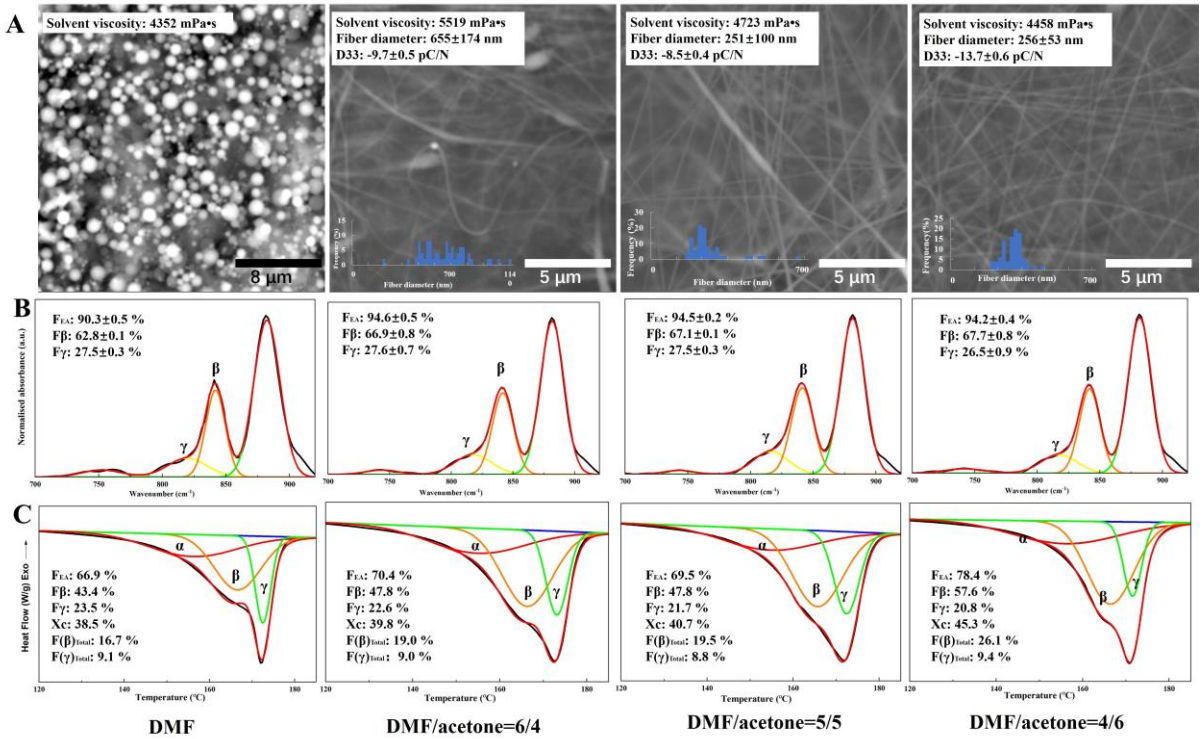

Figure 1. (A) SEM images, (B) The deconvolution of the IR spectra, (C) The deconvolution of the DSC curves of PVDF samples prepared from different solvents (25w/v% PVDF, TCD=20cm, needle: 20G, feed rate: 1 ml•h^{-1}, voltage: 20 kV. The F_{EA}, Fβ, Fγ, Xc, and $F(\beta)_{total}$ were obtained by the formula in ref [8,9]).

To quantitatively analyze the content of α, β, and γ phases in electrospun PVDF samples, the FTIIR spectra and DSC curves of electrospun PVDF samples are deconvoluted by OriginPro 2019 (OriginLab Corporation, MA, USA) and the results are shown in Fig.1 (B) and (C).

According to the results, the F_{EA} of electrospun PVDF samples prepared from mix-solvent is higher than that of PVDF samples prepared from DMF solvent. As the volume of acetone in the mix-solvent increases from 0 vol% to 60 vol%, the content of β phase (F(β)) increases significantly from 62.8 % (IR) and 43.4 % (DSC) to 67.7 % (IR) and 57.6 % (DSC). At the same time, the content of the γ phase decreases slightly with the increase of acetone in the mixed solvent.

The results of IR and DSC illustrate that adding acetone is beneficial to the formation of electroactive phase, especially β phase in PVDF during the electrospinning process. Volatile solvents allow the solvent to evaporate completely during the electrospinning process and reduces the structure of the beads, thus improving of F_{EA} [4]. However, it must be pointed out that the addition of acetone facilitates the formation of the electroactive phase in electrospinning PVDF samples limited to PVDF molecular weights of 220,000. Some studies have shown that excess volatile solvents do not promote the formation of the β phase [10]. For nanofibers with a large beads structure, adding acetone eliminates the structure of the bead and forms more β phases.

As the content of acetone in mix-solvent increased, the d33 of PVDF nanofiber membrane increased from -9.7 to -13.7 pC/N. The change in d33 is attributed to the increase of β phase in PVDF. When the acetone content in the solvent rose from 40% to 60%, $F(\beta)_{total}$ increased from 19.0% to 26.1%, and $F(\gamma)_{total}$ did not change significantly. The improvement of the β phase directly affects the enhancement of the piezoelectric properties of PVDF. The changing of acetone content in the solvent makes the β phase of electrospinning PVDF change significantly, thus affecting the piezoelectric properties of PVDF. However, the effect of γ on the piezoelectric properties of PVDF is not apparent.

CONCLUSION

The morphology and structure of electrospun PVDF samples were significantly changed using different volumes of DMF/acetone solvent. The addition of acetone reduced the presence of the beads and improved the nanofibrous structure of PVDF by increasing the solvent evaporation rate. According to the results of quantitative analysis of the effects of β phase and γ phase on piezoelectric properties of PVDF, the main phase affecting the piezoelectric properties of electrospinning PVDF is the β phase in the electroactive phase rather than the γ phase.

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