Effect of flow rate on the fabrication of P(VDF-HFP) nanofibers

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Abstract. In this study, different flow rates were used to produce electrospun Poly (vinylidenefluoridene-hexafluoropropylene) P(VDF-HFP) nanofibers to investigate the fiber diameter and water contact angle (WCA). The flow rate range for P(VDF-HFP) electrospinning started from 0.1 to 0.9 ml/h. The surface morphology of the nanofibers was studied by scanning electron microscopy. The intrinsic beta-phase and the degree of crystallization are confirmed from Fourier transform infrared spectroscopy and differential scanning calorimetry studies. The wettability of the nanofibers was also determined in terms of WCA. The results show continuous nanofiber mats. The P(VDF-HFP) mat at flow rate of 0.7 ml/h shows the highest values of fiber diameter of 835 nm and WCA of 152°. The electroactive beta-phase occurred during the electrospinning process is achieved with 86% of beta-phase fraction and 85% of crystalline degree. These results suggest that the as-received P(VDF-HFP) nanofibers can operate stably as the fiber strain sensor without being affected by sweat or water.

1. Introduction

Owing to the piezoelectric polymer, poly(vinylidene fluoride) (PVDF) and its copolymers such as polyvinylidene fluoride-hexafluoropropylene (P(VDF-HFP)) are attracting increasing interest in many applications in the areas of sensors and actuators, energy harvesting and biotechnology because of its flexibility, lightweight, thermal stability, and chemical robustness [1]. PVDF and its copolymer also present a naturally high hydrophobicity [2]. Electrospinning is known as one of the most efficient techniques to directly fabricate continuous fibers by exposing a polymer solution to an electric field. In particular, polymer fibers with hydrophobicity produced by electrospinning have been widely investigated in the field of self-cleaning materials and high-performance coatings [3]. In this study, different flow rates were used to prepare electrospun P(VDF-HFP) nanofibers mats to investigate the fiber diameter and water contact angle (WCA). The surface morphology, phase structure and thermal property were analyzed by scanning electron microscopy, Fourier transform infrared spectroscopy and differential scanning calorimetry, respectively. The dielectric property of as-prepared samples was also investigated.
2. Experimental details

The polymer solutions used in the electrospinning process were composed of Poly(vinylidenefluoridene-hexafluoropropylene) (P(VDF-HFP); Solef 11010/1001; Solvay) and N-Dimethylformamide (DMF; D158550; Sigma-Aldrich) without further purification. The P(VDF-HFP) powder was dissolved in DMF solvent with a certain ratio of 1:4 and by stirring for 2 h at 60°C. For the P(VDF-HFP) film, the solution was cast on a clean glass and further dried in the hot air oven for 6 h at 80°C. To form P(VDF-HFP) fibrous mats with different flow rates (0.1, 0.3, 0.5, 0.7, 0.9 mL/h), the electrospinning equipment was set in horizontal baseline. Nearly 20 mL of precursor solution was transferred into a plastic syringe. A syringe pump (Nz1000 NEWERA Pump Systems Inc., USA) was used to eject the mixture to induce 10 kV, a high voltage power supply (Trek model 610E, USA) was used. The positive electrode was connected to the needle tip, and the opposing one was attached to the aluminum ground collector, which was equipped at 11 cm. All samples were electrospun for 2 h at room temperature and the relative humidity was 60%.

The surface morphology of electrospun P(VDF-HFP) nanofibers was scanned by scanning electron microscopy (SEM, FEI Quanta 400, Netherlands), after coating with a thin gold layer to give electrical conductivity. Water contact angle (WCA) was determined on an OCA15 machine (Dataphysics, OCA-15EC, Germany) at ambient temperature. As compared to P(VDF-HFP) film, Fourier transform infrared (FT-IR; 8400s; Japan) and differential scanning calorimetry (DSC) were conducted to verify phase structure and thermal property, respectively. Dielectric property of the samples was measured by LCR meter (IM 3533 HIOKI, Japan).

3. Result and discussion

3.1. Morphological analysis of P(VDF-HFP) fibers

SEM images of P(VDF-HFP) fibers prepared at various solution flow rates are given in figure 1 and the magnifications of all SEM images were same at 3000x. The average fiber diameter measured by Image J processing is presented in table 1. As can be seen from the given figure, the bead-free fibrous mats are randomly distributed and interconnected. The P(VDF-HFP) fibers with 0.7 mL/h exhibit the maximum diameter of 835.3 ± 169.0 nm. The WCA values increased with the increase in diameter. At the flow rate of 0.9 mL/h, the lower WCA due to the decrease of diameter. Furthermore, the average diameter on 0.9 mL/h was under high fluctuating. However, the diameter distributions do not change much with the electrospinning solution’s flow rates.

![Figure 1. SEM images of P(VDF-HFP) nanofibrous mats with different flow rates.](image)

| Flow rate (mL/h) | 0.1     | 0.3     | 0.5     | 0.7     | 0.9     |
|------------------|---------|---------|---------|---------|---------|
| Average diameter (nm) | 632.2 ± 185.0 | 748.5 ± 251.1 | 780.3 ± 237.5 | 835.3 ± 169.0 | 694.0 ± 258.6 |
| WCA (°)          | 140.2 ± 2.1 | 142.9 ± 2.5 | 147.8 ± 3.2 | 152.5 ± 3.5 | 149.9 ± 2.7 |
3.2. WCA analysis
Figure 2 represents the WCA results of P(VDF-HFP) nanofibrous mats prepared with different flow rates. As introduced, fluoropolymers (such as PVDF, P(VDF-HFP)) usually exhibit high WCA values of around 85° to 130°, which confirm its inherent hydrophobicity [2]. As the results, the WCA values of all samples are in the range of $140.2 \pm 2.1^\circ$ to $152.5 \pm 3.5^\circ$, which gradually increases with the flow rates. Interestingly, it is achieved the superhydrophobicity with the WCA of $152.5 \pm 3.5^\circ$ in prepared P(VDF-HFP) nanofibers for flow rate of 0.7 mL/h. The obtained superhydrophobic surface is resulted from the largest diameter of the P(VDF-HFP) nanofibers, as reported in the SEM result. The significant increase in the optimal flow rate of 0.7 mL/h. Hence, the study focuses on optimizing the flow rate for B-phase analysis.

![Figure 2. WCA results of P(VDF-HFP) nanofibrous mats with different flow rates.](image)

3.3. FT-IR study
FT-IR analysis is usually used to identify chemical bonds, functional groups, and components of unknown sample mixtures. In this work, FTIR spectra were thus used to determine the phase structure and β-phase fraction presented in each sample. FT-IR spectra of the pristine P(VDF-HFP) film and electrospun nanofiber are shown in figure 3(a). As recorded, the absorption peaks situated at 490, 530, 615, 766, 795, 974 cm$^{-1}$ are attributed to nonpolar α-phase, while those observed at 511, 840 and 1276 cm$^{-1}$ are corresponded to polar β-phase [4]. By comparing the FT-IR spectra of P(VDF) film and nanofibers mat, it is observed that the P(VDF-HFP) film is represented the dominant peaks of α-phase at the wavenumber of 408, 614, and 766 cm$^{-1}$, whereas the P(VDF-HFP) fibrous mat is deducted the intensity of vibration band of α-phase. The peak of β-phase at 1276 cm$^{-1}$ is also prominently in the fiber, indicating that the α-phase can transform to β-phase during electrospinning processing by an electric force [5]. The β-phase fraction of film and fiber calculated from the equation same as the previous work is displayed in table 2. On comparing the P(VDF-HFP) fiber and film, the crystallization temperature ($T_c$) and melting temperature ($T_m$) show a similarly that is not statistically significant. The crystallinity ($X_c$) and the β-phase of nanofiber were found higher than film due to electrospinning relies on high electric fields.

| Sample            | β-phase fraction (%) | $T_c$ (°C) | $T_m$ (°C) | $\Delta H_c$ (J/g) | $\Delta H_m$ (J/g) | $X_c$ (%) | Dielectric constant (at 10Hz) | Loss tangent (at 10Hz) |
|-------------------|---------------------|------------|------------|--------------------|--------------------|-----------|--------------------------------|-----------------------|
| P(VDF-HFP) fiber  | 85                  | 137.25     | 157.57     | -24.75             | 88.67              | 84.77     | 3.8                             | 0.0056                |
| P(VDF-HFP) film   | 72                  | 140.63     | 159.14     | -23.87             | 68.16              | 65.16     | 7.9                             | 0.0008                |
3.4. Differential Scanning Calorimetry
Thermal property of the samples was analyzed using DSC measurements. Figure 3(b) and table 2 show respectively the DSC thermograms and thermal property of the P(VDF-HFP) film and P(VDF-HFP) nanofiber. Both the P(VDF-HFP) film and nanofiber exhibit an exothermic peak at around 160 °C, which is ascribed to its melting point [4]. This result is indicated that the as-received samples can use for device application at high temperatures.

3.5. Dielectric constant
The dielectric constant and loss tangent (at 10 Hz) of the P(VDF-HFP) film and nanofibers mat prepared with 0.7 mL/h flow rate are exhibited in table 2. It is found that the dielectric constant of P(VDF-HFP) film is higher than that of the fiber. The lower dielectric constant in the fiber is caused by some air gaps (voids) in the fiber network. The loss tangent of both samples is very low, as compared to the previous research [6].

4. Conclusion
In our research, achieving superhydrophobic P(VDF-HFP) fibrous mat is obtained by electrospinning. The P(VDF-HFP) mat at flow rate of 0.7 mL/h shows the highest values of fiber diameter of 835 nm and WCA of 152°. The polar β-phase occurred during the electrospinning process is achieved with 86% of β-phase fraction and 85% of crystalline degree. These results suggest that the as-received P(VDF-HFP) nanofibers can operate stably as the fiber strain sensor without being affected by sweat or water.

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