Enhanced beta-phase formation and dielectric properties of P(VDF-HFP) nanofibers composites filled with polyaniline

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Abstract. In this study, the polyaniline (PANI) with different contents was blended in Poly(vinylidenefluoridene-hexafluoropropylene) [P(VDF-HFP)]. The composite P(VDF-HFP)/PANI nanofibers were fabricated by electrospinning technique conducted with flow rate of 0.5 ml/h and electrical voltage at 17 kV. Scanning electron microscopy (SEM), water contact angle (WCA), Fourier-transform infrared spectroscopy (FTIR), and dielectric property of all P(VDF-HFP) fibers were studied. The SEM image shows that some beads appeared in the pristine P(VDF-HFP) nanofibers. After adding with PANI, the uniform fiber without any bead formation is achieved, which the average fiber diameter is ranged from 100 to 300 nm determined by ImageJ processing program. However, the WCA of the composite nanofibers is reduced with increase of PANI concentrations. The incorporation of PANI filler can improve the β-phase content and dielectric constant with low loss tangent. This work provides a potential strategy for the fabrication of high-performance P(VDF-HFP) nanofibers.

1. Introduction

Nanofibers, prepared by electrospinning technique, have been garnering increasing attention in intensive research for many emerging environmental applications due to their high specific surface area and interconnected porous structure. Moreover, the main advantage of this process is inexpensive, simple, and scalable method to fabricate into continuous fibrous structure with a variety of materials [1]. Poly(vinylidenefluoridene) (PVDF) are widely used as the polymer materials because of their excellent resistance, piezoelectricity, flexibility, durability, lightweight as well as strong hydrophobicity [2]. Recently, a copolymer of PVDF with hexafluoropropylene [P(VDF-HFP)] has attracted interest as a potential candidate. Compared with PVDF, P(VDF-HFP) copolymer exhibits better properties such as higher solubility, greater free volume, and better mechanical strength. In addition, the incorporation of HFP groups increases the fluorine content, which leads to the higher hydrophobicity of P(VDF-HFP) [3]. In this work, a nanofibrous mat based on P(VDF-HFP) copolymer was fabricated by electrospinning. The conductive polymer like a polyaniline (PANI) filler with different contents was blended in P(VDF-HFP) solution. The effect of PANI mass ratio on the structure, hydrophobicity and dielectric property of the composite P(VDF-HFP) fibers were investigated in detail.
2. Experimental details

2.1. Materials and fabrication of electrospun nanofiber films
Poly (vinylidenefluoridene-hexafluoropropylene) (P(VDF-HFP; Solef 11010/1001) was purchased from Solvay. N,N-dimethylformamide (DMF; D158550) from Sigma-Aldrich was used as a solvent for preparation of polymer mixture. Polyaniline (emeraldine base; 576379) with the particle size of 2-3 µm was obtained from Sigma-Aldrich and used as a filler, which added into polymer solution.

The electrospun P(HFP-HFP)/PANI composite films were prepared similarly to the previous work as follows [4]. Firstly, 25 wt% of dried P(VDF-HFP) in the DMF solvent containing different weight percentages of PANI (0.5, 1.0, 1.5, 3.0 and 5.0 wt %) with respect to P(VDF-HFP). The prepared polymeric solutions were then transferred into 20 mL plastic syringe with stainless-steel needle (gauge 20.5) connected to a syringe pump (Nz1000; New Era Pump Systems, USA) at a flow rate of 0.5 mL/h. The electrospinning instrument was placed in horizontal direction. The pure and composite P(VDF-HFP) solutions were spun into nanofiber with the electrical voltage of 17 kV at room temperature. The distance between the collector covered with an aluminium foil and tip of the needle was 10 cm. Finally, each collected-electrospun film was dried at 50 °C for 12 h to remove residual solvent.

2.2. Characterizations of electrospun nanofiber films
Scanning electron microscopy (SEM; FEI Quanta 400, Netherlands) was used to investigate the surface morphology of prepared nanofiber films. The average fiber diameter was measured using ImageJ processing program. The water contact angle of surface was characterized using the Dataphysics Contact Angle System (OCA-15EC, Germany) at the static sessile drop mode. The structural and dielectric properties of all samples were investigated by Fourier Transform Infrared Spectroscopy (FTIR; 8400s, Japan) and LCR meter (IM 3533 HIOKI, Japan), respectively.

3. Result and discussion

3.1. Fiber morphology
Figure 1 exhibits SEM photographs of pristine and composite electrospun P(VDF-HFP) fiber with various PANI concentrations. The average diameter of all samples is listed in table 1, as measured by the ImageJ processing program. From figure 1, it is clearly shown that some spindle-beads formation with non-uniform electrospun fibers are formed for the pure P(VDF-HFP) fibrous film, which has the average fiber diameter of 110.5 ± 50.5 nm. After adding PANI filler, the composite P(VDF-HFP)/PANI fibrous films present the randomly oriented fibers without bead formation together with increasing fiber diameter. The obtained fibers of composite fibers have the average diameter in the range of 250 ± 90.7 to 320 ± 105.6nm (table 1). This may be due to the complete solvent evaporation of the composite solution in electrospinning process [5]. When using the solution of 5 wt% PANI concentration, the structure is eventually produced the non-beaded and straight fibers.

![Figure 1. SEM images of P(VDF-HFP) nanofibrous films with different PANI concentrations](image-url)
Table 1. Average diameter, β-phase fraction, and dielectric property of P(VDF-HFP) fibers with different PANI concentrations.

| PANI concentration (wt%) | Average diameter (nm) | β-phase fraction (%) | Dielectric constant (at 100 Hz) | Loss tangent (at 100 Hz) |
|-------------------------|-----------------------|---------------------|---------------------------------|-------------------------|
| 0                       | 110.5 ± 50.5          | 77.92               | 1.5                             | 0.00003                 |
| 0.5                     | 250.1 ± 90.7          | 79.33               | 1.6                             | 0.00015                 |
| 1.0                     | 280.5 ± 80.5          | 81.77               | 1.9                             | 0.00041                 |
| 1.5                     | 265.3 ± 60.1          | 82.19               | 2.0                             | 0.0052                  |
| 3.0                     | 241.5 ± 48.6          | 81.18               | 2.1                             | 0.00697                 |
| 5.0                     | 320.4 ± 105.6         | 81.28               | 2.5                             | 0.01255                 |

3.2. Hydrophobicity

The hydrophobic property of P(VDF-HFP) nanofibrous mats with different PANI concentrations is determined by its value of water contact angle, as illustrated in Figure 2. The P(VDF-HFP) nanofibrous films without PANI filler is exhibited a very high contact angle of 138.7 ± 4.6°, indicating hydrophobic surface. This is caused by the fluorine atom in fluoropolymer with intrinsic low surface energy, which was further enhanced by the electrostatic charge produced in the electrospinning process [6]. For the composite P(VDF-HFP)/PANI nanofiber films, the amount of PANI gives effect to contact angle value, which is gradually reduced with increasing PANI concentration. The decrease in water contact angle of composite nanofibers could be attributed to the abundant amine groups contained in PANI, which is induced to the hydrophilic property [7]. In addition, high average diameter and straight fibers in composite P(VDF-HFP)/PANI films result in reducing surface roughness and water contact angle. However, the obtained values of water contact angle in composite nanofibers could be indicated in the hydrophobic surface.

Figure 2. Water contact angle of P(VDF-HFP) nanofibrous films with different PANI concentrations

3.3. FTIR

After observing the morphology and wettability of P(VDF-HFP) fibers, the crystal phase structure was studied by using FTIR spectrophotometry determined in different infrared wavelengths. Figure 3 demonstrates the FTIR transmission spectra of pristine P(VDF-HFP) and composite P(VDF-HFP)/PANI nanofibrous mats doped with various PANI concentrations. According to the literature, the typical peaks of α-phase are defined at 611, 766 and 979 cm⁻¹, whereas the absorption bands at 510 and 838 and 1276 cm⁻¹ are the characteristic of β-phase [8]. It is shown that the pure P(VDF-HFP) nanofibrous mat is dominant in the peaks of α-phase since the peaks of β-phase are relatively small. For the composite P(VDF-HFP)/PANI nanofibrous films, the crystalline α-phase peaks are reduced. By clear evaluation of the relative intensity of β-phase, the β-phase fraction [F(β)] can be calculated using the following equation: \( F(\beta) = \frac{A_\beta}{(1.26A_\alpha + A_\beta)} \). Where \( A_\alpha \) and \( A_\beta \) are the characteristic IR absorption bands of crystalline phase at 767 and 838 cm⁻¹, respectively [9]. The obtained F(β) values are represented in table 1, from which it is clear that compared to the pure P(VDF-HFP) fibers, the F(β) content is more for the composite P(VDF-HFP)/PANI nanofibrous mats. The obtained F(β) content for pristine P(VDF-HFP) nanofibers are indicated that the orientation of β-phase formation can
be directly formed by the molecular conformation and packing of their molecules in the electrospinning process. However, the F(β) values are saturated in the P(VDF-HFP)/PANI nanofibrous mats. This may imply that PANI content did not affect the structure and crystalline phase of P(VDF-HFP) fibers.

![Figure 3](image.png)

**Figure 3.** FTIR spectra of P(VDF-HFP) nanofibrous films with different PANI concentrations.

3.4. **Dielectric property**

The dielectric constant and loss tangent at 100 Hz of P(VDF-HFP) and composite P(VDF-HFP)/PANI nanofibers doped with different PANI concentrations are presented in Table 1. The dielectric constant is an increasing trend with the increase of PANI content because the conductive charge has probably increased the spatial charge density in addition to these within the matrix. Moreover, low dielectric loss values are found for the composite nanofibrous mats, which is highly preferred for energy storage and energy harvesting applications.

4. **Conclusion**

In summary, we have successfully prepared composite P(VDF-HFP)/PANI nanofibrous mats by electrospinning method. The uniform fibers without any bead formation are obtained with the average diameter in the range of 250 ± 90.7 to 320 ± 105.6 nm. The prepared P(VDF-HFP) nanofibrous mats are exhibited very high contact angle, indicating hydrophobic surface. However, the water contact angle of composite P(VDF-HFP)/PANI is reduced with increase PANI concentrations. The incorporation of PANI filler can improve the β-phase content and dielectric constant with low loss tangent. This work suggests the use of these nanofibers in energy storage and energy harvesting applications.

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