Nanocomposites of polyvinylidene fluoride copolymer-functionalized carbon nanotubes prepared by electrospinning method

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Abstract. Electrospun nanofiber membranes (ENM) have been utilized in varied applications like filters, sensors, scaffolds for tissue engineering, electronics and so on. In this study, polyvinylidene fluoride (PVDF) copolymer nanofiber was reinforced with functionalized multiwall carbon nanotubes (f-MWCNT) via electrospinning method with N,N-dimethylacetamide (DMAc) as the solvent. To ensure the dispersion of f-MWCNT in polymer solution, it was sonicated prior to addition of PVDF copolymer into the dispersion. The results showed that tensile strength and elongation at break increased by 9 % and 79 %, respectively, with the addition of f-MWCNT, when compared to pure PVDF copolymer nanofiber web. Incorporated f-MWCNT into PVDF copolymer nanofiber also resulted in an increase in the average nanofiber diameter from 312 nm to 445 nm but decrease the hydrophobicity. FTIR spectra and XRD pattern confirmed the increase of PVDF β-phase structure as the results of electrospinning process and addition of MWCNT.

Keywords: nanofibers; PVDF copolymer; MWCNT; electrospinning; electrospun membrane

1. Introduction

A combination of inexpensive materials with an ease and simple processing at large scale to produce multifunctional nanocomposites becomes a great challenge in materials engineering. Among many techniques, electrospinning is an attractive process because it is inexpensive, simple, and scalable processing method for fabricating continuous fibres from polymer solutions or melts [1]. This process utilizes high-voltage electrical force to produce fibres with diameter ranging from a few microns to about ten nanometers, depending on polymer types, voltage, and viscosity of the solution [2]. The electrospun nanofiber membranes (ENMs) exhibit excellent properties and more effective than conventional non-woven mats in particulate separation and liquid filtration [3], due to high surface area to volume ratio, high length to diameter ratio, and high porosity of the fibres. These characteristics are useful in many potential applications such as gas sensors [4], textile [5], antibacterial wound dressing [6], energy storage and conversion [1], and filtration/separation membranes [7].

Many polymers have been used to prepare the ENMs including polyvinylidene fluoride (PVDF) [8], polyacrylonitrile (PAN) [9], polyvinyl alcohol (PVA) [10,11], polycaprolactone (PCL) [12], polysulfone (PSU) [13], chitosan and hydroxyapatite [14], and so on. Among those polymers, PVDF is one of the most used materials for electrospinning and formed by polymerization of vinylidene
difluoride. It has gained considerable attention due to excellent properties such as high thermal stability, good chemical resistance, high membrane forming properties, piezoelectricity, flexibility, durability, lightweight, and relatively low acoustic impedance [15-18].

Although ENMs exhibit many excellent properties and can meet most of the requirements for many applications, their lack of mechanical integrity relative to conventional cast membrane is one drawback to use the membrane. Low mechanical properties come from weak bonding between nanofiber, highly porous structure as well as small fibre diameter [19,20]. Several techniques have been proposed to improve the mechanical properties of the ENM including heat treatment [21], incorporating with reinforcement [22,23], blending with other polymer [7], or solvent treatment [10].

Carbon nanotube (CNT) has attracted many interests because of their unique structures with dimension in nanometer scale as well as excellent electrical and mechanical properties [24]. Because of its characteristics, the incorporation of small amount of CNT into polymer matrix offers a great potential to enhance the properties of the composites. Many studies have shown improvement in mechanical properties of nanofibers by incorporated MWCNT with not only many kinds of synthetic polymers such as PAN [25], polymethyl methacrylate (PMMA) [26], PVA [27], but also with natural biopolymer such as cellulose derivative [28]. Incorporated MWCNT into PVDF by electrospinning process has been investigated by Huang et al. [29]. This study focused on investigation of polymorphism and crystal orientation of electrospun PVDF/CNT nanofibers. Thus, the mechanical and physical properties have yet to be demonstrated. In this work, functionalized MWCNT (f-MWCNT) were incorporated into PVDF copolymer nanofibers by using an electrospinning process. In order to ensure the good dispersion, f-MWCNTs were sonicated prior to mixing with the polymer. Morphology, structure, mechanical properties and hydrophobicity of the electrospun f-MWCNT/PVDF copolymer nanofiber were analysed and compared with that of pure PVDF copolymer nanofiber.

2. Experimental Method

2.1. Materials
Poly(vinylidene fluoride) (PVDF) copolymer was used as the membrane material and purchased from Arkema Inc. U.S.A. Multiwall carbon nanotubes (MWCNTs) with an outer diameter of 8-15 nm and purity of 95 % were supplied by He Ji Company, Hongkong. The nanotubes were functionalized by surface oxidation method using a mixture of sulfuric acid and nitric acid according to previous report [24]. The N,N-dimethylacetamide (DMAc), sulfuric acid (H₂SO₄) 95-97 %, and nitric acid (HNO₃) 65 % were from Merck and used without further purification.

2.2. Fabrication of f-MWCNT/cPVDF nanocomposites
Functionlized MWCNT (f-MWCNT) at a concentration of 0.1 % was dispersed in DMAc through 1-h sonication using Ultrasonic cleaner (120W, 40 kHz), followed by adding PVDF copolymer powder at the concentration of 24 % and continuous stirring for 24 h. The solution was then transferred to a 5 mL syringe fitted with a needle (inner diameter of 0.8 mm). Polymer nanocomposites were electrospun at 20 kV, flow rate of 1 mL/h, and tip to collector distance of 17 cm. The ENM was collected on to the aluminum foil wrapped over the drum collector for 60 mins. For comparison, pure PVDF copolymer nanofiber was prepared using the same procedure. All nanofibers were dried in room temperature for at least one day prior to characterization.

2.3. Characterization of electrospun membrane f-MWCNT/cPVDF nanocomposites
Surface morphologies of the obtained nanofibers were observed using scanning electron microscopy (SEM, JEOL JSM IT-300, Japan) operated at 10 kV. Prior to measurements, samples were sputtered coated with a layer of gold. The images were captured at 5000× magnification. The average diameters of the nanofibers were calculated on SEM images using ImageJ software from at least 200 data.
Fourier-transform infrared (FTIR) Nicolet iS5 ATR iD5 Thermo Scientific was used for analysis of structural interaction between PVDF copolymer and f-MWCNT in nanocomposites. XRD analysis were conducted by using an X-Ray Diffractometer (Bruker D8 Advance, Germany) with CuKα radiation ($\lambda = 1.5418 \text{ Å}$). The operating voltage and current were 40 kV and 40 mA, respectively. The samples were scanned from $10^\circ$ to $70^\circ$.

Mechanical properties of ENMs were tested using a universal testing machine (Orientec UCT-5T, Japan) to determine the tensile strength, elongation, and elastic modulus of the membranes. The membrane was cut into rectangular specimens of 35 mm long and 5 mm wide using a sharp scissor. Thickness of the films was measured using a dial gauge (Mitutoyo, Japan) with an accuracy of 0.01 mm at three random points. The distance between the jaws was 20 mm and the testing were conducted using a load cell of 100 kgf. All specimens were stretched at a constant speed of 10 mm/min. Each membrane was measured in three replicates and the average value was calculated.

Water contact angle was measured by drop shape method and calculated by the equation (1):
\[
\frac{\theta}{2} = \tan^{-1}\left(\frac{h}{d}\right)
\]
with $\theta =$contact angle, $d =$diameter, and $h =$height of the water droplet.

3. Results and Discussions

3.1. Morphological analysis
The SEM images of pure PVDF copolymer and f-MWCNT/PVDF copolymer nanofibers are presented in Figure 1. The nanofibers of pure PVDF copolymer have smooth and uniform structures with no beads on nanofiber string. The average diameter of pure PVDF copolymer nanofiber was 312 nm. Addition of 0.1 % f-MWCNT into PVDF copolymer increased the average diameter of the resulted nanofibers to 445 nm. This was attributed to the increase in the viscosity of electrospinning solution as a result of f-MWCNT loading. Furthermore, it is evident that the f-MWCNT embedded well within the nanofiber and there is no CNT was found on the surface of nanofiber as seen in Figure 1b. This indicates the optimum sonication period for breaking the aggregates or bundles of MWCNT to achieve good dispersion. Kearns and Shambaugh explained sonication might damage CNT when the sonication time is too long, but too short sonication process could result in inadequate dispersion [30].

3.2. FTIR analysis
The structure and the interaction between PVDF copolymer and f-MWCNT were confirmed by using FTIR. Figure 2 shows the FTIR spectra of PVDF copolymer and f-MWCNT/PVDF copolymer nanofiber prepared by electrospinning. The IR vibrational bands observed at 611 cm$^{-1}$ (CF$_2$ bending), 762 cm$^{-1}$ (skeletal bending), and 796 cm$^{-1}$ (CH$_2$ rocking) were related to the PVDF $\alpha$-phase. Incorporated f-MWCNT into PVDF copolymer matrix caused shifting peak at CF$_2$ bending group (613 cm$^{-1}$) and CH$_2$ function group (800 cm$^{-1}$). It is also confirmed the formation of PVDF $\beta$-phase from vibrational band at 839 cm$^{-1}$ (CH$_2$ rocking vibration), 877 cm$^{-1}$, and 1274 cm$^{-1}$ (CF stretching vibration) due to electrospinning process. The bands at 1400 cm$^{-1}$ and 1178 cm$^{-1}$ corresponded to CF$_2$ symmetrical stretching. The presence of f-MWCNT in f-MWCNT/PVDF copolymer nanofiber membrane caused shifting peak at 1176 cm$^{-1}$.
Figure 1. SEM images and diameter distribution of (a) PVDF copolymer, (b) f-MWCNT/PVDF copolymer nanofiber membranes.

Figure 2. FTIR spectra of PVDF copolymer and f-MWCNT/PVDF copolymer.
3.3. XRD analysis
X-ray diffraction (XRD) patterns for pure PVDF copolymer and f-MWCNT/PVDF copolymer nanocomposites are presented in Figure 3. Supporting analysis of FTIR spectra, the presence of PVDF \( \beta \)-phase was confirmed by the strong peak of piezoelectric crystal at 20.2°, which corresponds to 200 reflection, while another peak at 18.3° corresponds to 020 reflection of the \( \alpha \)-phase. For addition of 0.1% f-MWCNT, the \( \beta \)-phase peak is shifted to 20.1° but with higher intensity than that of neat PVDF copolymer nanofiber. On the other hand, the \( \alpha \)-phase peak at 20 = 18.2° is weakened compared to that of the PVDF copolymer. This is indicating that the \( \beta \)-phase is slightly increased while the \( \alpha \)-phase is suppressed with the addition of MWCNT. A similar result was also reported by Huang et al. where incorporated MWCNT into PVDF dissolved in a DMF/acetone mixture [29].

![XRD pattern of PVDF copolymer and f-MWCNT/PVDF copolymer](image)

**Figure 3.** XRD pattern of PVDF copolymer and f-MWCNT/PVDF copolymer

3.4. Mechanical properties
Typical stress-strain curves with calculated values of the two samples are presented in Figure 4. The pure PVDF copolymer nanofiber exhibited relatively low tensile strength of 0.71 MPa and elastic modulus of 1.85 MPa because of highly porous structure, as observed by SEM image. In addition, the small fiber diameters also resulted in declining of mechanical integrity of the membrane. However, PVDF copolymer nanofibers showed moderate elongation at break of 81%. With f-MWCNT, the tensile strength and elongation at break were significantly improved. The tensile strength was increased to 0.77 MPa, while elongation at break increased to 144%. The increase in tensile strength could be attributed to the strong interfacial interaction between MWCNT and the polymer matrix, hence the load during tensile force transferred effectively from polymer matrix to the MWCNT. Moreover, the higher average diameter of the f-MWCNT/PVDF copolymer could also contribute toward higher mechanical properties. It is assumed that MWCNTs oriented well along the fibre axes and acted as the reinforcement, so that the elongation was improved. A similar phenomenon was observed by others when incorporated MWCNT into cellulose acetate [28].
Figure 4. Mechanical properties of PVDF copolymer and f-MWCNT/PVDF copolymer nanofibers, inset: tensile strength, elongation, and elastic modulus of PVDF copolymer and f-MWCNT/PVDF copolymer nanocomposites

3.5. Contact angle
Surface hydrophobicity of the nanocomposite membrane was also found to be affected by the addition of f-MWCNT into the PVDF copolymer nanofiber. Figure 5 shows the contact angle of the surface of PVDF copolymer and f-MWCNT/PVDF copolymer nanofibers. Pure PVDF copolymer nanofiber has contact angle of 114°. Then, it reduced to 103° due to the addition of 0.1 % f-MWCNT, indicating that the surface of f-MWCNT/PVDF copolymer nanofibers appear to be more hydrophilic than pure PVDF copolymer nanofiber because of the hydrophilic nature of acid treated MWCNT. The carboxylic acid functional groups generated by acid treatment on the surface of MWCNT led to decrease hydrophobicity of the nanocomposite membrane.

Figure 5. Contact angle of PVDF copolymer and f-MWCNT/PVDF copolymer nanofiber membranes
4. Conclusion

Functionalized MWCNTs were successfully incorporated into PVDF copolymer solution via electrospinning process. It was demonstrated that the addition of f-MWCNT increased the diameter and mechanical properties of the nanocomposites. FTIR spectra and XRD patterns confirmed the increase in PVDF \( \beta \)-phase due to electrospinning process and addition of f-MWCNT. However, incorporated f-MWCNT slightly decrease hydrophobicity of PVDF copolymer ENM due to hydrophilic properties of f-MWCNT.

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Author Contribution

Indriyati is contributed as the main contributor of this work. All authors read and approved the final paper.

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