Effect of Carbon Nanotube Loading on Electrical Properties of Electrospun Polyvinylidene Fluoride (PVDF) Fiber

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Abstract. Polyvinylidene fluoride (PVDF) is a high purity thermoplastic fluoropolymer that use in the aircraft, electronics, and chemical industry. Carbon nanotube (CNTs) is made up of rolled up of graphite sheets, exhibits excellent chemical, thermal, mechanical properties, and large surface areas. PVDF fibers blended with CNTs were able to enhance the β-phase which contributes to piezoelectric properties. Electrospinning is the simplest and low-cost method to produce PVDF/CNT fibers by dissolving PVDF in solvent N, N-Dimethylformamide (DMF). 15wt% PVDF solution was used. CNT loading were varied at 0.0wt%, 0.35wt%, 0.80wt% and 1.00wt% with parameters of 20kV, tip-to-collector distance (TCD) 15cm and flow rate 1.0mLh-1. Scanning Electron Microscope (SEM), four-point probe and X-ray Diffraction (XRD) were used to determine the morphology and crystallinity of electrospun PVDF/CNT fibers. The SEM analysis concluded all fibers showed beaded structure due to low concentration of PVDF solution with insufficient ultrasonification and stirring, cause electrospaying and agglomeration. XRD and four-point probe analysis concluded PVDF/0.35wt%CNT showed the highest β-phase content with intense XRD peak and highest electrical conductivity. However, shift peak is observed among all fibres due to short electrospinning time leads to insufficient thickness of electrospun mat, which affects the mechanical properties of fibres and causes peak shift.

1 Introduction

Carbon Nanotube (CNT) is made up of a graphene sheet roll up to a hollow cylinder in axial symmetrical on tube axis. It exhibits high electrical conductivity, able to withstand high temperature, lightweight and high elasticity [1]. However, individual CNT has weak translation of its intrinsic properties into macroscopic form which makes it unsuitable to use in the form of powder. CNT is mostly use in combination with other materials in the form

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of alloys or blends composite materials [2]. The most common combination is by dispersing CNT as filler in polymer-based matrices in conventional polymers such as thermoplastics, thermosets or elastomers [3]. Polynanocomposite is one of the largest fields of application for CNTs. Integration of CNT increase the electrical properties of nanotube polymer composite. Polyvinylidenefluoride (PVDF) exists in 4 crystalline phases: α phase, β phase, γ phase and δ phase which is identifying by the chain conformations and packing of molecules [4]. The dipole moment of β phase is higher than other phase and contributes to the piezoelectric properties in PVDF itself [5]. However the β phase is thermodynamically unstable and pure PVDF normally exist in α phase. Hence nanoparticles such as fillers like CNT were added into PVDF to obtain β phase. Electrospinning is a simple and low cost method to produce PVDF/CNT fibers. There are few parameters that affect the electrospinning process, which are polymer solution flow rate, type of collector, tip-to-collector distance (TCD), applied voltage, and concentration of polymer solution as they have remarkable effect on nanofibers morphology and diameter of nanofibers [6]. Electrospinning of PVDF/CNT will increase its electrical properties as CNT loading increase until the percolation threshold at 1.0 wt%. Xu Yue et al. [7] found out that the XRD characteristics peaks of α phase decrease in intensity and increase β phase at 2θ = 20.6° correspond to (110)/(200) planes. In this study, the morphology, phase and electrical properties of PVDF at different CNT loading were investigated.

2 Experimental

2.1 Materials

The solvent used to dissolve PVDF/CNT fibers is N,N-Dimethylformamide (DMF) which is supplied by Fisher Scientific Company, Polyvinylidene fluoride (PVDF) in the form of powder is supplied by Sigma-Aldrich Company and carbon nanotube (CNT) in the form of powder.

2.2 Solution Preparation

PVDF powder were used as raw material in this study. 10 wt% of PVDF solution was used in this study. Pure PVDF solution was prepared by dissolving PVDF powder into N,N-Dimethylformamide (DMF) at room temperature in two step method. 0.8330g of PVDF powder was added in to 10ml of DMF to form PVDF/DMF solution. The solution was stirred for 10 minutes using magnetic stirrer until it was dissolved. Next, the remaining 0.8330g of PVDF powder was added into the solution and was stirred for another 1 hour and 50 minutes at room temperature. The solution was covered with aluminium foil to avoid evaporation. PVDF/0.35wt% CNT, PVDF/0.80wt% CNT and PVDF/1.00wt% CNT were prepared by adding CNT powders into 10ml of DMF. The solution was sonicated using ultrasonic homogenizer for 1 hour to break the CNT bundles. Half of the portion of PVDF powders were added into the mixture and stirred for 10 minutes using magnetic stirrer, and follow by another 1 hour and 50 minutes stirring by adding the remaining PVDF powder until the powder was fully dissolved in mixture.
Table 1. Mass and wt% of CNT for all 4 samples

| Sample | Volume of DMF/ml | Mass of PVDF/g | CNT (wt%) | Mass of CNT/g |
|--------|------------------|----------------|-----------|--------------|
| A      | 10.00            | 1.6659         | 0.00      | 0.00         |
| B      | 10.00            | 1.6659         | 0.35      | 0.039        |
| C      | 10.00            | 1.6659         | 0.80      | 0.086        |
| D      | 10.00            | 1.6659         | 1.00      | 0.1122       |

Electrospinning was conducted after mixture prepared. The PVDF solution was transferred into a 10ml syringe with 0.8mm syringe nozzle inner diameter, which was placed horizontally at syringe pump on injection holder. The parameters used in electrospinning were kept constant, which were 1.0mL/h of flow rate, 20kV voltage, and 15cm tip-to-collector (TCD) distance. Aluminium foil was wrapped around flat metal plate which act as nanofibers collector, that was placed perpendicular to the tip of syringe nozzle. The syringe was rubbed with sandpaper until needle stay flat on surface. Clipper was clamped on the needle to supply voltage from power source. Pump machine and voltage supplier is switched on to allow the PVDF solution to flow from needle tip to flat metal plate. The fibers of PVDF was collected from aluminium foil.

2.3 Morphological Study

Morphology of PVDF fibers were examined by scanning electron microscope (SEM), Hitachi TM3000. The samples were prepared in size of 1cm × 1 cm.

2.4 Electrical Properties

The electrical conductivity of PVDF fibers were measured using four-point probe technique. The conductivity was tested by Keithley 6221 AC/DC source and Keithley 2182A nanovoltmeter. The samples were measured in the present of 100V of voltage.
2.5 Phase Analysis

The phase of PVDF fibers were analyzed by using X-Ray Diffraction (XRD) analysis with model XRD-600, Shimadzu, Tokyo, Japan of X-Ray Diffraction (XRD). The composition and phase of PVDF and PVDF/CNT fibers were determined. The scan rate was 0.02°/s and the 2θ scan range is between 5° to 30°.

3 Results and Discussion

3.1 Morphological Study

Fig. 2. shows morphology of electrospun PVDF fiber with different CNT loading under magnification of ×5000. All of the electrospun PVDF fiber showed beaded structures due to low PVDF concentration and insufficient ultrasonification and stirring time. Low concentration of PVDF induce electrospraying process which produce beaded fibers [9]. Hao Shao et al. [10] stated that beaded PVDF fibers were produced when the polymer concentration is lower than 20wt%. The electrospun PVDF fiber was non-beaded at 20wt%. With increment in PVDF concentration from 20wt% to 26wt% increase the fiber diameter that decrease the β-phase of PVDF. In comparison, electrospun PVDF/0.35wt% CNT fibers showed the least beaded fibers.

3.2 Electrical Properties

Fig. 3. showed the average resistance and average conductance of samples with different wt% CNT loading, that are measured with four-point probe technique. The electrical resistance of sample B is the lowest, with highest average conductance of 548.88 Ω and 1.6×10⁻³ Siemens respectively, which indicates it has the highest electrical conductivity.
The electrical conductivity increase as CNT loading increase until 0.35 wt%, and decrease as CNT further increase from 0.35 wt% to 1.00 wt%. However, this result does not match with research paper from Wang, S.-H. [11] and Alhasssan, Z. A. [12], the electrical conductivity increases with CNT loading until 1.2 wt%. The density of CNT-CNT junction increases with an enhancive conductivity as CNT loading increase from 0 wt% until 1.2 wt%. The electrical conductivity stays constant as CNT loading increase further from 1.2 wt%, as the three-dimensional network had been constructed. This experiment result does not match with the previous research finding due to improper parameters in electrospinning process, such as low concentration of PVDF solution, insufficient ultrasonification and stirring, and insufficient electrospinning time.

![Fig 3.](a) Average resistance of samples using four-probe measurement, (b) Average conductance of samples using four-point probe measurement

### 3.3 Phase Determination

Fig. 4. showed the diffraction angle of pure PVDF and 3 different wt% of PVDF/CNTs at 20kV were enlighten by X-Ray Diffraction patterns from scan range of 5° to 30°. According to studies from Gregorio et al. [13,112] and Esterly et al. [14,113], the samples should show up an intense peak around 20.26° correspond to β-phase. However, from the result of XRD in Fig. 2., it is shown that the peak showed up at range of 22.2° to 22.64° instead. It is believed that the main reason for shifted peak in this XRD analysis is cause by the crystallite size and lattice strain effect of the samples [15,114]. The decrease performance of the samples in terms of Young's modulus result in a shorter fibre-fibre junctions which disrupts the fibre ability to reorganized according to the increasing strain [16,118]. Hence, it can be concluded that the electrospun samples do not achieve the desirable thickness which in turn affects the mechanical properties that result in a peak shift in XRD analysis. The result of this research does not support with finding from Indriyati, Primadona, I. [17,111] and Ahn, Y. , Lim 18,[112] as the characteristics peaks intensity of α phase at 2θ=18.0°,18.6°, 20.2° and 26.8° decrease when CNT loading increases. It was showed a prominently increase in characteristic β phase peak at 20.26° when CNT increase. Hence, the difference in result of this research work and previous research are due to insufficient electrospinning time which leads to insufficient electrospun mat thickness.
4 Conclusion

In this study, the effect of carbon nanotube (CNT) loading on electrical properties of electrospun PVDF fibers were investigated. However due to improper parameters of electrospinning process, such as low PVDF concentration, insufficient ultrasonification and stirring in solution-preparing step and inadequate thickness of electrospun mat causes a shift in fibers diameter, beaded fibers, shifted in XRD peak and electrical conductivity. It is vital to first finalized the electrosprining parameters before proceeding with effect of CNT loading on PVDF fibers.

References

1. Yu, M.-F., Files, B. S., Arepalli, S., & Ruoff, R. S., Phys. Rev. Lett., 849 (2000)
2. Q. Li, A. Vierreckl, C. Rottmair, C. A. & Singer, R. F., Compos. Sci. Technol. 69 (2009)
3. P. Saini, Syn., Prop. and App. (2015)
4. A. Lund, B. Hagström, J. of App. Poly. Sci. (2010)
5. Schwartz, Mel. En. of Smart Mater., (2002)
6. N. Bhardwaj, S. C. Kundu, Biotechnol. Adv. 28 (2010)
7. S. K. Rath, S. Dubey, G. S. Kumar, S. Kumar, A. K. Patra, J. Bahadur, A. K. Singh, G. Harikrishnan, & T. U. Patro, J. of Mater. Sci., 49, 1 (2014)
8. Y. Xu, W. T. Zheng, W. X. Yu, L. G. Hua, Y. J. Zhang, & Z. D. Zhao, Chem. Res. in Chinese Uni., 26, 3 (2010)
9. F. Mokhtari, M. Latifi, & M. Shamshirsaz, The J. of The Text. Ins. (2015)
10. H. Shao, J. Fang, H. Wang, & T. Lin, RSC Advances, 5, 19, (2015)
11. S. -H Wang, Y. Wan, B. Sun, L. Z. Liu, & W. Xu, Nanoscale Res. Lett, 9, 1 (2014)
12. Z. A. Alhasssan, Y. S. Bureqz, R. Nair, & N. Shehata, J. of Nanomat, (2018)
13. R. Gregorio, J. of App. Polym. Sci., 100, 4 (2006)
14. D. M. Esterly, & B. J. Love, J. of Polym. Sci. Part B: Polym. Phys., 42, 1 (2003)
15. S. K. Mishra, H. Roy, A. K. Lohar, S. K. Samanta, S. Tiwari, & K. Dutta, IOP Conf. Ser.: Mater. Sci. and Eng., 75 (2015)

16. A. A. Conte, K. Sun, X. Hu, & V. Z. Beachley, Front. in Chem., 8 (2020)

17. Indriyati, I. Primadona, F. Dara, A. Syampurwadi, & M. Nasir, IOP Conf. Ser.: Earth and Envi. Sci., 483, 1 (2020)

18. R. F Gregorio, J. of App. Polym. Sci., 100, 4 (2006)