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Morphology and thermal properties of PVDF electrospun nanofiber

[1]M. Buddhakala and [2]A. Muakngam

[1]Division of Physics, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Klong 6, Thanyaburi, Pathumthani 12110, Thailand
[2]College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand

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ABSTRACT

Polyvinylidene fluoride (PVDF) membranes was prepared by electrospinning technique using 11 - 15 wt.% PVDF solution in mixed solvent of *N*,*N*-dimethylacetamine (DMAc):acetone at a ratio of 4:6 with the applied voltage of 10 kV, tip to collector distance of 10 cm and flow rate of 1 mL/hr. The morphology of the PVDF membranes was investigated by scanning electron microscope (SEM). The effect of polymer concentration on the average fiber diameter of PVDF membranes were discussed. Level of crystallinity of electrospun PVDF was investigated by differential scanning calorimetry (DSC). It was found that polymer concentration have signigicant influence on the thermal properties of PVDF membranes.

INTRODUCTION

Poly (vinylidene fluoride) (PVDF) has received great attention as a membrane material with its outstanding properties such as thermal stability, high mechanical strength and chemical resistance. PVDF membranes have been studied for applications in membrane distillation, rechargeable batteries, gas removal and separation, and biological applications. A variety of techniques such as chemical treatment, chemical grafting, and dip coating have been developed to improve the membrane surface. However, pore and pore size distribution are difficult to control. As a result, electrospinning is introduced in this study.

Electrospinning is an efficient fabrication process that gives fibrous and porous membranes with an average diameter ranging from 100 nm to 5μm [1-2], which are at least one or two order of magnitude smaller than the fibers produced from melt or solution spinning. Electrospinning technology has recently been extended in various fields like preparation of porous filters, biomedical materials, reinforcing components, cloths for electromagnetic wave shielding, sensors, electronic devices, etc. [3-6]. Electrospinning is a process by which sub-micron polymer fibers can be produced using an electrostatically driven jet of polymer solution. A pendant droplet of the polymer solution at the capillary tip is deformed into a conical shape under the electrostatic field. When the electrostatic forces overcome the surface tension, a charged jet is ejected. The jet moves towards a ground plate acting as a counter electrode (or collector). A grounded counter electrode is placed against the capillary. A thin polymer fiber is deposited on the collector. There are reported that electrospun PVDF membranes was used as polymer electrolyte [7-9]. In general, electrospun nanofiber mat has a lower physical properties due to the non-woven state without interfiber bonding. In this study, we prepared electrospun PVDF nanofibers from different solution concentration. The polymer membranes are characterized by scanning electron microscope for morphology. The thermal properties are studied by differential scanning calorimetry.

Materials And Methods

Polyvinylidene fluoride (M_w= 534,000, Sigma Aldrich) were used as fibrous PVDF membrane material. *N, N*-dimethylacetamide (DMAc) and acetone were purchased from Sigma-Aldriche Co. The electrospun fibers were prepared from 15 wt.% solution of PVDF in mixed solvent (acetone/DMAc) 6:4 by weight. Fig. 1 shows the schematic of electrospinning setup. It consists of syringe pump, DC high voltage and collector, etc. In this study we use cylindrical rotating as collector. During electrospinning, a stainless steel needle was kept in contact to a positive high voltage and the collector was grounded. The spun membranes was collected on an aluminium foil and kept at 35°C for 6 h before further use.

Corresponding Author: M. Buddhakala, Division of Physics, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Klong 6, Thanyaburi, Pathumthani 12110, Thailand
E-mail: morak555@gmail.com Tel. 0225494186-7

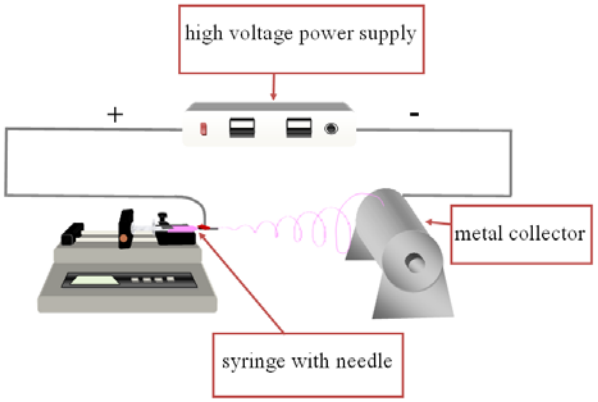


Fig. 1: Scheme of an electrospinning equipment.

Morphology of the electrospun fibrous membranes was observed with a scanning electron microscope (SEM-JEOL JSM 5600) The average was calculated using the ImageJ software based on SEM images. The thermal properties of PVDF membranes was determined by differential scanning calorimetry (DSC). DSC data were obtained in the temperature range of 40-200 °C and rate of 10 °C/min. Surface hydrophilicity was characterized on the basis of an optical angle measurement system at ambient temperature. Static contact angle of membrane was determined from the image with calculation software.

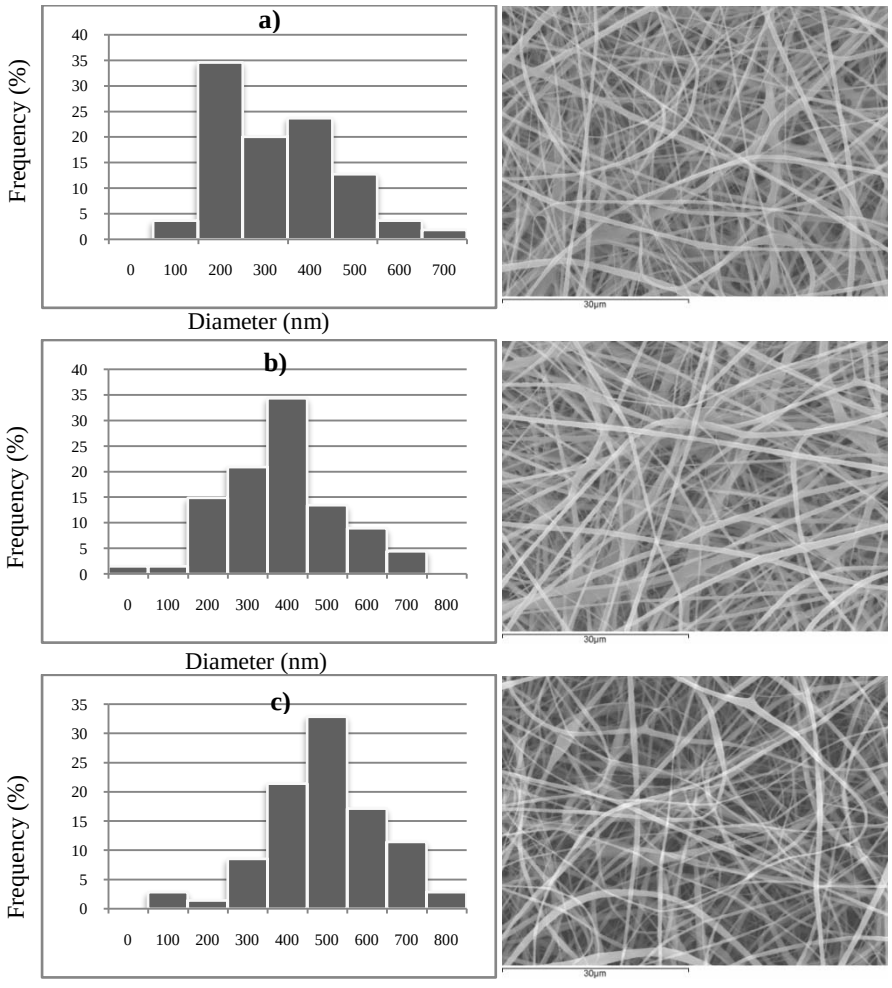
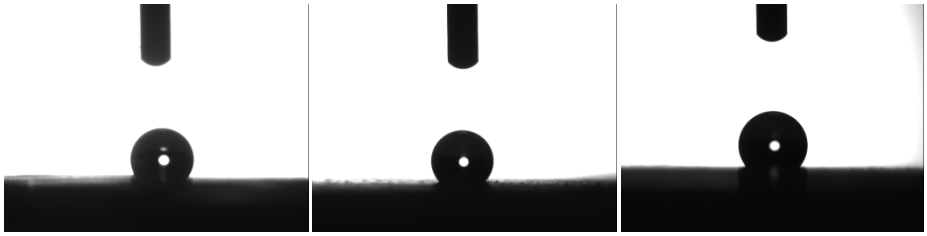


Fig. 2: Diameter distribution of the electrospun PVDF nanofibers with concentration a) 11 wt.% b) 13 wt.% c) 15 wt.%

Results And Discussion

Fig. 2 shows the SEM images and the distribution of fiber diameters. The average fiber diameters of nanofibers increased from 351 nm to 542 nm with an increase in solution concentation from 11wt.% to 15 wt.%. An increases in the concentration will result in greater polymer chain entanglements within the solution which is necessary to maintain the continuity of the jet during electrospinning. When the polymer concentration is increased the charge on the electrospinning jet will be able to fully stretch the solution with the solvent molecules distributed among the polymer chains. With increased polymer concentration, the diameter of the fiber also increases due to the greater resistance of solution to be stretched by charge on the jet.



(a) (b) (c)

Fig. 3: Water droplet on electrospun PVDF a) 11 wt.% b) 13 wt.% c) 15 wt.%

The water contact angle of electrospun PVDF nanofiber are shown in Fig. 3 which are found the change in the contact angle measurment of electrospun nanofibers according to the PVDF concentration. The concectration of 11 wt.% 13wt.% and 15 wt.% are $126.22^{o} \pm 3.27^{o}$, $127.03^{o} \pm 0.98^{o}$ and $129.96^{o} \pm 3.27^{o}$, respectively. All most concentration of PVDF solution contribute to the hydrophobic of the electrospun PVDF nanofiber.

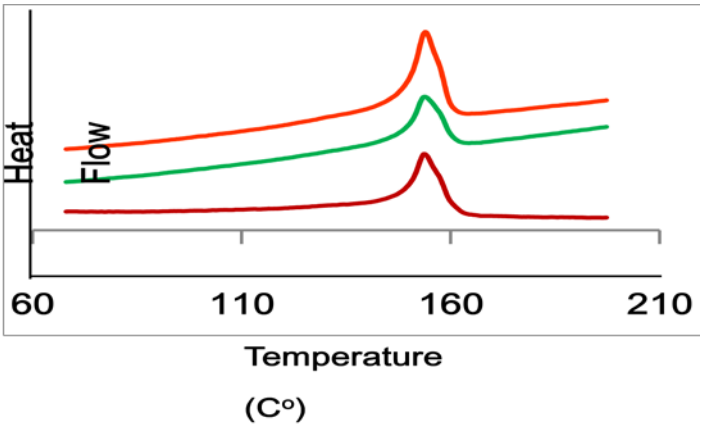


Fig. 4: DSC thermograms of the electrospun PVDF nanofibers a) 11 wt.% b) 13 wt.% c) 15 wt.%

In order to determind the formation in crystal structure and thermal properties of PVDF membrane, The DSC measurement was carried on electrospun PVDF. Fig. 4 shows DSC thermograms of the electrospun PVDF nanofibers. The melting temperature (T_m) are nearly the same at 158 C^{o}. Degree of crystallinity (χ_c) of the sample was determined from its DSC curve using the following equation [10]:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^*} \times 100\ \%$$

When and ΔH_f is melting enthalpy of the perfectly crystalline PVDF and the melting enthalpy of the samples, respectively. In this study, value of 104.5 J/g was used as ΔH_f^* . The crystallinity of electrospun PVDF nanofibers increased from 25.4 % to 35.1% with a increase in the average diameter from 351nm to 542 nm. This can be attributed to a higher resistance of the solution to be stretched by charge on the jet with the increase of the solution concentration. The crystallinity of electrospun PVDF are lower than pure PVDF.

Conclusion:

The electrospinning technique was used to fabricate PVDF membrane. The effect of solution

concentration on the morphology and thermal properties of electrospun membrane were investigated. It was shown that higher concentration PVDF solution favoured the formation of continuous nanofibers with no bead-like textures. The average diameter of nanofiber is increased with increasing solution concentration. DSC results indicated that the electrospun PVDF exhibited the weaken crystallinity and has hydrophobic nature.

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