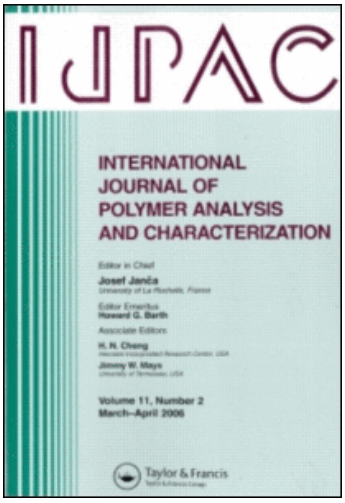

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Huang, Fenlin , Wei, Qufu , Cai, Yibing and Wu, Ning(2008) 'Surface Structures and Contact Angles of Electrospun Poly(vinylidene fluoride) Nanofiber Membranes', International Journal of Polymer Analysis and Characterization, 13: 4, 292 — 301
To link to this Article: DOI: 10.1080/10236660802190963
URL: http://dx.doi.org/10.1080/10236660802190963

International Journal of Polymer Anal. Charact., 13: 292–301, 2008

ISSN: 1023-666X print
DOI: 10.1080/10236660802190963

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Surface Structures and Contact Angles of Electrospun Poly(vinylidene fluoride) Nanofiber Membranes

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Abstract: Poly(vinylidene fluoride) (PVDF) nanofiber membranes with different surface structures were obtained by controlling operating parameters in the electrospinning process. The diameters and assembling morphology of the PVDF nanofibers were characterized by scanning electron microscopy, nitrogen adsorption based on the BET (Brunauer, Emmett, and Teller) principle was applied to measure the specific surface area of the nanofiber membranes, the contact angles on the nanomembrane were evaluated by static micro-drop observation, and a modified Yang equation was applied to analyze the contact angles. The results revealed that the BET specific surface area was the key factor affecting the contact angles.

Keywords: Contact angle; Electrospinning; Poly(vinylidene fluoride); Specific surface area

Received 19 March 2008; accepted 9 May 2008.

This work was supported by the Program for New Century Excellent Talents in University (NCET-06-0485), Innovation Project of Jiangsu Graduate Education (No.: CX07B-152Z), and Program for Innovative Research Team of Jiangnan University.

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INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has drawn a great attention in recent years due to its attractive properties such as piezo-, pyro-, and ferroelectricity, as well as flexibility, light weight, and good processability.[1] These properties have been increasingly applied to various fields such as filtration, air cleaning, and rechargeable batteries,[2,3] Surface properties, especially surface tension, play the most important role in these applications of PVDF materials.

Electrospinning has been established as a simple and versatile method to produce polymer fibers with diameters at nanometer or submicron scale. This technique has also been employed to fabricate PVDF nanofibers and fibrous thin films for various applications. Continuous fibers can be collected in the form of nonwoven fibrous membranes or as aligned yarns.[4] Nanofibers prepared by electrospinning have many superior properties, such as good pore structure and high surface porosity.[4,5] Recently, several research groups have proved that the surface energy of materials was closely related to the surface properties, especially surface roughness,[6] which presented a new way to control material surface wettability.

In this study, the surface energy of nanofibrous PVDF membranes was investigated by static contact angle measurements. The effect of the fibrous structures on the contact angle of nanofibrous membranes was analyzed.

EXPERIMENTAL SECTION

Materials

PVDF with average molecular weight (Mn) of $5.5 \times 10^5\,g\,mol^{-1}$ was supplied by Haina Co., Ltd. (China). *N*,*N*-Dimethyl formamide (DMF) and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification.

Preparation of PVDF Nanofibers

PVDF nanofiber membranes with four different fiber diameters were prepared in this study. All membranes were electrospun from solutions with concentrations of 15 wt. % prepared by dissolving the polymer in a mixture of DMF and acetone (1:4, v/v) at room temperature. A mechanical stirrer was employed to obtain a homogeneous solution. The

prepared solution was kept for one hour in a dark place before electrospinning in order to remove air bubbles in the solution.

The apparatus for electrospinning included a glass syringe, an 18 gauge stainless steel needle, a microinfusion pump (Medical Instrument Co., Zhejiang, China), a high-voltage power supply (Dongwen Co., Tianjing, China), and aluminum foil as the collector. PVDF solution was drawn horizontally from the needle tip by the electrostatic force generated from the high voltage applied between the tip and the collector. The PVDF solution formed a Taylor cone and jetted through the tip of needle to the collector. The distance between needle tip and collector was kept at 15.0 cm. The applied voltage as the controlling parameter was set at 10.0, 13.0, 16.0, 19.0, and 22.0 KV, respectively. The corresponding nanofibrous membranes were labeled P1, P2, P3, P4, and P5, respectively. The nanofibers deposited on the aluminum foil collector in the form of a nonwoven mat after the evaporation of the solvent. The electrospun membranes were dried under vacuum before they were detached from the aluminum foil.

Scanning Electron Microscopy

The fiber diameters and surface structure were examined by a scanning electron microscope (SEM) (JSM-5610LV). The electrospun nanofibers were sputter-coated with gold before the SEM observations. The diameters of the electrospun nanofibers were measured using an image analyzer (Adobe Photoshop CS3.0) and calculated by measuring at least 12 fibers at random.

BET Specific Surface Area

The BET specific surface area of the samples were examined using low-temperature (77.38 K) nitrogen adsorption isotherms measured over a wide range of relative pressures from 0.02 to 1. Adsorption measurements were performed on a Micromeritics ASAP2010 volumetric adsorption apparatus. High-purity nitrogen (99.9999%) was used. Prior to measurement, the samples were degassed at 373 K for 3 h in the degas pot of the adsorption analyzer.

Contact Angle Measurements

The contact angle was measured on a Drop Shape Analysis System DSA100 produced by Kruss Company. Deionized water was dropped

onto the sample from a needle on a microsyringe during the test. A picture of the drop was taken a few seconds after the drop set onto the sample. The contact angles could be calculated by analyzing the shape of the drop.

RESULTS AND DISCUSSION

Structural Characterization

PVDF nanofibers electrospun using the voltage of 10.0 KV are shown in (Figure 1(a). It was found that the electrospun membrane is composed of randomly oriented fibers with a wide range distribution of fiber diameters from 500 to 2000 nm; the average diameter is about 978 nm. The image in Figure 1(a) also shows that the fibers assemble loosely and the fibers are bent and flexural. It is well known that the structures of electrospun nanofibers are mainly affected by the combination of the electrostatic forces and the viscoelastic behavior of the polymer solution.[7,8] The electrostatic forces applied play the most important role in this study since the concentration of the polymer solution is fixed.[9,10] In this work, the voltage is used as the main parameter to investigate the alteration of nanofiber diameters. The lowest voltage selected in this experiment is 10.0 KV, which produces weak electrostatic forces but high enough to overcome the surface tension. Accordingly, low voltage causes inadequate drawing and extension of the charged jets, resulting in the coarse and bended fibers as shown in Figure 1(a).

The low electrostatic field formed by low voltage also brings instability during electrospinning, which may lead to the formation of bent and coarse fibers. The drawing rate of the nanofibers can be enhanced by increasing the electric field strength. A shifting trend in the fiber diameter distribution towards a lower size is noted in Table I, and the results indicate that the average fiber diameter decreases with increased electric field strength. As the applied voltage altered from 10 to 13 KV, the average fiber diameter reduced by 175.3 nm, from 978 to 803.3 nm, which is shown in (Figure 1(b). However, the average fiber diameter only decreases by 101.4 nm when the same solution is spun by 16 KV. It can be seen in Figure 1(c) that the nanofibers tightly accumulate without curving. The average diameter of the electrospun fibers drops to 578.4 nm with a standard deviation of 69 nm.

It is well known that the difference in fiber size leads to great changes in basic web properties such as specific surface area. Electrospun nanofibers have diameters that are one to two orders of magnitude smaller than traditional fibers, which leads to a corresponding increase in fiber surface area. The specific surface areas of the electrospun PVDF nanofibrous

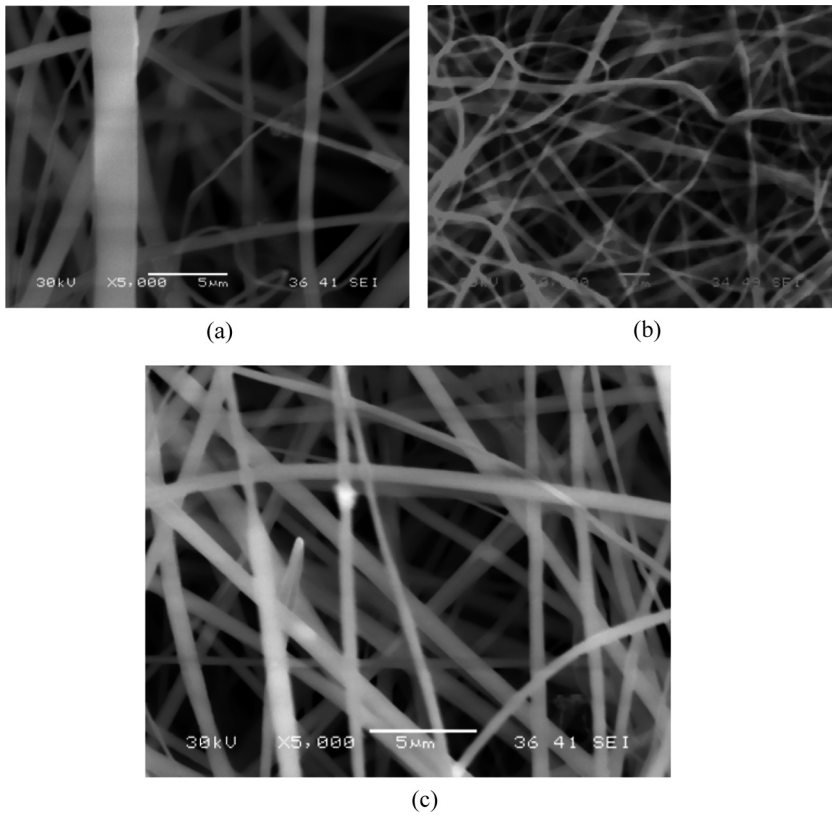

Figure 1. SEM image of nanofibers electrospun at (a) 10.0 KV, (b) 13 KV, and (c) 22 KV.

membranes investigated by nitrogen adsorption measurements at 77.38 K are summarized in Table I. The results indicate that the specific surface area of sample P1 electrospun at 10 KV is about 8.12 m^2/g with a significant increase compared to normal fibrous membrane.[11] The specific

Table I. Diameters and specific surface areas of PVDF nanofibers

Sample	Diameter (nm)	BET specific surface area (m^2/g)
P1	978.6	8.12
P2	803.3	8.96
P3	701.9	12.43
P4	641.1	15.22
P5	578.4	21.44

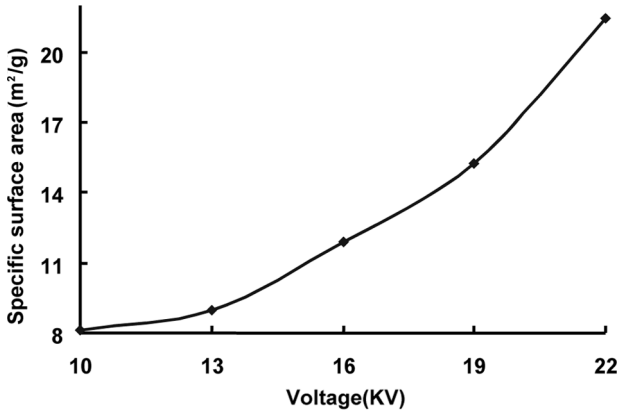

Figure 2. Distribution of specific surface areas of membranes electrospun with different voltages.

surface area increases to 21.44 m^2/g as the average diameter of the nanofibers is reduced to 578 nm, electrospun at the voltage of 20 KV. The BET specific surface area has a tendency to increase with the decline of fiber diameters, which is presented in Figure 2. Table I clearly reveals the effect of electrostatic voltage on the fiber diameter and specific surface area. The decrease in fiber diameter becomes slower as the voltage increases from 10 to 22 KV, which can be attributed to the combined effect of the electrostatic force and surface tension. The specific surface area of the nanofiber membrane, however, increases faster as the voltage increases from 10 to 22 KV. This is due to a higher voltage, which generates a more compressed assembly of the nanofibers and fiber nanofibers.

Contact Angle Analysis

The results of the static contact angle measurements are shown in Figure 3. It clearly reveals that the contact angles of the nanofiber membranes are all over 90°. The image in Figure 4(a) presents a water droplet formed on the PVDF nanofiber membrane electrospun at 10 KV with a contact angle of 91.8°. The contact angle increases to 132.3° when the voltage for the electrospinning increases to 22 KV, as illustrated in Figure 4(b). The high contact angle in the image clearly reveals the hydrophobic behavior of the nanofiber membrane. The curve in Figure 3 indicates that the contact angle increases with the specific surface area formed by different voltages. This phenomenon can be interpreted in terms of the Young equation and its modification.

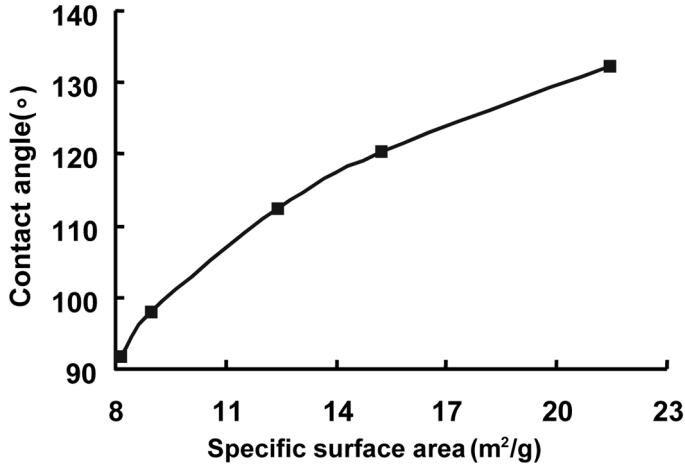

Figure 3. Contact angles of PVDF nanfibrous membrane along the specific surface area.

The Young equation is the common model to describe the contact angle on a surface:

$$\cos\theta = \frac{\gamma sv - \gamma sl}{\gamma lv} \tag{1}$$

where θ is the contact angle, and γsv, γsl, andγlv are surface energies for liquid-vapor, vapor-solid, and solid-liquid interfaces, respectively.

Most practical surfaces, however, are rough and heterogeneous to some extent. Accordingly, different modifications of the Young equation have been proposed to apply to rough surfaces.[12,13] In this study, it is assumed that all of the nanofibers under the water drop have contact with the water. A roughness factor r is the relation between the real area

Figure 4. Micrograph of static contact angle: (a) electrospun at 10 KV, (b) electrospun at 22 KV.

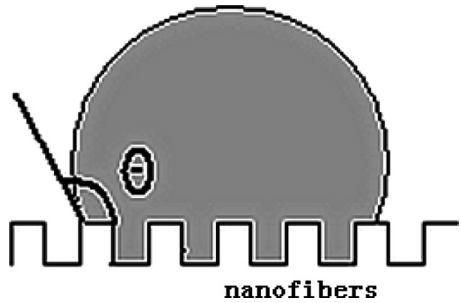

Figure 5. Contact angle model for nanofibrous membrane.

and the projected area. The model of contact angle for nanofiber membrane is shown in Figure 5. Thus, the contact angle of a nanofiber membrane can be denoted by

$$\cos\theta' = \frac{r(\gamma sv - \gamma sl)}{\gamma lv} = r\cos\theta \tag{2}$$

The increase in contact angle with voltage is attributed to the change in roughness factor r, as described by Equation (2). Roughness, however, is so complicated that it is difficult to develop a general method for roughness measurement. In this study, specific surface area based on the BET method is used for roughness characterization:

$$B = \frac{Sr}{m} \tag{3}$$

$$r = \frac{Sr}{Sp} = \frac{mB}{Sp} \tag{4}$$

where S_r is the real surface area of nanofibrous membrane, S_p is the projected area, B is the specific surface area, and m represents the mass of a membrane.

For a given nanofibrous membrane, the mass m and projected area Sp are constant and can be easily measured. Consequently, the modified Young Equation (2) can be derived:

$$\cos\theta' = r\cos\theta = \frac{mB}{Sp}\cos\theta \tag{5}$$

It can be seen from Equation (5) that the contact angle, θ', of the membrane depends on the ideal contact angle, θ, and surface roughness, and the specific surface area plays an important role in the material's contact angle. Larger specific surface area leads to higher contact angles, as shown in Figure 3.

CONCLUSION

PTFE nanofibrous membranes were electrospun using a self-made electrospinning apparatus. The surface structures, diameters, and specific surface areas of the electrospun nanofibers were successfully controlled by altering the electrostatic voltage. SEM observations revealed an increase in nanofiber diameter with applied voltage. The experimental results also proved that the static force applied on the jet might be the key factor affecting the surface structure, as well as the specific surface area. It was concluded by the analysis of the modified the Yong equation that specific surface area played the most important role in contact angles of the nanofibrous membrane. The larger specific surface areas resulted in high contact angles.

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