Effect of Inorganic/Organic Hybrid on the Wettability of Polymer Nanofibrous Membranes

Ning Wu, PhD, Ying Sun, Yanan Jiao, Li Chen

Tianjin Polytechnic University, CHINA

Correspondence to:
Li Chen email: chenli2012s@gmail.com

ABSTRACT

We report a new approach for improving the wettability of a poly (vinyl acetate) (PVAc) nanofiber membrane. The pure PVAc and hybrid PVAc/titanium dioxide（TiO_2）nanofibrous membranes can be obtained by electrospinning the PVA solution and PVA/TiO_2 hybrid sol with different TiO_2 contents, respectively. The resultant samples were characterized by scanning electron microscopy (SEM), nitrogen volumetric adsorption apparatus (NVAA), water contact angle (WCA), atomic force microscopy (AFM) energy dispersive X-ray spectroscopy (EDX) and transmission electronic microscopy (TEM). It was found that the WCA of composite fibrous membranes was decreased from 109 to 36° as the TiO_2 content increased. The AFM, EDX and TEM analysis indicate that the wettability of PVAc/TiO_2 hybrid nanofibers was mainly improved by surface roughness and surface hydrophilic groups.

Keywords: Electrospinning; Hybrid nanofibers; Surface characterization; Wettability

INTRODUCTION

Materials with nanofibrous structure have focused much attention because of their several specific characteristics such as very large specific surface area and very high porosity compared with other known forms of material [1]. Electrospinning has been recognized as a simple and versatile technique for preparing nanofibers. In the electrospinning process, a high electric field is applied to viscous polymer solution, inducing a charge density on the liquid drop surface. As Mutual charge repulsion on the drop surface overcomes surface tension, a charged polymer jet is elongated and accelerated by the electric field, undergoing a variety of instabilities, dries, and deposited on a substrate as a random nanofiber web [2].

PVAc nanofiber membranes are widely used in the development of polymer intermediates, various functional base materials [3-5]. PVAc is a homopolymer synthesized from vinylacetate monomer via a free-radical polymerization technique, so it is water-insoluble but able to absorb water to a slight extent [6]. The poor hydrophilicity of PVAc limits its application in many fields, for example, drug delivery, textile materials and controlling the release areas. Various techniques have been tried to improve the wettability of PVAc nanofibers, such as plasma treatment and surface chemical grafting [7, 8]. But plasma treatment may lead to the loss of mechanical properties and the surface chemical grafting can destroy the nanofibrous structure.

Organic/inorganic hybrid materials possess both the advantages of the organic materials such as lightweight, flexibility, and of inorganic materials such as high strength, heat-stable, and chemical resistance [9]. Sol-gel synthesis is widely used to prepare hybrid materials [10-12]. This method has the advantage of being a low temperature process and including the combination of networks of inorganic precursor and polymers at a molecular level, so the final materials have more homogenous than conventional composite materials [13].

In this work, PVAc/TiO_2 hybrid spinning solutions were prepared in sol-gel method. Electrospinning was used to fabricate nanofibers. The diameter distribution, porosity structure and wettability of the hybrid nanofibers were characterized by SEM, NVAA and WCA. Additionally, the surface roughness and surface chemistry components were also investigated by AFM, TEM and EDX.

EXPERIMENTAL

Materials

Polyvinyl acetate (PVAc) with a molecular weight 30000-50000, obtained from Sinopharm Chemical Reagent Co, Ltd, China, was used. Tetrabutyl Titanate (TBT) of chemically pure reagent grade was used for preparing partial hydrolysis TiO_2 sol. The Ethanol and acetone used were of analytical grade. Ethyl acetate was used as the inhibiting agent for the hydrolysis process of TBT.

The Preparation of PVAc and PVAc/TiO_2 Hybrid Nanofiber Membranes

1.0mL Ethyl acetate and 5.0mL TBT were added to 14.0mL ethanol with constant stirring (solution A). 1.0mL distilled water mixed with 9.0mL ethanol (solution B). Then solution B was added drop wise into the solution A with vigorous stirring for 7 h at room temperature. After uniform mixing, stable and transparent TiO_2 sol was obtained. Eq. (1-3) illustrated the three step TBT hydrolysis reaction process for TiO_2 sol preparation (R is tertbutoxycarbonyl group):

$$nTi(OR)_4+nH_2O\rightarrow nHOTi(OR)_3+nCH_3CH_2CH_2CH_2OH \quad (1)$$

$$nHOTi(OR)_3+nH_2O\rightarrow n(OH)_2Ti(OR)_2+nCH_3CH_2CH_2CH_2OH \quad (2)$$

$$n(HO)_2Ti(OR)_2+nH_2O\rightarrow n(OH)_3Ti(OR)+nCH_3CH_2CH_2CH_2O \quad (3)$$

PVAc solution with a concentration of 12wt% was prepared by dissolving the PVAc particles in acetone. A controlled amount of prepared TiO_2 sol was drop wisely added into the acetone PVAc solution, then reacted at room temperature for 24h.Thus,five transparent PVAc/TiO_2 hybrid solution with different TiO_2 sol content (0wt%,0.25wt%,0.5wt%,0.75wt%, 1.0wt%) were obtained.

In the electrospinning process, a high voltage power (15KV) was applied to the solution contained in a syringe via an alligator clip attached to the syringe needle. The solutions were delivered to the blunt needle (the nozzle diameter is about 0.7mm) tip via a microinfusion pump (WZ-50C2, Zhejiang, China) to control the solution flow rate in 0.8ml/h. The electrospun fibers were collected on an electrically grounded aluminum foil. The distance between needle tip and aluminum foil was 15cm.

Characterization

The fibrous structures of the nanofibers were observed with a SEM (HITACHI S-4800, Japan) after a gold coating. The average fiber diameter of the electrospun nanofibers was measured by Photoshop CS3 software. The SEM Quanta 200 equipped with EDX was used to examine the element compositions of the hybrid nanofibers. An accelerating voltage of 20 kV with accounting time of 100s was applied. The specific surface areas and pore structures of the grafted nanofiber membranes were examined using low temperature nitrogen adsorption isotherms measured over a wide range of relative pressure from 0.02 to 1. Adsorption measurements were performed on an ASAP2010 volumetric adsorption apparatus. DSA100 apparatus produced by KRUSS Company was employed to measure the static contact angle. The surface morphology of single nanofiber was analyzed based on the AFM observations. The AFM scanning was performed on a CSPM4000 AFM (Benyuan Co, Ltd, China), scanning was carried out in tapping mode. The electrospun nanofibers for TEM observation were collected on a 300 mesh copper grid during the electrospinning. The TEM images of the hybrid nanofibers were obtained by using a TecnaiG220 microscope with an accelerating voltage of 200 kV.

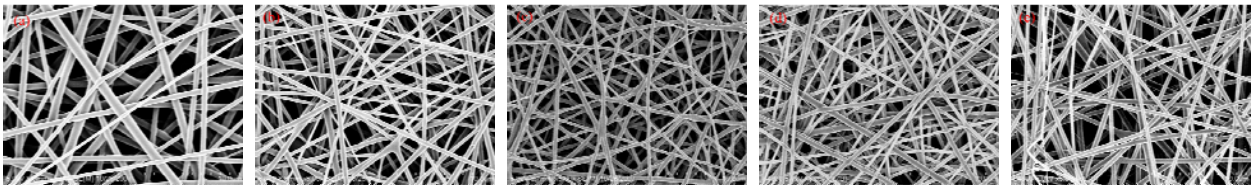

FIGURE 1. SEM images of the electrospun PVAc nanofiber membranes with different TiO_2 contents (a) 0 wt%, (b) 0.25 wt% (c) 0.5 wt% (d) 0.75wt% (e) 1wt%.

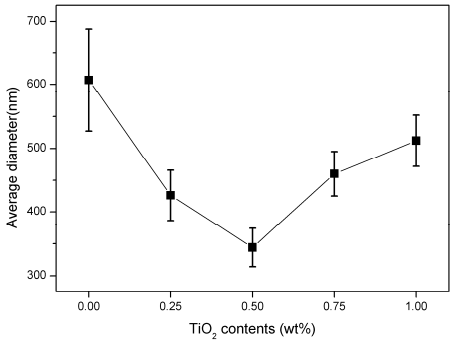

FIGURE 2. Average diameters of PVAc/TiO_2 nanofiber membranes with different TiO_2 contents.

RESULTS AND DISCUSSION

Fibrous Structure Analysis of PVAc and PVAc/Tio_2 Nanofiber Membranes

Figure 1 shows the SEM images of the nanofibers electrospun from PVAc and PVAc/TiO_2 solutions. *Figure 1* presents the PVAc and PVAc/TiO_2 fibrous structure formed. They are randomly distributed and formed a porous membrane with a wide pore diameter distribution. The average fiber diameter of the resultant fibrous membranes is shown in *Figure 2*. It can be seen from *Figure 2* that the diameters of electrospun PVAc and PVAc/TiO_2 nanofiber are significantly affected by the amount of TiO_2 added. At first, the average diameter of the PVAc/TiO_2 nanofiber decreases when the TiO_2 content increases in the polymer. This is caused by the TiO_2 sol which contains ethanol solvent which reduced the concentration of PVAc/TiO_2 sol system. Over 0.5%, the average diameter increased. This phenomenon is caused by the combined actions of molecular interactions between PVAc and TiO_2 sol molecules in preparation process.

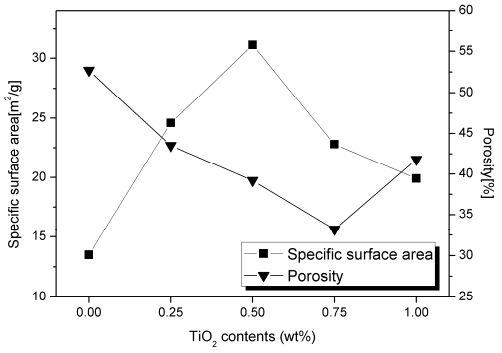

FIGURE 3. Specific surface area and porosity of PVAc/TiO_2 nanofiber membranes with different TiO_2 contents.

Different fiber diameter distributions and fiber tightness leads to the variation of membrane structures such as specific surface area and pore size distribution. The BET specific surface areas of the nanofiber membranes are summarized in *Figure 3*. It can be seen from *Figure 3* that BET specific surface area has an adverse tendency with average diameter in *Figure 2*. The specific surface area changed from 13.5 to 31.1 and to 19.9m^2/g as the diameter variety changed from 607 to 344 and to 512 nm. A shifting trend in the porosity of the PVAc/TiO_2 membrane is also revealed in *Figure 3* and the results indicate that the porosity doesn't show a monotone decrease, when the TiO_2 content come to 0.75wt%, the nanofiber membrane has lowest porosity.

Wettability Analysis of PVAc and PVAc/TiO_2 Nanofiber Membrane

Figure 4 reveals the effect of TiO_2 content on the contact angle of these nanofibrous membranes. It can be seen that the contact angle of these membranes is sharply replaced when TiO_2 content increases, from 109 to 36. Larger specific surface area and higher porosity promotes obtaining better wettability, but this tendency is completely misfit with the variation of specific surface area and porosity's in *Figure 3*. So it can be concluded that surface microstructure variation is not the main influence factor to lead to the wettability of PVAc nanofiber membrane modification. Except the surface microstructure, surface roughness and surface chemistry also play important roles in governing the wettability of nanofiber surface normally.

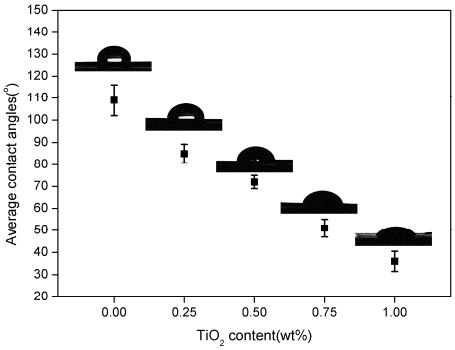

FIGURE 4. Static contact angle of water droplet placed on surfaces of the nanofibrous membranes with different TiO_2 content.

Roughness of Single PVAc and PVAc/TiO_2 Nanofiber

It is well known that the surface roughness is one of the key parameter to influence the surface wettability. The AFM 3D images and the cross section profiles

along the single nanofiber's length direction of single PVAc and PVAc/TiO_2 nanofibers are presented in *Figure 5*. The AFM image in *Figure 5a* shows the PVAc nanofiber has a relatively smooth surface and the cross section curve is mild. Compared to *Figure 5a*, the PVAc/TiO_2 hybrid nanofiber in *Figure 5b* is observed a rough surface with irregularity concave-convex structure along the direction of length.

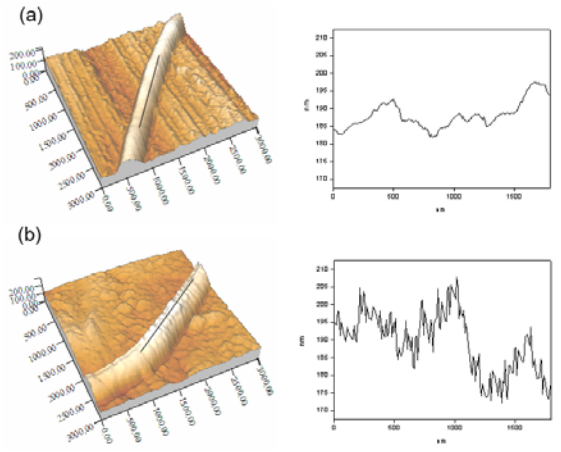

FIGURE 5. AFM images and the cross section profiles along the marked directions (a) PVAc and (b) PVAc/TiO_2 nanofiber.

Surface Chemistry Analysis of PVAc/Tio_2 Nanofiber

The TEM images of PVAc/TiO_2 hybrid nanofibers are presented in *Figure 6*. From this figure it can be found that some black steaks with various lengths distributed in the nanofibers, which maybe the mixture of TiO_2 and other hydrolysis products. It can also be observed from *Figure 6* that not all of the inorganic parts dispersed in the nanofibers, some of them extended on the surface. From AFM and TEM analysis, it can be regarded that the irregularity concave-convex structures on hybrid nanofiber surface are attributed to the inorganic products dispersed in the surface and inner of nanofibers. EDX scans were used to verify the surface compositions of PVAc/TiO_2 nanofibers. As it is shown in *Figure 7*, the EDX elemental analysis reveals that beside H, the hybrid nanofibers are composed of C, O and Ti elements. The Ti element has three energy levels (Ti-L, Ti-Kα, and Ti-Kβ). Eq. (1-3), we see that a large amount of TiOH is generated in the hydrolysis process, so the increase of TiO_2 sol content leads to an increase of hydrophilic group (–OH). Now it can be concluded that the increase of surface hydrophilic groups is the main influencing factor to give rise to the monotonous decrease of water contact angle value.

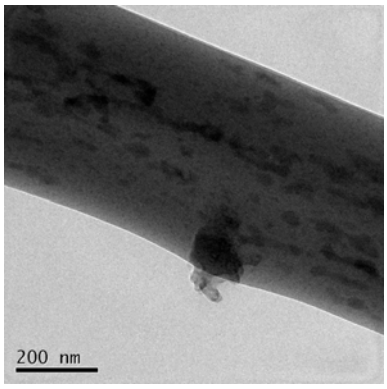

FIGURE 6. TEM images of PVAc/TiO_2 nanofibers.

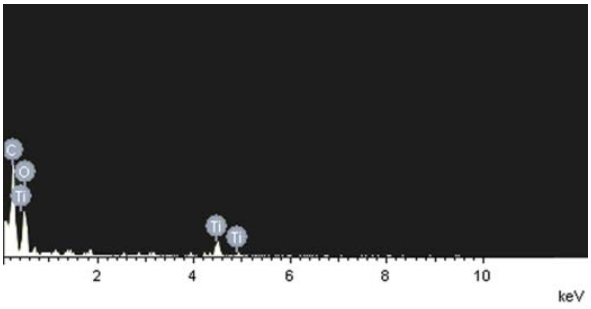

FIGURE 7. EDX spectra of PVAc/TiO_2 nanofibers.

CONCLUSION

This study explored the effects of fibrous structure, surface roughness and surface chemistry of nanofiber on the wettability of the electrospun PVAc/TiO_2 hybrid nanofiber membranes. The fibrous structure analysis revealed that the average diameters, specific surface area and porosity were largely changed with the variation of TiO_2 content. The static contact angle test indicated that the change of fibrous structure was not mainly influence the tendency of wettability properties of PVAc/TiO_2 hybrid nanofiber membranes. AFM, TEM and EDX analysis indirect indicated the increasing amount of hydrophilic group (-OH) existed on the surface of PVAc/TiO_2 nanofiber as the increase of TiO_2 content. It is concluded that the superhydrophilic PVAc/TiO_2 nanofiber membranes was ascribed to the combined effects of the high surface roughness of the hybrid nanofiber membrane and the hydrophilic group modification. It is likely that other polymer nanofiber membrane materials may be similarly modified by composited with partial hydrolytic inorganic oxide sol.

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REFERENCES
[1] Huang Z., Zhang Y., Kotakic, *Compos. Sci. Technol.*2003, 63, 2223 – 2253.
[2] Dzenis Y., *Science* 2004, 304, 1917-1919.
[3] Kim S., Kim H,; *Thermochim. Acta* 2006,444, 134–140.
[4] Vassiliou V., Barboutis I., Karastergiou S., *J. Appl. Polym. Sci.* 2007, 103, 1664 – 1669.
[5] Kim S., Kim H., *Macromol. Mater. Eng.* 2007, 292, 339–346.
[6] Park J., Lee H., Bea G., *J. Ind. Eng.Chem.* 2008, 14, 707-713.
[7] Xia X., Zhang Y., Wei Q., *J.Tianjin Poly. Univer.* 2011, 30, 8-10.
[8] Wu Y., Xu X., Wu G., Lu J., *Des. Mono. & Polym.* 2003, 6, 23-29
[9] Chronakis I., J. *Mater. Process. Technol.* 2005,167, 283-293.
[10] Sanchez C., Ribot F., *New J. Chem.* 1994, 18, 1007-1047.
[11] Yang Y., Wang P., *Polymer,* 2006, 47, 2683–2688.
[12] Sengupta R., Bandyopadhyay A., Sabharwal S., *Polymer,* 2005, 46, 3343–3354.
[13] Pomogailo A., *Colloid J.*, 2005, 67,658–677.

AUTHORS' ADDRESSES
Ning Wu, PhD
YingSun
Yanan Jiao
Li Chen
Institute of Textile Composite Key Laboratory of Advanced Textile Composite Materials
Ministry of Education
Tianjin Polytechnic University
CHINA