ENHANCED HYDROPHOBICITY OF ELECTROSPUN POLYVINYLIDENE FLUORIDE-CO-HEXAFLUOROPROPYLENE MEMBRANES BY INTRODUCING MODIFIED NANOSILICA

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Abstract

Electrospun nanofiber membranes consisting of Polyvinylidene fluoride-co-hexafluoropropylene blended with nanosilica nanocomposites were successfully prepared using electrospinning technique in this paper. The neat PdH, PdH-nanosilica, and PdH-modified nanosilica nanocomposite membranes were characterized by water contact angle, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM), respectively. Results showed that the addition of nanosilica increase the hydrophobicity of the membranes. Blended with 5 wt% modified nanosilica, the water contact angle of membrane could reach up to a maximum value (136°). Membrane morphological analysis presented that the resultant membrane had the thinnest diameter and roughness surface, which confirmed the enhancement of hydrophobicity of the membrane.

Introduction

Nanotechnology and nanoscience have been a highly novel area in the recent decades and constitutes two major branches: one is the synthesis of different materials with diverse morphologies, and the other is the construction/assembly of these as-synthesized nanostructures [1,2]. Construction of the synthesized nanostructures is necessary with the increasing requirements in energy, material and biomedical fields and the resulting assemblies generally show innovative or better performance. It has been demonstrated that selfassembly technique is the most effective way, in which the constituent components are spontaneously connected and integrated through direct interactions (e.g., van der Waals interaction, electrostatic interaction, molecular surface forces) or indirectly using template or external fields (e.g., carbon nanotubes (CNTs), magnetic, electronic, flow field, and liquid interfaces). [3]

Electrospinning is a efficient, convenient, and low-cost technique for fabricating extremely long polymer fibers with diameters ranging from 2 nanometers to several micrometers, utilizing electrical forces [4,5].

Electrospun films consisting of a continuous, nonwoven web of nanofibers usually have complex porous structure, high specific surface area, unique physical and mechanical properties. Specifications of the electrospun fiber, such as fiber size, porosity, and morphology, can be controlled by process parameters, such as deposition time, applied voltage, and nozzle-to-collector distance, and by material properties such as polymer concentration and solvent evaporation rate, etc. So far, electrospinning has been used to fabricate a huge range of nanofibers, such as polymers, metals, ceramics and composites. Electrospinning technology is not only a processing technique, but also can be used as a simple and effective method for the self-assembly of polymer and nanoparticles together in preparation of functional nanofiber material. A recent review article [6] thoroughly summarized the electrospinning fabrication of functional fibers from polymeric materials with various nanoparticles. It correlated the fabrication and applications of nanoparticles-electrospun fiber composites and give an overview on this emerging field combining nanoparticles and electrospinning. Using composite materials made from the combination of nanosized inorganic and organic materials can provide advantages over the use of a single organic or inorganic material. The incorporation of a small amount of inorganic nanoparticles, such as titania and zinc oxide, can improve the wetting, mechanical, thermal, optical, antimicrobial, antifouling and catalytic properties of a polymer matrix [7].

The wetting behavior of a liquid on a solid surface is a very crucial aspect of surface properties, which plays important roles in industry, agriculture, and daily life [8]. Studies of non-wettable surfaces with a water contact angle (WCA) close to or higher than 150° and facile sliding of drops, also called superhydrophobic surfaces [9]. Electrospinning has been used to fabricate nanostructured surfaces with varying degrees of hydrophobicity and water adhesion, including various hydrophobic polymers [10,11] and inorganic silica [12,13] with or without subsequent chemical treatment. Besides hydrophobicity, the silica can be used to preparation high performance
polymer composite material. Where silica particles are introduced to epoxy resin for reducing the coefficients of thermal expansion (CTE), lowering shrinkage on curing and mechanical reinforcement. [14]

In this work, we investigate the effect of nanosilica and modified nanosilica on the hydrophobic property of polyvinylidene fluoride-co-hexafluoropropylene (PcH) fiber membrane, respectively. The resultant modified nanosilica/PcH fiber membrane had a roughness surface morphology caused by hydrophobic nanoparticles, and thus achieving a highest water contact angle (136°). The surface morphology, hydrophobicity and preparation methods were discussed in detail.

Experimental

Materials

Polyvinylidene fluoride-co-hexafluoropropylene (PcH, average Mw ~400000, average Mn ~130000, pellets) was purchased from Sigma-Aldrich Chemie GmbH. APTES (3-aminopropyltriethoxysilane) and N,N dimethylacetamide (DMAc, 99.5%) were provided by Shanghai Pure Biochemical Polytron Technologies Inc. Acetone (analytical grade, Scharlau) was supplied by Rich Joint Chemical. Nano silica (SiO$_2$, 99.5%, metals basis, 30nm) was obtained from Aladdin Industrial Corporation.

Modification of SiO$_2$

The surface modification of SiO$_2$ with APTES coupling agent was carried out in liquid phase. In a typical process, SiO$_2$ powder (5 g) was first dispersed well in 150mL of ethanol, added with 0.5 mL of silane coupling agent APTES. The mixture was stirred and kept at 50°C for 12 h, then the grafting reaction was realized. The obtained SiO$_2$-NH$_3$ particles were filtered from the mixture, washed with ethanol and deionized water five times, and dried under vacuum.

Preparation of electrosprun solutions

Three solutions were prepared for electrospinning: the first one was 16 wt% neat PcH solution, the last two contained 5 wt% of SiO$_2$ and SiO$_2$-NH$_3$ w.r.t. to the amount of PcH respectively. All PcH solutions was prepared by dissolving a certain amount of PcH pellets in DMAc/acetone (70/30 V/V) solvent solution by overnight stirring at room temperature. Before electrosprinig, the SiO$_2$/PcH and SiO$_2$-NH$_3$/PcH solutions were sonicated again for 2 h to disperse the silica. All solution had the same concentration of PcH.

Membrane fabrication by electrospinning

The electrospinning setup used in this study consisted of a 10-mL syringe, a syringe pump to control flow rates, a stainless needle with a flat tip (inner diameter of 0.60 mm) used as a spinneret, a high voltage DC power supply (0-50KV) and an aluminum sheet as a flat receiver. The distance between the nozzle tip and the outer surface of the collector was fixed at 18 cm. The emitted electrode of positive polarity was attached to the needle and ground attached on the flat receiver. The flow rate was maintained at 0.6 ml/h and the collection time was fixed at 1 h. After electrosprinning, the nanofiber membranes deposited on the aluminum foil were peeled off from the collector and dried in an oven at 60°C for 24 h to evaporate the residual solvents.

Characterization and measurements

The FT-IR spectra were recorded between 0 cm$^{-1}$ and 4000 cm$^{-1}$ on a Nicolet NEXUS 670 Fourier transform infrared spectrometer to characterize untreated silica and APTES-treated silica.

The morphological appearance of the electrospun fibers was observed with a Quanta FEG 250 field emission scanning electron microscopy. Specimens for scanning electron microscopy (SEM) observation were prepared by cutting an aluminum sheet covered with the electrospun materials and carefully affixed to copper stubs. Each specimen was gold-coated with a sputtering device before observation under SEM. The diameters of the electrospun fibers or beaded fibers were measured directly from selected SEM images with Image-Pro software. The reported diameter values for each of the samples were averaged from at least 50 measurements. For the beaded fibers, the fiber diameters were measured between beads.

The water contact angle (CA) of the samples was measured using a standard contact Angle measurement instrument (KRUSS, German) with an image processing software. A volume of 5µL of deionised (DI) water was dropped carefully on the membrane surface, wherein the drop is captured by a camera, and the imaging software estimates the CA directly. At least 5 measurements were taken for each membrane sample and the average value is reported in this paper.

Results and discussion

FT-IR spectra curves of nano silica

As the FT-IR spectra curves of Figure 1 shows, the main peaks of SiO$_2$ spectra curve at 467, 799, 1100,1640 and 3450 cm$^{-1}$ are designed as bending vibration of Si-O-H, stretching vibration of Si-OH, stretching vibration of Si-O-Si, bending vibration of O-H and stretching vibration of -OH, respectively. Several minor bands at around 2800 to

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3000 cm\(^{-1}\) were detected in the spectra of SiO\(_2\)-NH\(_2\), which were attributed to the C-H stretching vibration of the hydrocarbon chains of the grafting APTES. The spectra curve at 3400-3500 cm\(^{-1}\) was enhanced because of the bending vibration of N-H on the APTES-treated silica.

Figure 1. FT-IR spectra curves of pristine SiO\(_2\), SiO\(_2\)-NH\(_2\).

**Surface Morphology of PcH Nanofibers**

As shown in the Figure 2, all membranes showed randomly-oriented, ultrafine, and interconnected nonwoven fibers and pore structure. The neat PcH nanofibers (Fig 2. 1) show bead-free surface, with smooth and cylindrical nanofibers at an average fiber diameter of 271 nm. The SiO\(_2\)/PcH and SiO\(_2\)-NH\(_2\)/PcH nanofibers resulted to thinner fibers (258 nm and 216 nm, see Table 1), shows that the addition of nano silica can reduce the fiber diameter. The solution containing silica had more charges and consequently more elongation and thinner fibers. At the same time, beads were formed on the membrane when SiO\(_2\) and SiO\(_2\)-NH\(_2\) were added into the PcH solution. In general, the surface of a membrane can be modified by controlling process parameters such as the operating conditions and the precursor’s thermophysical properties. The process parameters determine the appearance or disappearance of bead-on-string or bead-free nanofibers. The electrical conductivity of the spinning precursor greatly affected the bead formation along the nanofibers. The concentration of PcH was not change weather the solution had the silica or not, and the electrospinning parameters were changeless. These beads could be due to the agglomeration of nano silica in the composite solution, as well as the change of the viscosity and the conductivity of the composite solutions.

In an electrospun membrane, beads are generally considered as demerits as they provide additional stress points that can affect the membrane's mechanical properties. However, the micro or nanobeads on the electrospun membrane can serve as additional roughness to the membrane surface that can enhance the membrane hydrophobicity, if properly designed [15]. The surface morphology of the nanofiber membrane shows large amounts of protrusions, and hills and valleys, providing microscale and nanoscale roughness that could possibly increase the hydrophobicity of the surface [16].

![Figure 2. Morphological images of electrospun fibers 1 PcH, 2 SiO\(_2\)/PcH, and 3 SiO\(_2\)-NH\(_2\)/PcH.](image)

Table 1. Statistical data of the diameter of electrospun fibers.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average diameter (nm)</th>
<th>SEM Images</th>
</tr>
</thead>
<tbody>
<tr>
<td>PcH</td>
<td>271±50</td>
<td>1</td>
</tr>
<tr>
<td>SiO(_2)/PcH</td>
<td>258±50</td>
<td>2</td>
</tr>
<tr>
<td>SiO(_2)-NH(_2)/PcH</td>
<td>216±50</td>
<td>3</td>
</tr>
</tbody>
</table>

The hydrophobicity (contact angle) of the fibers

The presence of beads has increased the surface roughness through microscopic inspection. Many studies have demonstrated that porous beaded fibers exhibit increased hydrophobicity due to increased surface roughness. Figure 3 shows the CA measurements of the

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different fabricated membranes in this study. The neat PcH fibers showed a CA of 119°. On the other hand, the SiO$_2$/PcH nanofiber had a CA of 124°, which is higher than the neat PcH fibers that is mainly attributed to the rougher surface structure of the overlapping layers of nanofibers. While the CA of the SiO$_2$-NH$_2$/PcH fibers was 136°.

It should be noted that the hydrophobicity of SiO$_2$-NH$_2$/PcH fibers was better than both of the neat PcH and SiO$_2$/PcH fibers. The formation of beads with nano silica in/on the surface increases the surface roughness at a nanoscale level, which affects the wettability of the surface and increases its hydrophobicity. Besides, the surface modification of SiO$_2$ with APTES coupling agent shows more significant effect on the hydrophobicity of the composite nanofibers.

Figure 3. Contact angle measurements of electrospun fibers

Conclusions

To study the effects of nano SiO$_2$ on the hydrophobic properties of PcH fiber membrane, the untreated SiO$_2$ and APTES-treated Silica were added into the PcH electrospun solution respectively. The contact angle (CA) of composite nanofibers was higher than that of a neat PcH membrane. The nano SiO$_2$ without modification increase the hydrophobicity of PcH fiber membrane slightly, while the APTES-treated Silica significantly increased the hydrophobicity of PcH fiber membranes. The incorporation of nano silica in/on the nanofibers could enhance the hydrophobicity of electrospun PcH membrane. The presence of SiO$_2$ in/on the nanofibers produced beads on the surface of the membrane, that is the nano silica provides microscale and nanoscale roughness. As the roughness of SiO$_2$/PcH and SiO$_2$-NH$_2$/PcH nanofiber membrane was equivalent, in comparison to producing the beads, the surface modification of SiO$_2$ with APTES coupling agent was a more effective way to increase the hydrophobicity.

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