

Preparation of a New Superhydrophobic Nanofiber Film by Electrospinning Polystyrene Mixed with Ester Modified Silicone Oil

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ABSTRACT: A new superhydrophobic nanofiber membrane with certain mechanical strength was prepared by electrospinning the polystyrene (PS) with ester modified silicone oil (EMSO). To increase the roughness and tensile strength, the EMSO with low energy as hydrophobic macromolecular substance was added into PS precursor solution. Then during the process of electrospinning, some of the ester modified silicone oil was distribution on the surface of substrate (PS) fiber films to generate double structure which led to the superhydrophobicity. We probed into the relationship between the surface wettability, morphologies, mechanical property, and the mass ratios of ester modified silicone oil /PS, and with the increasing of EMSO, the water CA value increased from $135 \pm 0.5^\circ$ to $152 \pm 0.2^\circ$ and the tensile strength grown from 0.23 MPa to 0.92 MPa. The film shows a network structure consisting of numerous randomly oriented fibers, the diameters of which changed from $0.5 \mu\text{m}$ to $2.0 \mu\text{m}$ belong to relatively big diameter fibers, which has great significance to the research of superhydrophobic membrane with big diameter fibers and also this method is easy, convenient and environment friendly. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40718.

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INTRODUCTION

Surfaces with water contact angles larger than 150° are typically considered to be superhydrophobic surfaces or super water-repellent surfaces.^{1,2} Such surfaces appear omnipresently in nature, such as insect legs,³ insect wings,⁴ and the leaf of many plants.^{5–7} So far, researchers have made great progress in the manufacture of superhydrophobic surfaces^{8,9} by imitating “lotus effect.” These surfaces have attracted considerable interest on account of their special properties such as self-cleaning and anticontamination, which have a wide application in daily life and industrial applications including self-cleaning coating for automobiles,¹⁰ nonviscous coating for power line and antennas¹¹ and so on.

In general, there are two thoughts to prepare superhydrophobic surfaces, one of which builds rough structure on the surface of low energy surface material, the other takes advantage of low surface energy to modify the materials that have fine structure themselves. On the basis of these two thoughts there are many different techniques that have been developed to produce superhydrophobic surfaces, for instance, phase separation,¹² sol-gel methods,¹³ electrochemical deposition,¹⁴ hydrothermal,¹⁵ self-assembly,¹⁶ solution-immersion,¹⁷ and etching and photolithography.¹⁸ Among these techniques, multistep processes, high

cost problem, especially the imitation in large-scale superhydrophobic surfaces production hampered the further application. The newly developed technology of electrospinning has been gaining increased interest in nanotechnologies with attractive feature of simplicity and inexpensive setup of required device.

Electrospinning as a simple and promising technique has been used to produce various polymer mats of polymer nanofibers as well as composite nanofibers since its first description in 1934.¹⁹ So far, the fabrication of fibrous films with high surface roughness and surface-to-volume ratio by electrospinning has been widely reported.^{20,21} Recently, composite materials with better properties than a single organic or inorganic material have received a lot of attention in material science.^{22,23} Because polystyrene (PS) is hydrophobic, dielectric, cheap, atmosphere-stable, and electrospinnable, this material can be modified by many different additives to create two-ductal structures, which has long been diffusely used to produce high water repellent electrospun membrane by electrospinning.^{24–26} A novel three-dimensional surface structure of PS mats with tunable wettability via incorporating titania nanoparticles between polystyrene nanofibers were reported by Lee et al.²⁴ Zhu et al.²⁵ mixed PS solution with polyaniline (PANI) to produce superhydrophobic conductive substrates exhibited static

water CA of 167° (0° on the flat surface) with very low roll-off angles (<5°) showing self-cleaning properties. Asmatulu et al.²⁶ presented a surfacephobic surface with a water CA reaching to 177.5° by electrospun PS blended with 8% concentration of TiO₂ nanoparticles. Among these papers, in order to construct two-dimensional structure of fibers on the surface morphology, most require a significant reduction in the concentration of the spinning solution to appear as fiber-bead structure, along with a reduction in the fiber diameter, poor mechanical strength, and easily broken; however, the superhydrophobic fiber mats with larger diameter and high mechanical strength are reported less.

In our work, a relatively large diameter nanofiber membrane with superhydrophobicity and certain mechanical strength was prepared succinctly through electrospinning the mixture solution of PS and ester modified silicone oil. The ester modified silicone oil was dispersed in PS precursor solution, during the process of electrospinning, a part of the ester modified silicone oil was decentralization on the surface of substrate (PS) to generate double roughness structure so that the modified PS has superhydrophobicity. We also have explored the relationship between superhydrophobicity and the mass ratios of ester modified silicone oil /PS, and also explored which affect the fibers membrane morphology, wettability, and mechanical strength.

MATERIALS AND METHODS

Materials

Trimethylolpropane allyl ether was purchased from Sigma-Aldrich. Octamethylcyclotetrasiloxane (D₄), hexamethyldisiloxane (HMDS), and polymethylhydrogensiloxane (PMHS, $M_w = 2000$), were all provided by CNPC Jilin Chemical Industry Co., Polystyrene ($M_w = 220,000$) was supplied by Beijing Yanshan Petrochemical Company. The octanoyl chloride and chloroplatinic acid hexahydrate was purchased from Aladdin. Dimethylformamide (DMF), toluene, triethylamine, dichloromethane, and isopropanol were all from Beijing Chemicals Co., China.

Characterization

The composition of 2-(allyloxymethyl)-2-ethylpropane-1, 3-diyl dioctanoate (AEDD) and ester modified silicone oil (EMSO) were confirmed by Fourier transform infrared (FTIR) spectra. KBr pellets were applied to the FTIR measurement. ¹H NMR spectra was recorded on AVANCEIII400 MHz NMR spectrometer using tetramethylsilane as internal standard and CDCl₃ as solvent. The images of electron surfaces and the corresponding element distributions on the surface were taken using a cold field-emission scanning electron microscope (SEM SU8000 Series). The contact angles measurements of the electrospun films were carried with a drop shape analysis system (Krüss DSA100) in the sessile mode at ambient temperature. Stress-strain analysis was carried out at room temperature in a material testing station (Instron5869) using standard procedures (ASTM standard 882 for thin films and membranes). Several specimens with lengths of 20 mm and widths of 10 mm were prepared for each tensile test.

Synthesis of 2-(allyloxymethyl)-2-ethylpropane-1, 3-diyl dioctanoate (AEDD)

We used acyl chloride method to synthesize AEDD. The process was following, 17.4 g (0.1 mol) trimethylolpropane allyl ether diluted with dichloromethane and 35 mL (0.24 mol) triethylamine as acid binding agent were added to a 250 mL three-path round-bottomed flask with a dry pipe. The reaction was stirred at -5°C-0°C for 6 h, after 41 mL (0.24 mol) octanoyl chloride was added dropwise, under magnetic stirring, to the flask, which was placed in an ice-water bath. The AEDD compound was separated by filtering triethylamine hydrochloride, washed with water for three times, dried over anhydrous Mg₂SO₄, and then the solvent was distilled off to obtain a yellow oily liquid.

Synthesis of Ester Modified Silicone Oil (EMSO)

The EMSO was preparation by hydrosilylation. Ester (AEDD), obtained in the previous step experiment dissolved with a quantity of toluene was added to a three-path round-bottomed flask, and then a certain amount of the catalyst was added. The system was warmed to 40°C, stirred for 30 min and then under N₂ environment, low-hydro silicone oil (SH copolymer) diluted with toluene was added dropwise. The Si-H bond and C=C bond were placed into the reaction vessel at the mole ratio of 1 : 1.05. The reaction system was heated to reflux for 6 h, and after completion of the reaction, activated carbon decoloration. Then distilling off the solvent (such as toluene and the low-boiling substances) to obtain a pale yellow transparent shiny silicone oil.

Preparation of PS Precursor Solution

First, PS precursor solutions with the concentration of 20 wt % were prepared by dissolving set number of PS in DMF. The PS solutions were stirred for 12 h at ambient temperature to attain sufficient viscosity required for the further experiments. Then several groups of precursor solutions that have different mass ratios of EMSO/PS (0.05 : 1, 0.15 : 1, 0.25 : 1, 0.35 : 1, 0.45 : 1, and 0.60 : 1) were manufactured, respectively. At room temperature, the precursor solutions were stirred so strongly for 12 h that EMSO was dispersed equably in PS solutions used for electrospinning.

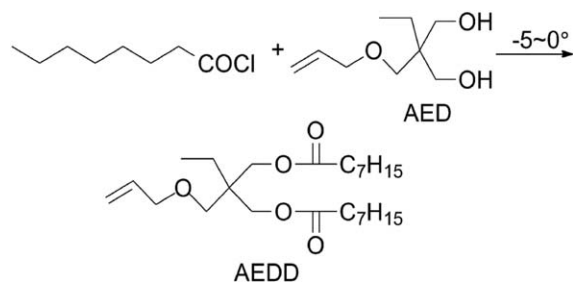
Superhydrophobic Membrane Preparation by Electrospinning

The basic electrospinning set-up consists of three main components: a high-voltage power supply, a feeding system, and a grounded collector. The needle of electrospinning was attached to a high-voltage supply that can provide direct voltages up to 50 kV. A 14 kV direct voltage was putted into used across a settled collection distance of 12 cm between the collector and the tip of the needle. A syringe pump was used to control the feed rate of the precursor solution. During electrospinning, the applied electrical field was strong enough to overcome the surface tension of the polymeric solution, then ejected a continuous jet by which nanofibers are produced on the collector surface with subsequent solvent evaporation and bending.

RESULTS AND DISCUSSION

Synthesis and Characterization of 2-(allyloxymethyl)-2-ethylpropane-1, 3-diyl dioctanoate (AEDD)

The 2-(allyloxymethyl)-2-ethylpropane-1, 3-diyl dioctanoate (AEDD) was synthesized by using trimethylolpropane allyl ether (AED) and octanoyl chloride as the initial materials, which is



Scheme 1. Reaction to produce (AEDD).

showed in Scheme 1. In order to confirm the chemical composition of AEDD, two techniques of the FTIR and ^1H NMR has been used. The infrared figures of AEDD and AED are shown in Figure 1(a,b) respectively. Compared with Figure 1(b), the peak of $3200\text{--}3500\text{ cm}^{-1}$ belong to hydroxide radical disappears in the Figure 1(a), at the same time, the peaks of 1743 cm^{-1} and 727 cm^{-1} correspond to stretching vibration of $\text{C}=\text{O}$ and stretching vibration of more than four CH_2 appear, which indicate esterification reaction had been occurred. It is also proved by asymmetric and symmetric stretching vibration absorption peaks of $\text{C}-\text{O}-\text{C}$ of ester group at 1110 cm^{-1} and 1170 cm^{-1} . From the ^1H NMR spectrum of AEDD in Figure 2, we can see that characteristic peak for CH_2 (NO.4 of ester) at 3.29 ppm is singlet due to no adjacent hydrogen proton so we chose it as the standard to compute the integral area of the rest of hydrogen. It also shows the complete disappearance of $-\text{OH}$ resonance at 4.78 ppm and associated with the peaks at ($\delta = 2.31, 1.27, 1.23,$ and 0.89) ppm which are the peaks of CH_2 and CH_3 resonance absorption (NO.5, 6, 7, and 8) separately were produced. In addition, the integral areas of different chemical shift hydrogen are almost in conformity with the structural formula of AEDD. Through the analysis of FTIR and ^1H NMR spectrum of the AEDD, we can confirm this esterification reaction was successful.

Synthesis and Characterization of EMSO

The EMSO which contains ester groups on the side-chain was synthesized from the hydrosilylation reaction of poly (methyl-

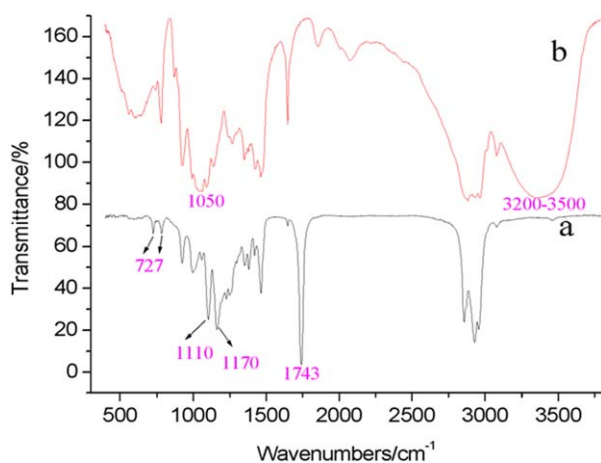


Figure 1. FTIR spectrum of AEDD (a) and EMSO (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

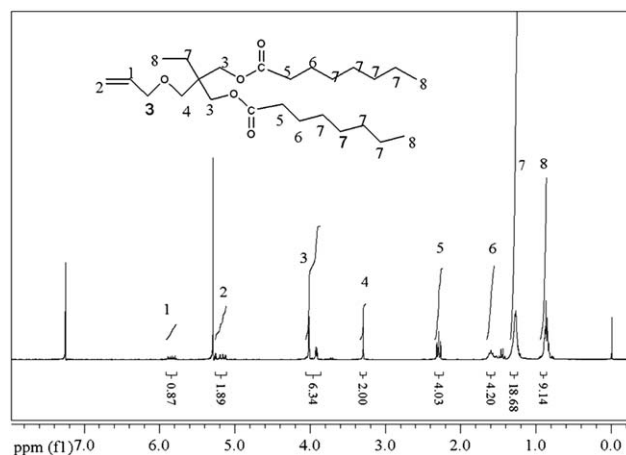


Figure 2. ^1H NMR spectrum of AEDD.

drosiloxane) copolymer (SH) and 2-(allyloxymethyl)-2-ethylpropane-1, 3-diyl dioctanoate is showed in Scheme 2. The SH copolymer was obtained by the acid-catalyzed equilibration of D_4 and PMHS with hexamethyldisiloxane as an end-capper [eq. (1)]. The SH copolymer was then hydrosilylated with AEDD in presence of a Pt-catalyst to gain the ester-siloxane copolymer [eq. (2)]. The FTIR spectrum of SE copolymer and SH copolymer (Figure 3(a,b)) shows the peaks of $2156, 915$ and 1645 cm^{-1} correspond to characteristic absorption of $\text{Si}-\text{H}$, bending vibration of $\text{Si}-\text{H}$ and stretching vibration of $\text{C}=\text{C}$ respectively practically vanish in Figure 3(a) accompany with stretching vibration of $\text{C}=\text{O}$ and CH_2 generating at 1743 cm^{-1} and 2856 cm^{-1} . The ^1H NMR spectrum of SE copolymer is showed in Figure 4. It illustrates characteristic peak of $\text{Si}-\text{Me}$ at 0.07 ppm which is spit into two peaks ($\delta = 1.22$ and $\delta = 1.57$) due to the adjacent $\text{Si}-\text{Me}$ atom. It also shows the disappearance of the $\text{Si}-\text{H}$ resonance ($\delta = 4.7\text{ ppm}$) and the concomitant disappearance of the vinyl group of AEDD ($\delta = 5.2$ and 5.8 ppm). In addition, the peaks ($\delta = 1.6\text{ ppm}$) are the resonance peaks of $-\text{Si}-\text{CH}_2-\text{C}-$ group and $\beta\text{-CH}_2$ of ester group, whereas those

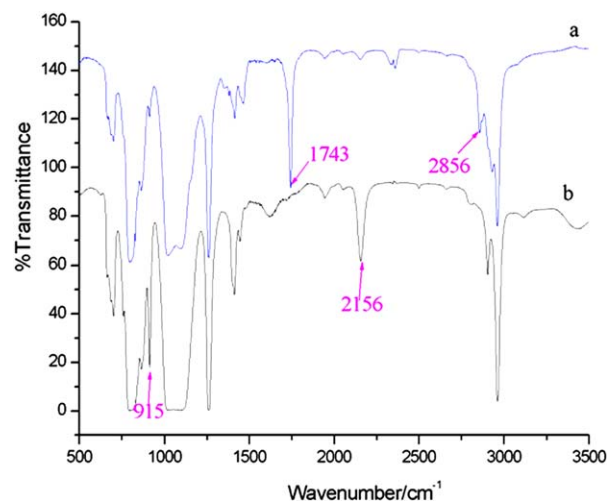
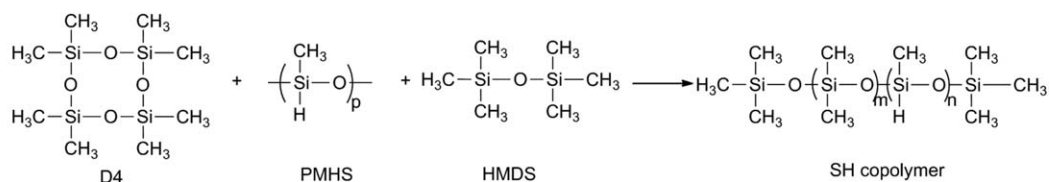
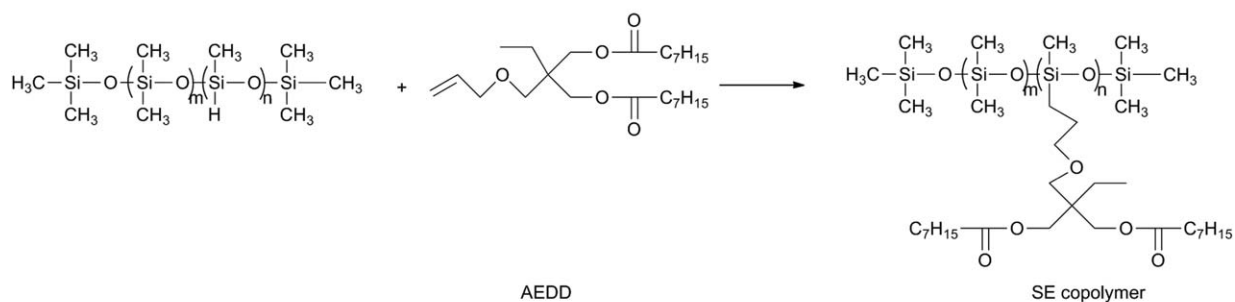


Figure 3. FTIR spectrum of SE copolymer (a) and SH copolymer (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Equation 1



Equation 2

Scheme 2. Reaction to produce SH copolymer [eq. (1)] and reaction to produce copolymer. [eq. (2)].

($\delta = 2.38$ ppm) represent the resonance peaks of α -CH₂ of ester group the epoxide group and also the peaks of —CH₂—O—CH₂— are at $\delta = 3.1$ and 4.0 ppm. These results sufficiently demonstrate that the AEDD has been successfully bonded to the Si—H of SH copolymer.

Morphologies of PS Fibers Membrane

From the SEM image of a 20 wt % PS/DMF solution in this work which is displayed in Figure 5(a), we can see that the film has a network structure consisting of numerous, randomly oriented heterogeneous nanofibers and microfibers, and a small number of diamond beads. The magnification SEM picture shows that most of the fiber surface is smooth apart from covering with a handful of micropapillanes. In this article, estimating the average diameter (D) of nanofibers is taken advantage of the following equation:

$$D = \frac{1}{n} \sum_{i=1}^n X_i^* \frac{B}{L} \quad (3)$$

where n refers to the quantity of the nanofibers in SEM pictures, X is the diameter of every nanofiber, B delegates the scale bar, and L represents the length of the scale bar.²⁷ Consequently, the average diameter of polystyrene (PS) fibers is about 1.09 μm . The water contact angle of this electrospun membrane reaches to $135 \pm 0.5^\circ$ [Figure 5(b)], demonstrating that PS surface is hydrophobic. However, the contact angle is far below the 150° threshold required for superhydrophobic materials so that this membrane surface could not supposed to have superhydrophobicity.

Morphologies of Modified PS Nanofibers Membrane

A series of composite films comprising of EMSO and PS were prepared, and the mass ratios of EMSO /PS varied from 0.05 : 1 to 0.6 : 1. To discover the influence of the surface of the film wetting properties, we made use of some SEM images and water

CA pictures (Figure 6) to represent the film morphologies and wettability with disparate mass ratios of EMSO/PS. From these images, it can be seen that these electrostatic spinning films still have a type network structure, at the same time the diamond beads disappear with the incorporation of EMSO. The diameters of these fibers are not uniform, which change from 0.5 μm to 2.0 μm of the range, and the average diameter reckoned by eq. (3) is 1.0 μm . The magnification SEM pictures indicate some of the synthetic EMSO was dispersed on the surface of fibers then successfully play an important function of creating a two-level surface roughness on the membrane surface.

Figure 7 shows the distribution of EMSO, which is represented by silicon elemental along the nanofibers direction and on the fiber cross-section. It is obvious that the area of red dots of the image of EDX perfectly overlap the area of fibers of the SEM, which demonstrates the EMSO is distributed uniformly in or on the PS fibers.

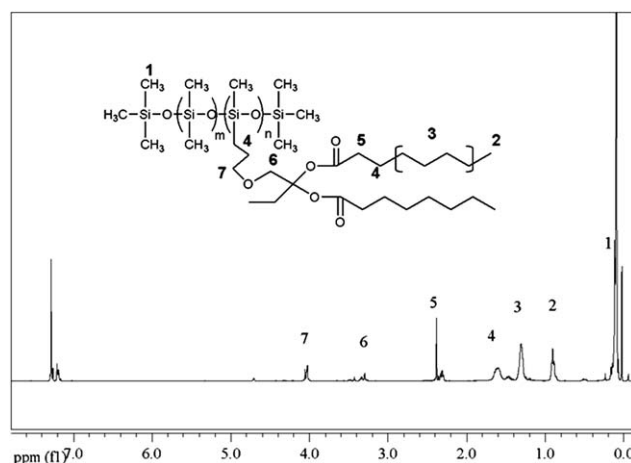


Figure 4. ¹H NMR spectrum of SE copolymer.

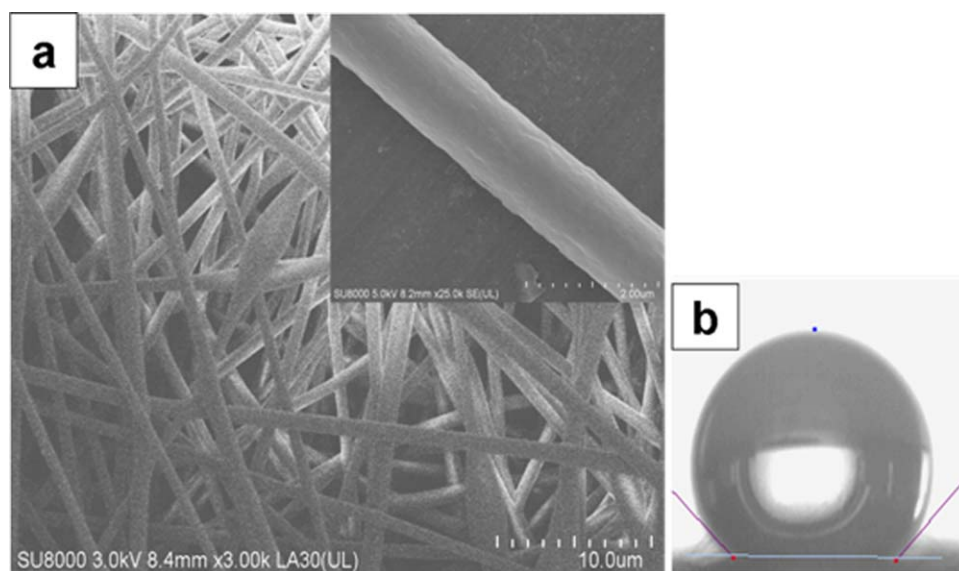


Figure 5. (a) SEM image of electrospun film prepared from 20 wt % PS/DMF solution. (b) Behavior of a water droplet on its surface. $CA = 135^\circ \pm 0.5^\circ$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

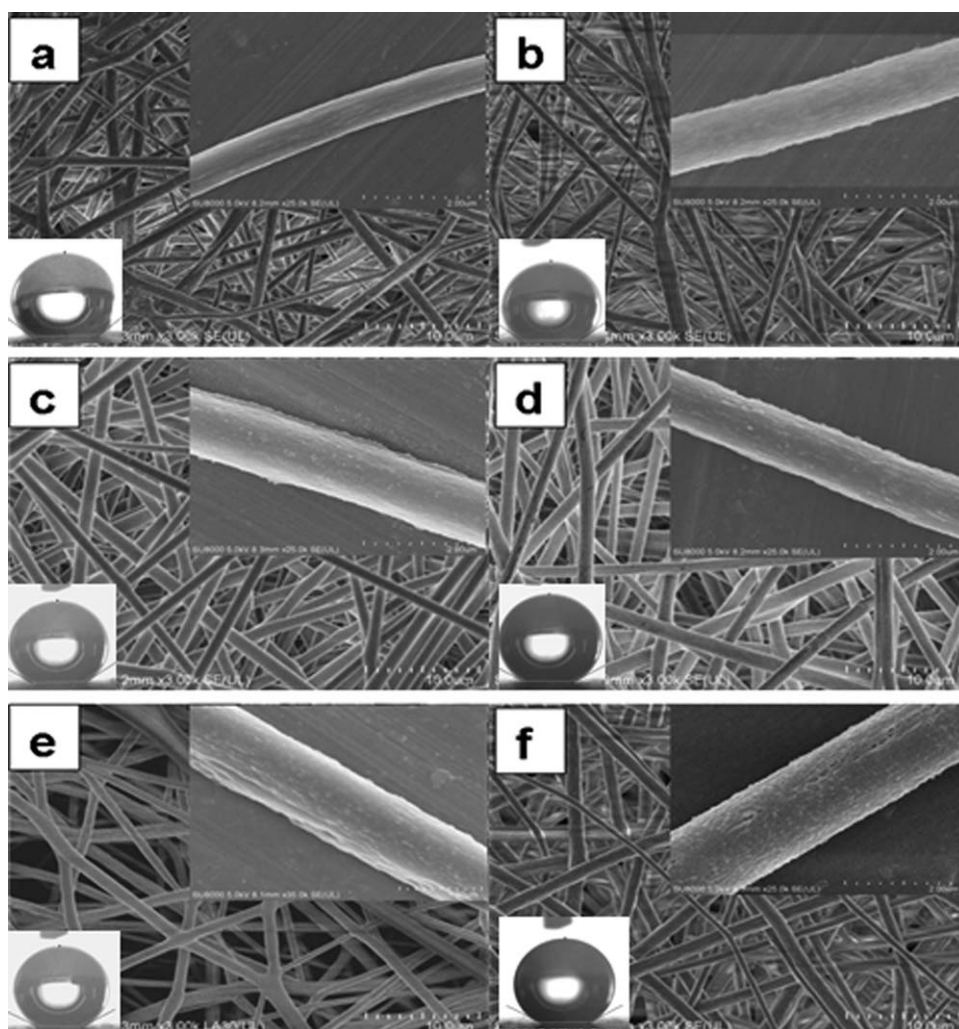


Figure 6. SEM images and water CA of electrospun composite films comprised of different weight ratios of EMSO/PS: (a) 0.05 : 1, (b) 0.15 : 1, (c) 0.25 : 1, (d) 0.35 : 1, (e) 0.45 : 1, (f) 0.6 : 1.

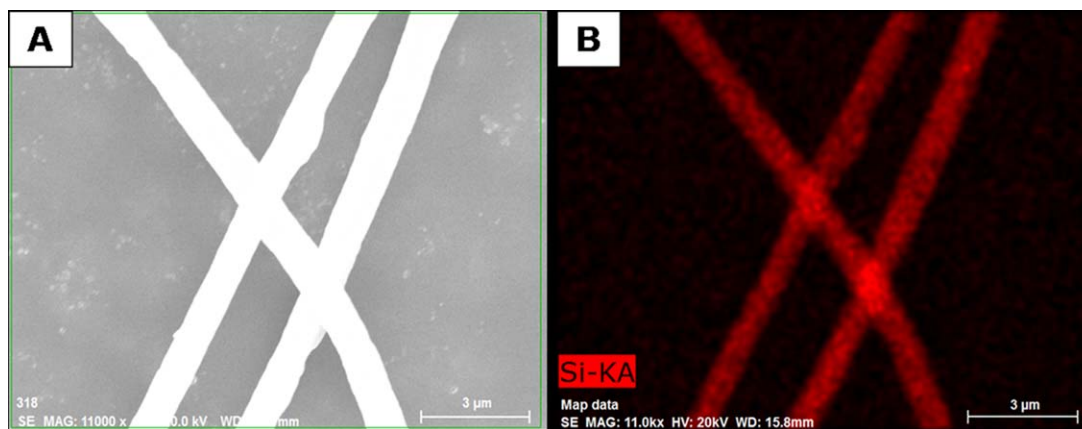


Figure 7. SEM image of the EMSO modified PS fibers surface (A) and silicone elemental distribution by EDX (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Stress–Strain Curves of Modified PS Nanofiber Membrane

The tensile stress–strain curve that stands for the mechanical property of electrospun mats prepared from PS and EMSO is shown in Figure 8. As can be seen from Figure 8, with the amount of EMSO increasing in the prepared mats, the mats demonstrate an enhanced tensile strength with high elongation. This behavior may be attributed to the EMSO can enter into the gaps of PS fibers that generated during the electrospinning, due to the unique characteristics of EMSO, exhibits a good lubricity, liquidity, and softness characteristic. When the weight ratios of EMSO (EMSO)/polystyrene (PS) varied from 0.00 : 1 to 0.60 : 1, the tensile strength of composite films have grown from 0.23 MPa to 0.92 MPa, which indicated that the presence of EMSO contributed to an obvious reinforcement of PS composite mats.

Wettability of Modified PS Nanofibers Membrane

Wettability is one of the significant properties of a solid surface, and the contact angle (CA) of a water droplet on the surface is a direct description of the wettability of a solid.²⁸ There are two factors that decide the wettability of a solid surface, its chemical

composition and the topographic structure of the surface, respectively.²⁹ The PS is chemically hydrophobic on account of its relatively low surface energy, and the static CA on this smooth polystyrene (PS) surface is 95°. ³⁰ Up to now, many authors used electrospinning in order to increase the roughness of polystyrene substrates, constantly producing two-level micro/nanostructures, and also some papers^{31,32} have researched the effect of electrospinning parameters to the surface roughness and hydrophobicity of the producing mats.

Along with the augment weight ratio of EMSO, it can be found that the CA values of modified PS membranes tend to rise as shown in Figure 9. It shows that the more EMSO there is, the more easily the surface will not be wetted. When the mass ratio is reduced to 0.15 : 1, the water CA value of modified PS membranes is $143 \pm 0.3^\circ$ smaller than 150° , which is the critical contact angle of superhydrophobic surface. When the mass ratios of EMSO/PS reaches 0.6 : 1, the static water CA value can be achieved $152 \pm 0.2^\circ$, That is due to EMSO distribution on the surface of substrate (PS), fiber increases the roughness of fibers' surface which lead to the superhydrophobicity. However, when

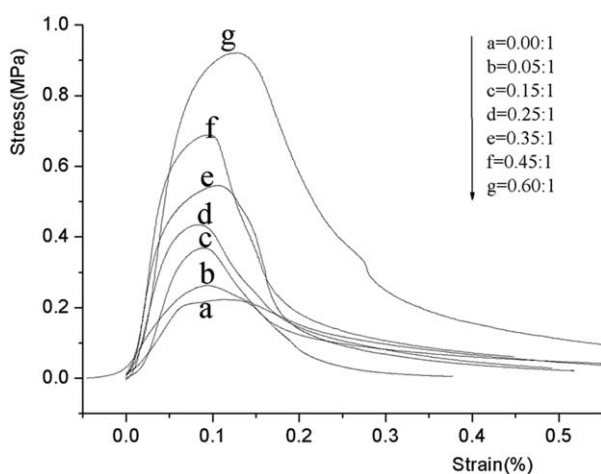


Figure 8. Stress–strain curves of composite electrospun mats composed of various weight ratios of EMSO/PS.

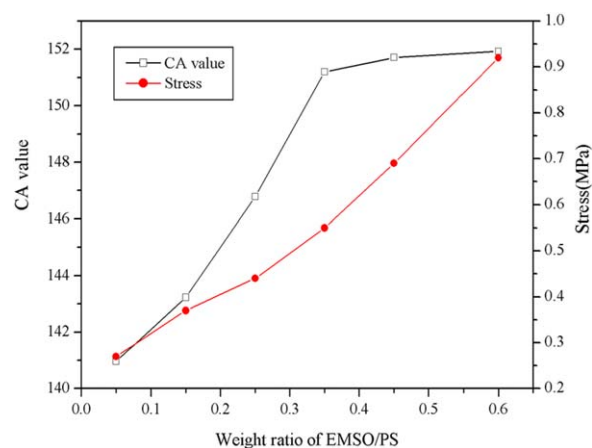


Figure 9. Variation of CA value of composite films based on different weight ratios of EMSO/PS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the mass ratio is larger than 0.45 : 1, the increase of the water CA becomes slow sharply because of the disadvantage of this morphology film on which there is so much ester modified silicone oil that PS microsized fibers surface are nearly covered entirely by ester modified silicone oil. This leads to the system of dual-scale structure destroyed and less air trapped in the pocket on the surface. In addition, we dropped a drop of water on the modified PS fibers membrane and raised a certain angle, it was found that the water drop was hardly to roll on the surface freely. This is a kind of super-hydrophobic material with a certain viscous force, about which there are many literatures reported.^{33,34}

It is well known that the roughness has a great impact on the wettability of a solid surface. There are two models to suppose the wetting on the roughness surfaces, namely Wenzel (homogeneous) wetting,³⁵ where the liquid can completely infiltrate the roughness grooves, and Cassie–Baxter (composite) wetting,³⁶ where the liquid cannot be able to replace the air in the roughness grooves. The second model usually accounts for the observed wetting behavior and the transition between these models³⁷ has an important role in superhydrophobicity. Cassie and Baxter raised an equation to describe the relation between the contact angles of a water droplet on a smooth surface (θ_2) and a rough surface (θ_1) consisted of air and a solid [eq. (4)].

$$\cos \theta_1 = f_1 \cos \theta_2 - f_2 \quad (4)$$

where f_1 and f_2 are the fractions of solid surface and air in touch with liquid, and $f_1 + f_2 = 1$. The θ_2 of the smooth PS membrane surface is 95° , and the θ_1 of roughness PS membrane surface is 152° from Figure 9, then the numerical values of f_1 and f_2 are about 0.129 and 0.871, respectively, which imply that only 13% of this PS membrane surface is in direct contact with water, at the same time approximately 87% is coverage with air. The entrapment air stopped the water droplet from permeating the surface, which made the drops of water suspended on the surface and brought about that the nanofiber membrane surface had superhydrophobicity.

CONCLUSIONS

A novel superhydrophobic PS nanofibers film was successfully prepared by electrospinning the mixed solution consisting of the ester modified silicone oil and PS precursor solution, and were characterized by SEM, CA, and EDX. During electrospinning, the ester modified silicone oil was uniformly distributed in or on the fibers resulting in a dual-scale micro/nano structure that caused a superhydrophobic phenomenon on the membrane surface. With the increasing of the mass ratios of ester modified silicone oil/PS, the CA value reaches to $152 \pm 0.2^\circ$ at the mass ratio is 0.6 : 1 and also the electrospinning membranes have relatively large diameters with no beads, the more the fibers have a certain mechanical strength, which has great significance to the research of big diameter fibers superhydrophobic surface and also this method is easy, convenient, and environment friendly.

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