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Water-permeable polylactide blend membranes for hydrophilicity-based separation

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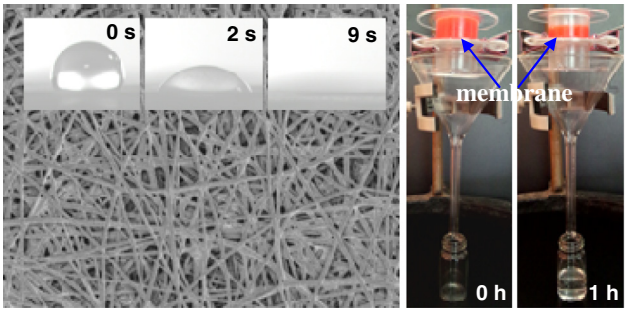
HIGHLIGHTS

- Polymer membranes are good candidates for separation of oil/water emulsion.
- Removal of oils from the emulsion was realized by superhydrophobic membranes.
- Water-permeable PLA blend membranes are produced by electrospinning.
- The blend membranes exhibit superior removal of water from the emulsion.

GRAPHICAL ABSTRACT



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ABSTRACT

Polymer membranes produced by electrospinning have great potentials in the separation of oil/water emulsion under gravity. Removal of oils from the emulsion has been realized by superhydrophobic membranes due to selective penetration of oils. In this study, we demonstrate that blend electrospinning of polylactide (PLA) with a biodegradable and biocompatible polyester (P34HB) produces membranes with complete water permeability. In contrast, PLA membranes are highly hydrophobic and cannot be penetrated by water. The water permeability is correlated with more hydrophilicity of P34HB than PLA and especially with structural porosity of the membranes. The water-permeable membranes exhibit superior removal of water from the emulsion under gravity, exactly opposite to the situation encountered by superhydrophobic membranes.

1. Introduction

Polymer membranes produced by electrospinning consist of numerous pores among intertwined nanofibers. This peculiar texture makes electrospun membranes have great potentials in the application as separation materials [1–7]. As compared to porous membranes prepared by phase inversion methods [8–10], electrospun membranes have outstanding characteristics, e.g. extremely high flux and very low operation pressure. What is more, separation of liquids by electrospun membranes can be carried out under gravity without external driving force [11,12], which is a convenient and energy-saving process.

To date, two types of separation have been realized by electrospun membranes. The first is based on size exclusion, determined by pore size of electrospun membranes and the size of separated substances [13,14]. That is, electrospun membranes can only retain and separate substances with size larger than their pore size. Due to relatively large pore size, electrospun membranes are mostly used for separation of substances with submicron and micron size. The second is related to surface wettability of electrospun membranes towards liquids, which is widely applied in the separation

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of oil/water emulsion. For instance, superhydrophobic membranes can repel water but allow penetration of oils, resulting in removal of oils from the emulsion [11]. However, superhydrophobic membranes are easily adhered and fouled by oils, deteriorating the separation efficiency. This dilemma could be solved by penetration of water but repellence of oils. As demonstrated in the previous studies [15,16], superhydrophilic membranes after hydration meet this requirement; and water can be effectively removed from oil/water emulsion.

Polylactide (PLA), a biodegradable and biocompatible material, has attracted much attention in many applications. Due to high surface area electrospun membranes from PLA are mainly used as the scaffolds for drug delivery and tissue engineering [17]. Electrospun PLA membranes are highly hydrophobic [18], as a result of the increased surface roughness. Thus, water cannot penetrate electrospun PLA membranes and only remains on the surfaces. Incorporation of other polymers into PLA via blend electrospinning is possible to improve water permeability of electrospun membranes. In the past, poly (ε-caprolactone), poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and chitosan were respectively blended with PLA to produce electrospun membranes [19–21]. These studies were mainly concentrated in the factors affecting morphology of electrospun membranes; and little attention was paid to water permeability of electrospun membranes and related hydrophilicity-based separation of oil/water emulsion.

In this study, a biodegradable and biocompatible polyester (P34HB) was mixed with PLA in the solutions for blend electrospinning. Different from PLA counterparts, the membranes consisting of blend fibers exhibit superior water permeability and thus highly efficient removal of water from oil/water emulsion under gravity.

2. Experimental

2.1. Materials and blend electrospinning

The poly (L-lactide) (abbreviated as PLA) was purchased from Changchun Sinobiomaterials Co., Ltd., China and had a viscosity-average molecular weight of 193 kg/mol. The poly (3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB) was supplied by Shenzhen Ecomann Biotechnology Co., Ltd., China. It had a Mw and Mn of 536 and 261 kg/mol, respectively, and the molar fraction of 4-hydroxybutyrate was 10%. PLA and P34HB were dissolved in a mixture of dichloromethane and ethanol (9:1, v/v) at room temperature. The percentage of P34HB in the PLA/P34HB blends was 30 and 50 wt%, respectively; and total polymer concentration in the solutions was 40 mg/ml. Solution electrospinning was carried out by a setup consisting of a syringe and a metal collector with a distance of 15 cm under a voltage of 20 kV at room temperature. For comparison, PLA membranes were also fabricated under the identical electrospinning conditions. Prior to measurements the obtained membranes were vacuum dried at room temperature to remove the residual solvents.

2.2. Characterizations

The morphology was probed by a Nova NanoSEM 450 scanning electron microscope (SEM); and a thin gold layer was sputtered before observations. The conductivity and relative viscosity of the solutions were measured by a DDS-11A conductivity meter and an Ubbelohde viscometer at 25 °C, respectively. The contact angle of membranes was evaluated by a JC2000C contact angle measuring instrument at room temperature. A very small drop of water was placed on the surface of membranes and its time-dependent shape was recorded to deduce the water contact angle. Fourier transform infrared spectroscopy (FTIR) measurements were conducted by a Thermo Nicolet FTIR spectrometer with a resolution of 2 cm^{-1} at room temperature. Thermal behaviors were measured by a TA Q2000 differential scanning calorimetry (DSC) instrument at a heating rate of 10 °C/min under nitrogen atmosphere. The elements of membranes were analyzed by a X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos Co., UK) using focused monochromatised Al Ka radiation at 15 kV. The crystalline phase was evaluated by a Bruker D8 ADVANCE X-ray diffractometer (XRD) at room temperature; and the wavelength of the X-ray was 0.154 nm.

2.3. Separation of oil/water emulsion

A mineral oil for vacuum pump was mixed with water under vigorous stirring to form an oil/water emulsion, and volume ratio of the oil to water was 1:1. The oil was dyed by Sudan Red for better visual observation. To test separation of the emulsion, membranes supported by a stainless steel mesh were firmly sandwiched between a pair of cylinders with diameters of 33 mm. No leakage of the emulsion was observed during separation process. The emulsion was poured into the top cylinder and the separation spontaneously proceeded under gravity. The permeate was collected to evaluate the separation efficiency of water from the emulsion.

3. Results and discussion

Fig. 1 shows SEM micrographs of electrospun membranes from the solutions of PLA and its blends with P34HB. Ultrafine fibers with surface porosity are produced from the PLA solutions. Incorporation of P34HB in the PLA solutions results in significant variation of fiber morphology. First, surface porosity is reduced and disappears completely in the blend fibers containing 50 wt% P34HB. Second, the diameter of blend fibers is smaller than that of PLA counterparts, which becomes significant with increasing P34HB content (Fig. 1d). The generation of surface porosity in the PLA fibers should be related to condensation of moister in the atmosphere during electrospinning. The insolubility between water and dichloromethane results in the formation of small water droplets and thus numerous pores on the PLA fibers after solidification. This phenomenon was called as breath figure effects in the previous studies.[22,23] As for the blend fibers, the decrease in surface porosity suggests that addition of P34HB in the solutions alleviates or suppresses the breath figure effects. It could arise from more hydrophilicity of P34HB than PLA. This speculation is further supported by electrospinning of PLA solutions with more ethanol in the mixed solvents. For instance, surface porosity on the PLA fibers almost disappears while a mixture of dichloromethane and ethanol (7:3, v/v) was used as solvents for electrospinning.

To understand the decrease in the fiber diameters with addition of P34HB, conductivity and relative viscosity of the solutions for electrospinning were measured. As given in Fig. 2a, conductivity is increased with incorporation of P34HB in the solutions. The increase in the conductivity corresponds to enhanced interactions between the solutions and the electrical field. It benefits significant deformation of the solutions and thus the decrease in the fiber diameters. On the other hand, deformation of the solutions under the electrical field is similarly favored by the reduced viscosity. The addition of P34HB in the solutions results in the decreasing of relative viscosity (Fig. 2b), also responsible for the small diameters of blend fibers.

Fig. 3 depicts the structural changes in the PLA and blend fibers upon electrospinning. As demonstrated by the XRD profiles (Fig. 3a), diffraction peaks are almost absent for the PLA fibers. It corresponds to little crystallization of PLA during electrospinning