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Hydrophilic modification of HDPE microfiltration membrane by corona-induced graft polymerization

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ABSTRACT

Hydrophilic modification of high-density polyethylene membrane was performed with the introduction of peroxide onto the membrane surface by corona discharge treatment, followed by graft polymerization with acrylic acid. The surface graft polymerization was confirmed by attenuated total reflection-infrared and X-ray photo spectroscopy. Surface hydrophilicity was investigated by measuring the contact angles and moisture adsorption of the modified membrane. The results indicated that the modified membrane showed a significant increase in hydrophilicity. And water flux of the film increased from $102\,\mathrm{L/m^2\,h}$ of the virgin film to $200\,\mathrm{L/m^2\,h}$ of the grafted film, while the bovine serum albumin solution flux of the membrane increased from $43\,\mathrm{L/m^2\,h}$ of the virgin film to $98\,\mathrm{L/m^2\,h}$ of the modified membrane.

Keywords: Microfiltration membrane; Surface grafting; Hydrophilic; Corona discharge treatment

1. Introduction

High-density polyethylene (HDPE) is widely used in various applications due to abundant supply, good process ability, high specific modulus and strength, and resistance to chemicals and harsh environments. The use of polyethylene (PE) microporous membranes for various separations is generally taken account for its advantages over other commercial polymers, such as nontoxic, high specific modulus and strength, availability and low cost of raw material. Nonetheless, when used as microfiltration and ultrafiltration processes, the performance of PE membrane decreases because of fouling, which is likely related to the hydrophobic character [1,2]. Hydrophilic polymer membranes, however, are susceptible to chemical and thermal impacts in their applications because such materials readily adsorbed water and the membrane characters can be changed dramatically by the adsorbed water [3]. Modification of membrane surface is an attractive approach to altering the character of polymer surface. It is possible to combine the low-fouling properties of hydrophilic surfaces with the stability of hydrophobic PE membranes by surface modification. Numerous methods have been developed to prefunctionalize the substrate surfaces, such as γ-ray and UV irradiation [4–6], plasma [7,8], ozone [9],

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corona [10] or chemical initiators [11], and then the polymerization of hydrophilic monomers onto the membrane surface. Corona discharge treatment is one of the most commonly used techniques to improve the wetability and printability of polymers in industry [12], because it can be carried out at atmospheric ambience and seems the more simple and lower operation cost route. Therefore, considerable attention has been devoted to the use of corona discharges for surface modification of polymer membranes. For example, grafting of acrylic acid (AA) on the polyethersulfone membranes endowed the modified membranes with enhanced permeability and antifouling properties [13].

In this work, hydrophilic modification of HDPE membrane was performed with introduction of peroxide onto the membrane surface by corona discharge treatment, followed by graft polymerization with AA. The surfaces of the modified membrane were characterized by attenuated total reflection-infrared (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS). The film surface hydrophilicity was investigated by measuring the contact angles and moisture adsorption. Moreover, pure water and bovine serum albumin (BSA) solution fluxes of the membrane were also investigated.

2. Experimental procedures

2.1. Materials

HDPE microporous membrane was self-made by extrusion and extension method. The porous sheets used all possessed a 40–45% pore volume, a 0.3 μm mean pore size. The AA monomer, with analytical grade, was purified by vacuum distillation prior to use.

2.2. Corona discharge treatment and grafted polymerization

The HDPE membrane was treated by corona discharge treatment, which was generated by corona generator (GX-3,000, Changzhou Aofu electron instrument Ltd. Co., Jiangsu, China). The treated membrane was immediately immersed into AA aqueous solution for graft polymerization, with the nitrogen gas bubbled into the solution to exclude oxygen out from the reaction system. The graft polymerization was allowed to proceed in a shaking incubator at 37 ℃ with a shaking speed of 150 rpm for 6 h. Then, the membrane was taken out and extracted with deionized water for 10 h in Soxhlet extractor to remove the residual monomer and homopolymers. The membrane was dried at 60℃ in vacuum for 10 h, and the modified membranes were obtained.

2.3. Characterizations

The changes of chemical structure between the unmodified and the modified PE membranes were investigated by Fourier transform infrared spectroscopy (FTIR, Nicolet Magna-IR spectroscopy 550, Japan) with an attenuated total reflection unit. All spectra were recorded at 25℃ at a nominal incident angle of 24. The XPS spectra of the samples were performed by using a PHI-5300 spectrometer (Perkin-Elmer Instruments, USA) using $\mathrm{AlK}_{\mathrm{a}1,2}$ and $\mathrm{Mg}_{\mathrm{a}1,2}$ as X-ray source. The pressure in the sample analysis chamber was 10^{-9} mbar. The spectra were recorded in fixed radiation mode. The contact angle was measured by an OCA-20 instrument (German). The moisture absorption was performed by an instrument equipped with a steam generator. And the absorbed moisture of the membranes was defined as follows:

$$\text{Absorbed moisture } (\%) = \frac{w_1 - w_0}{w_0} \times 100$$

where w_1 and w_0 are the weights of the starting and absorbed membrane, respectively.

The filtration performance of the unmodified and modified HDPE membranes were investigated by a 10 cm^2 diameter dead ended stirred ultrafiltration cell. The effective membrane area was 22.1 cm^2. The flux of deionized water ($J_{\mathrm{w}0}$) was measured under 0.05 MPa by weighing permeation until the recorded value was constant for at least three points. The stirred cell and solution reservoir were then emptied and refilled with 4,000 mg/L BSA solution. The filtering experiment was performed at 0.1 MPa until 10 mL of permeate was collected. The permeate flux at the end of BSA solution filtration was denoted as Jp.

3. Results and discussion

The surface modification procedures and the associated grafting mechanism for the modification of HDPE membranes are briefly that the HDPE membrane surface exposed to corona discharge was firstly oxidized to generate peroxide. Then, the generated peroxide was decomposed to initiate graft polymerization at mild temperature. In the subsequent step, the monomer solutions were grafted onto the active substrate. The grafts attached to both the exterior membrane surface and the interior pore surfaces. ATR-FTIR spectra in reflection mode were recorded as shown in Fig. 1, which showed the presence of AA grafted on the membrane surface, confirmed by the

C=O vibration peak at 1,700 cm^{-1}. Comparing with that of the corona treatment membrane, the C=O vibration peak had a little shift. Moreover, the intensity at 1,700 cm^{-1} was increased with increasing the corona treatment time, suggesting that a larger amount of AA was grafted with longer treatment time.

Fig. 2 shows the XPS spectra of the nascent and the corona-treated membranes as well as the AA grafted membranes. For the unmodified HDPE membrane, a major emission peak corresponding to a 284.7 eV binding energy of $C_{(1s)}$ was observed. However, for the modified membrane, an additional emission peak (533.8 eV binding energy) of $O_{(1s)}$ was detected, as shown in Fig. 2(b–d). Furthermore, the peak intensity for $O_{(1s)}$ increased with the grafting degree of AA. The high-resolution spectra of the HDPE membrane corresponding to $C_{(1s)}$ showed that the nascent HDPE membrane only showed a single symmetry peak (284.7 eV binding energy), corresponding to C–H and C–C. For the corona-treated and AA-grafed membrane, the $C_{(1s)}$ spectrum can be resolved into three peaks, corresponding to C–H and C–C (−284.7), C–O (−286.0) and C=O (−287.4 eV). However, the area of C–O and C=O peak of the AA-grafted membrane greatly enhanced compared with that of the corona-treated membrane.

Although contact angle measurements are difficult to interpret for synthetic membranes due to capillary forces within pores, contraction in the dried state, roughness, the relative hydrophilicity of each sample can be easily obtained by this measurement. The average static water contact angles of the HDPE are 109˚. After modification, all of the membranes contact angles tended to decrease, and showed highly hydrophilic. As shown in Fig. 3, the water contact angle of the grafted membranes dramatically decreased with increase in AA grafting degree. The contact angle of 6.0% grafting degree of membrane was 46˚ and showed approximately a half of that of the unmodified membrane. And water drop on the modified membranes with 24.3% AA grafting degree disappeared so soon that the intrinsic contact angle

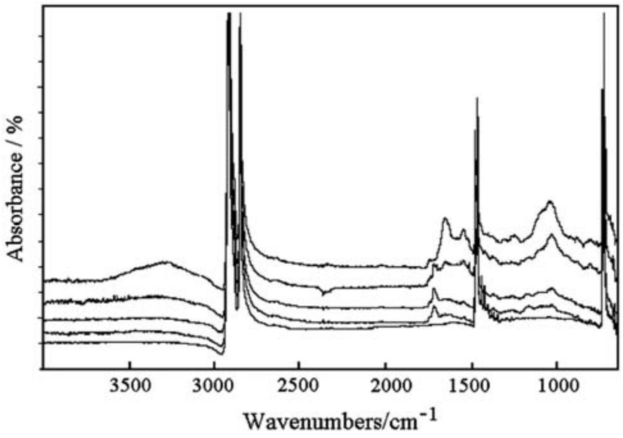

Fig. 1. ATR-FTIR spectra of virgin and AA grafted membranes (from bottom to top: 0, 30, 60, 90 and 120 min of corona treatment time).

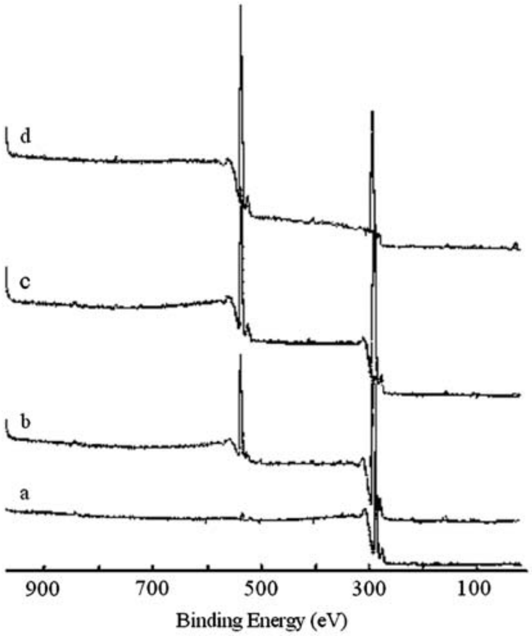

Fig. 2. XPS spectra of HDPE microporous membrane (a) nascent membrane, (b) corona-treated membrane, (c) 6.3% of AA-grafted membrane, and (d) 13.8% of AA-grafted membrane.

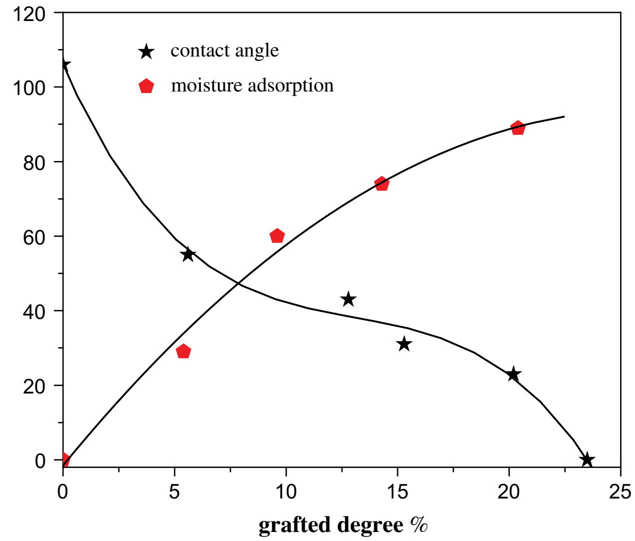

Fig. 3. Contact angle and moisture adsorption of membrane with grafting degree.

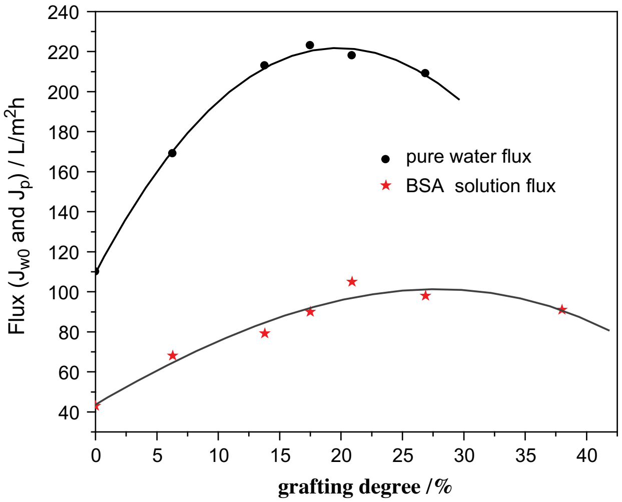

Fig. 4. Pure water and BSA solution flux with grafting degree.

cannot be read, supporting the fact that the membrane surface became highly hydrophilic with grafted AA.

Moreover, the hydrophilicity of membrane surface can also be characterized by the determination of moisture absorption. The HDPE membranes grafted with a higher percentage of AA had excellent moisture adsorption. The moisture adsorption of the modified membrane increased with AA grafting degree was shown in Fig. 3. The adsorption moisture was increased from 0.2% of the virgin film to 91.0% of the 21.5% AA grafting degree. These results showed that the hydrophobic HDPE membrane was effectively hydrophilized by grafting of AA onto the HDPE membrane surface.

The fluxes of deionized water and BSA solution through the unmodified and the modified membranes depending on the grafted degree are shown in Fig. 4. It can be seen in Fig. 4 that the deionized water and BSA solution flux increased with increase in grafting degree at first and then decreased when AA grafting degree exceed 18.0 and 24.0 wt%, respectively. The increased flux of the modified membrane would be ascribed to the hydrophilicity of membrane surface and the weakening of hydrophilic interactions between BSA molecules and hydrophilized membrane surface. While the decrease in the flux could be explained on the basis that the excessive AA grafting induced the decrease in pores and hence reduced the effective free cross-section for water and BSA solution flow.

4. Conclusions

In conclusion, AA grafted onto microporous HDPE membranes has been shown to reduce membrane hydrophobicity without significant adverse effects on membrane performance. ATR-FTIR and XPS spectra indicated the chemical changes of the modified membranes. Incorporation of polar functionalities caused a decrease in contact angle of the membrane with pure water and increased in moisture adsorption. The flux of pure water and the BSA solution through the grafted membranes increased significantly within 18.0 grafting degree.

Acknowledgments

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