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Formation behavior and performance studies of novel antifouling EVAL/PEO–PPO–PEO blend membranes for oil/water separation

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ABSTRACT

Novel anti-fouling poly (ethylene-co-vinyl alcohol)/polyethylene oxide-polypropylene oxide-polyethylene oxide (EVAL/PEO–PPO–PEO) blend membranes were prepared by immersion precipitation method with different EVAL/PEO–PPO–PEO ratios. Thermodynamic and kinetic parameters which govern the formation of membrane were studied by viscosity and precipitation kinetics. Polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO–PPO–PEO) content in the membrane solution controls phase separation by thermodynamic enhancement and kinetic hindrance. The addition of PEO–PPO–PEO is favorable for the formation of spongy like pores and higher porosity surface, which results in larger water flux and higher oil rejection rate through the membrane. Improved hydrophilicity and fouling resistance which have great significance in oil/water separation field were observed by the presence of PEO–PPO–PEO in the membrane. Fourier transform infrared spectroscopy results proved the residual PEO–PPO–PEO in the blend membranes.

Keywords: PEO–PPO–PEO; Poly (ethylene-co-vinyl alcohol); Blend membrane; Oil/water separation; Antifouling property

1. Introduction

Oily wastewater is one of the major pollutants in the aquatic environment and, as such, water treatment and fluid filtration are of interest to many industries [1,2]. Compared to conventional gravity separation and skimming, air flotation, coagulation, and flocculation methods, the membrane-based oil/water separation process has received increasing attention due to its advantages of low cost, simplicity of operation/installation, energy efficiency, and high process flexibility [3,4]. However, one bottleneck, which comes from serious fouling caused by deposition and adsorption of emulsified oil droplets on the membrane surface and/or inside the membrane pores, limits its efficiency and wide application [5,6].

It has been generally agreed that the enhancement of a membrane hydrophilicity could reduce its fouling [7,8]. Therefore, hydrophilic membranes, such as polyethylene-co-vinyl-alcohol (EVAL) membrane, have become a preferential choice for oil/water separation. EVAL, as an environmental-friendly material, becomes a promising membrane material, thanks to its low price, moderate chemical resistance, good biocompatibility, and high hydrophilicity [9–11].

In the past two decades, phase inversion via immersion precipitation has been widely studied and adopted for the preparation of EVAL membrane due

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to its facile manipulation and device availability. The mechanism related to immersion precipitation phase inversion is very complex, and the core issues are focused on thermodynamics [12,13] and kinetics [14]. To manipulate the membrane formation process, many researchers introduced different kinds of additives in casting solution. For example, Riyasudheen et al. added polyvinylpyrrolidone in the EVAL/Dimethylsulfoxide (DMSO) casting solution, which successfully endow EVAL membranes with high separation performance and superior antifouling property simultaneously [15]. Avramescu et al. prepared EVAL membrane for ligand coupling affinity separation from quaternary EVAL/1-propanol/DMSO/water systems using 1-propanol as an additive. Nevertheless, these above-mentioned additives are hydrophilic and often thought to have strong interaction with water in a coagulation bath [16]. The addition of these additives to a casting solution is apt to result in a faster phase separation thermodynamically, which leads to the formation of many macro-voids in the final membranes. Polymer asymmetric membranes with macro-voids always have weak mechanical properties that are not much desired for oily wastewater treatment. Attempts have been made to tune EVAL membrane structures using a series of water immiscible *n*-alcohols as additives [16]. But their hydrophobic characteristics will partially damage the hydrophilicity and antifouling properties of EVAL membrane. Therefore, it is probably more reasonable and necessary to choose an amphiphilic polymer as additive to improve separating, mechanical, and antifouling performance of EVAL membranes because of its appropriate hydrophilic–hydrophobic property.

Polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO–PPO–PEO) triblock copolymers are a kind of typical amphiphilic copolymers containing hydrophilic PEO segments and hydrophobic PPO segments, which can be commercially available as Poloxamers or Pluronics. Many research groups have found that the addition of PEO–PPO–PEO into a casting solution could significantly improve the permeation performance of an ultrafiltration membrane [17–19]. Furthermore, since the PEO segment is highly hydrophilic, PEO–PPO–PEO was also proved to be an excellent hydrophilic modifier in a membrane fabrication process [20,21].

In the present study, we report the preparation of novel EVAL/PEO–PPO–PEO blend membranes for oil/water separation via immersion precipitation method. The thermodynamic and rheological properties in the EVAL/PEO–PPO–PEO/DMSO/water quaternary system were studied. Furthermore, morphology, hydrophilicity, antifouling properties, and permeation characteristics like oil/water flux and oil rejection of the EVAL/PEO–PPO–PEO blend membranes were also investigated.

2. Experimental

2.1. Materials

EVAL containing ca. 38 mol% ethylene with a polymerization degree of 960 was kindly supplied by Kuraray Co. Ltd. Japan and was vacuum dried at 50˚C for 24 h before being used. PEO–PPO–PEO with the number-average molar mass 12,600 g/mol, corresponding to molecular formulas of EO_{98}–PO_{67}–EO_{98}, was purchased from Sigma-Aldrich, Inc. DMSO and sodium dodecyl sulfate (SDS) were purchased from National Pharmaceutical Group Chemical Reagent Co. Ltd., China. Soybean oil with density of 925 kg m^{-3} and average viscosity of 325 mPa s at room temperature was obtained from a local grocery store. All reagents were used without further purification.

2.2. Membrane preparation

EVAL/PEO–PPO–PEO blend membranes were prepared by the method of immersion precipitation and the formulations of the casting solutions are given in Table 1. In a typical membrane preparation process, EVAL and a certain amount of PEO–PPO–PEO were dissolved in DMSO and stirred at 80˚C for 24 h, and then left for 24 h to allow a complete release of bubbles. After being cooled to room temperature, the solution was cast on a glass plate with a steel knife and then immediately immersed in deionized water. Sub-

Table 1
Formation of casting solutions for preparation of the EVAL/PEO–PPO–PEO blend membranes

	Composition of casting solution				
Membrane	EVAL (g)	PEO-PPO-PEO (g)	DMSO (g)	PEO–PPO–PEO loading (wt.%)*	Retention rate of PEO–PPO–PEO (wt.%)
M-0	14	–	100	0	–
M-5	14	0.7	100	5	1.67
M-10	14	1.4	100	10	2.99
M-15	14	2.1	100	15	4.55
M-20	14	2.8	100	20	6.27

*The weight ratio of PEO–PPO–PEO to EVAL in the casting solution.

sequently, a pristine membrane was peeled off from the glass plate and washed thoroughly with deionized water to remove residual solvents. The as-prepared membrane had a wet thickness of 200–250 μm and was kept in deionized water until being used. To determine the amount of PEO–PPO–PEO remaining in a blend membrane, a piece of wet membrane was thoroughly dried in ambient air for sufficient time and weighed (the mass can be designated as M_2). The total mass of EVAL and PEO–PPO–PEO in the casting solution for preparing the membrane can be designated as M_1. Then, the weight difference between M_1 and M_2 is the weight loss of PEO–PPO–PEO in the process of membrane preparation. The retention rate of PEO–PPO–PEO in EVAL/PEO–PPO–PEO blend membranes was supplied in Table 1.

2.3. Cloud point determination

The cloud points of the EVAL/DMSO/water systems with and without PEO–PPO–PEO were determined by titrimetric method at room temperature [15]. In this method, a series of EVAL/DMSO/PEO–PPO–PEO casting solutions (see Table 1) were prepared. Then, a small amount of Milli-Q water acting as nonsolvent was added into each homogenous solution and local gelation occurred. Stirring was carried out to make the solution homogenous again. The process was repeated until the cloud points reached, at which permanent turbidity was observed visually. Then, the water contents at cloud points were recorded.

2.4. Viscosity of casting solution

Rheological characteristic of the casting solutions was measured by a rheometer (BROOKFIELD RVDV-3, USA). The measurements were carried out using a CP52 measuring plate under the steady-state shear rate ranging from 10 to 200 r/min at 25℃. The viscosity of the casting solutions was taken at the shear rate of 100 r/min.

2.5. Characterization of EVAL/PEO–PPO–PEO blend membranes

The infrared ray (IR) absorption spectra of membranes were taken through an FTIR–ATR spectrometer (NICOLET NEXUS 470, Thermo Electron Corporation, USA) over the range of 700–4,000 cm^{-1} using a spectral resolution of 6 cm^{-1}. For each IR spectrum a number of 64 scans were averaged.

The surface and cross-section morphologies of the prepared membranes were observed by a scanning electron microscopy (SEM) (Hitachi S4800, Japan) with 2–3 kV accelerating voltage. The membranes frozen in liquid nitrogen were broken and sputtered with gold before SEM analysis.

The water contact angle of each membrane was determined using a contact angle system (OCA40, Dataphysics Instruments with GmbH, Germany) equipped with video capture at 25 ± 1℃ and 60% relative humidity. Ten measurements were performed for each sample to get an average value [22].

Stretching testing of membranes was performed at room temperature on an electronic universal testing machine (Shenzhen, China) with a crosshead speed of 30 mm/min. Before testing, the membranes were cut into rectangle-shaped strips with the dimension of 50 mm × 10 mm (length × width). The tests were repeated for at least five times for each sample.

In order to evaluate the fusion enthalpy of EVAL and EVAL/PEO–PPO–PEO blend membranes, differential scanning calorimetry (DSC) analyses were carried out on a Perkin–Elmer DSC-7 equipment over the temperature range of 20–200℃ with a heating rate of 10℃/min.

2.6. Oil/water emulsion preparation and characterization

The oil-in-water emulsion was prepared as follows: 0.9 g soybean oil and 0.1 g SDS were added to 1,000 mL deionized water. The solution was then stirred by FJ200-S digital high-speed homogenizer (Shanghai Sample and Model Co.) for 30 min. The size of the oil droplets, which was measured using a particle size analyzer (ZetaPALS, Brookhaven Instruments Corporation, USA), was in the range of 0.12–2.3 μm with a volume average particle diameter of 0.8 μm.

2.7. Filtration experiment

Filtration experiments were conducted on a cross-flow filtration unit having an effective area of 13.8 cm^2. Under a cross-flow velocity of 2 m/s and a trans-membrane pressure of 0.02 MPa, the flux of pure water (J_{W1}) was obtained from the volume of permeated water within 1 h. After that, the oil/water emulsion was forced to permeate through the membrane at the same pressure for 1 h, and the flux was recorded as J_P. Oil rejection ratios were calculated by the following equation:

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \tag{1}$$

where c_p and c_f are the oil phase concentrations of permeate and feed solutions, respectively, measured by TU-1901 dual-beam UV/visible-spectrophotometer at the wavelength of 531 nm [21].

In order to evaluate the oil-fouling-resistant ability of EVAL/PEO–PPO–PEO membranes, pure water flux (J_{W2}) was measured again after the membrane was washed with deionized water for 2 h. The oil/water emulsion flux decay ratio (FDR) and flux recovery ratio (FRR) were calculated as follows:

$$\mathrm{FDR} = \left(1 - \frac{J_P}{J_{W1}}\right) \times 100\% \tag{2}$$

$$\mathrm{FRR} = \frac{J_{W2}}{J_{W1}} \times 100\% \tag{3}$$

3. Results and discussion

3.1. Membrane morphologies

Fig. 1 presents the SEM images of pure EVAL membrane and EVAL/PEO–PPO–PEO blend membranes, respectively. The surface morphology is slightly changed depending on PEO–PPO–PEO loading in EVAL membrane. As the PEO–PPO–PEO loading increases, the porosity on the membrane surface tends to be higher. The cross-sections of all membranes exhibited the typical asymmetrical structure consisting of a dense top layer and a finger-like porous sub-layer. Moreover, for the membranes with higher PEO–PPO–PEO loading, the distance from the top surface to the ending point of macro-void formation became shorter and the porous sub-layer in the asymmetric structure had a more sponge-like structure.

The changes of EVAL membrane morphologies are believed to be associated with the thermodynamic and kinetic effects caused by the addition of PEO–PPO–PEO into the casting solution. Fig. 2 shows the cloud point and viscosity of the casting solutions with different PEO–PPO–PEO loadings. Cloud point data of the system, consisting of four components viz. water, DMSO, EVAL, and PEO–PPO–PEO, was obtained by titration method. The onset of cloudiness is due to the optical inhomogeneities, which can be induced by liquid–liquid or solid–liquid de-mixing. Therefore, the composition at which the cloudiness begins can be used to express phase separation of the system induced by the addition of nonsolvent. It can be seen that the water content at the de-mixing point of EVAL/DMSO is 12.73 wt.%, and that of EVAL/DMSO/PEO–PPO–PEO with 10 wt.% PEO–PPO–PEO loading is increased to 13.56 wt.%. Further, the addition of PEO–PPO–PEO followed the same trend and a cloud point at 14.58 wt.% of water was observed for the casting solutions with 20 wt.% PEO–PPO–PEO loading. From these cloud point data, it is clear that the addition of PEO–PPO–PEO favored the stability of casting solution thermodynamically. Similar phenomenon was also observed in other membrane-forming systems where amphiphilic copolymers are used as additives, and it was explained that the de-mixing of casting solution was retarded due to the surfactivity of amphiphilic copolymers [23].

In addition, as the amount of EVAL and solvent were fixed, the addition of PEO–PPO–PEO enhanced the viscosity of the casting solution (see Fig. 2) and slowed down the exchanging rate of solvent-nonsolvent during membrane formation. It is likely that both the increase in thermodynamic stability and the decrease in solvent-nonsolvent exchanging rate promoted delayed de-mixing, which is in favor of the formation of sponge-like pore structure in EVAL/PEO–PPO–PEO membranes with higher PEO–PPO–PEO loadings.

3.2. FTIR–ATR analysis

Fig. 3 presents the FTIR–ATR spectra of EVAL membranes with or without PEO–PPO–PEO. The characteristic peaks of EVAL membrane were 3,326, 2,926, and 1,090 $\mathrm{cm^{-1}}$, which are corresponding to the stretching vibration of O–H, CH_3, and C–O bonds, respectively. All the above three peaks appeared at the same position for EVAL/PEO–PPO–PEO blend membranes. PEO–PPO–PEO had a characteristic absorbance at 1,241 $\mathrm{cm^{-1}}$, which can be attributed to the asymmetric stretching vibration band of C–O–C. It can be seen from Fig. 3 that there were adsorption peaks appearing at 1,241 $\mathrm{cm^{-1}}$ for the EVAL/PEO–PPO–PEO blend membranes, and their intensity increased with an increase of PEO–PPO–PEO loading. From this result, it is evident that the residual PEO–PPO–PEO content in EVAL/PEO–PPO–PEO membranes follows the same order as that of the casting solutions, which is in consistence with the retention rate values of PEO–PPO–PEO in blend membranes supplied in Table 1. Furthermore, the interaction between the polymer segments can be deduced from the hydroxyl peak broadening, which can be attributed to the hydrogen bonding existing between EVAL and PEO–PPO–PEO segments. Though PEO–PPO–PEO is a kind of water-soluble copolymer and may dissolve in coagulation bath during the process of membrane preparation, the FTIR–ATR result shows that a portion of the added PEO–PPO–PEO has been embraced in the blend membranes surface

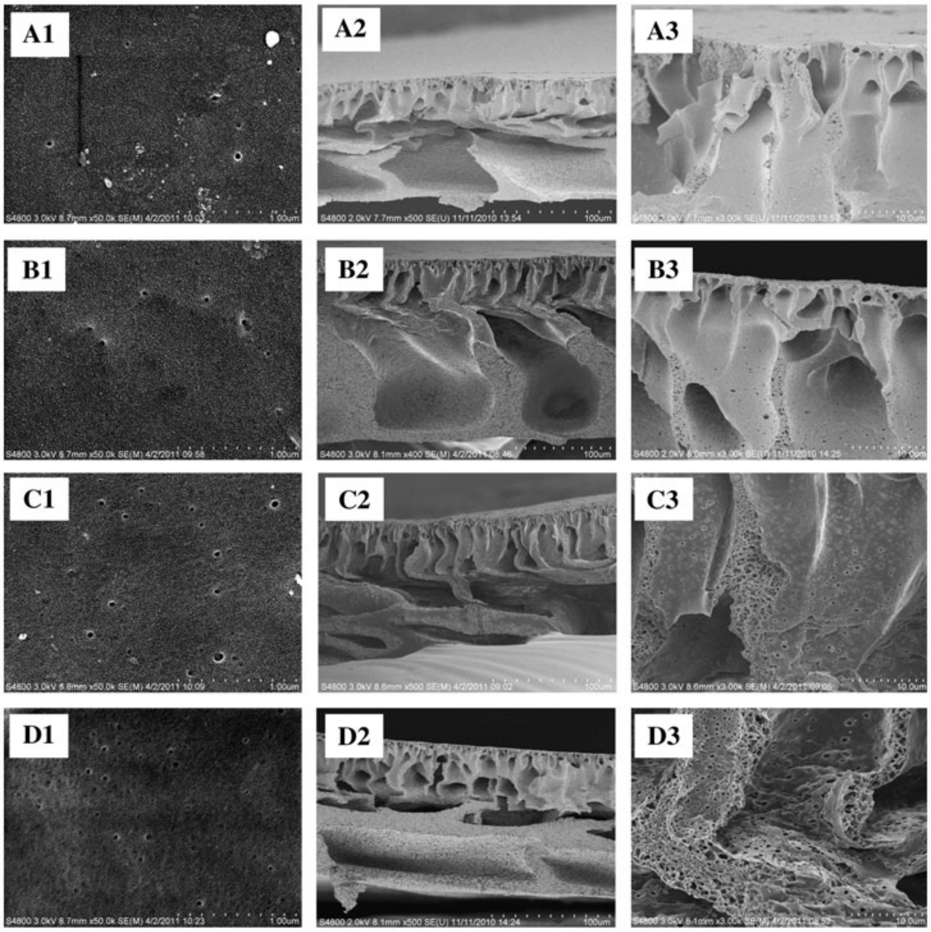

Fig. 1. Surface (left), cross-section (middle), and magnified cross-section (right) SEM images of the membranes with different PEO–PPO–PEO loading. (A) 0 wt.%, (B) 5 wt.%, (C) 15 wt.%, (D) 20 wt.%.

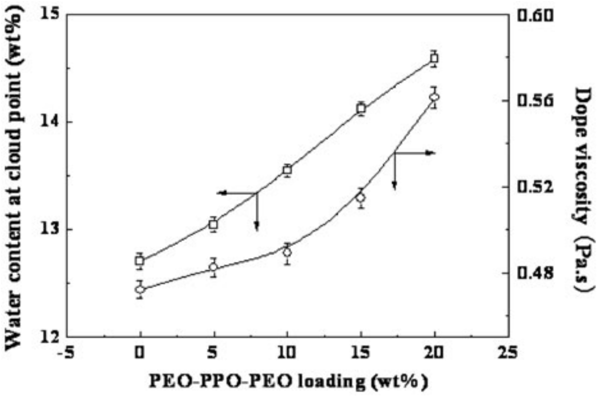

Fig. 2. Water content at cloud point and viscosity of casting solution in EVAL/PEO–PPO–PEO/DMSO systems.

because of the entanglement and hydrogen bonding interaction between EVAL and PEO–PPO–PEO segments.

3.3. DSC

Fig. 4 shows the DSC curves of PEO–PPO–PEO, EVAL, and their blends. From the curves of EVAL/PEO–PPO–PEO blends, it can be found that all the EVAL/PEO–PPO–PEO blends showed only one melting peak and T_g. In general, when two polymers are miscible, DSC characterization shows one single T_g (melting peak) because two polymers interact with each other [24]. Therefore, the DSC result indicated that EVAL and PEO–PPO–PEO are compatible.

3.4. Hydrophilicity of membranes

Contact angle measurement is the general technique to quantify the wettability of a membrane. It is very difficult to measure the static contact angle of a porous polymer membrane because the drop of the liquid rapidly disappears into the pores upon

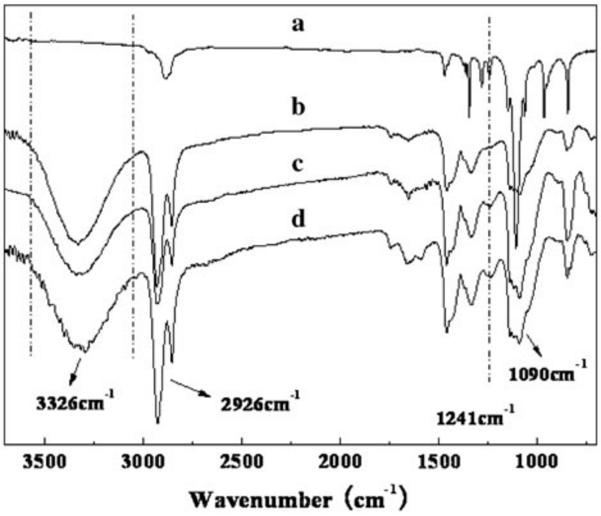

Fig. 3. FTIR–ATR spectra of PEO–PPO–PEO (a) and the EVAL membranes with 0 wt.% (b), 10 wt.% (c), and 20 wt.% (d) PEO–PPO–PEO loading.

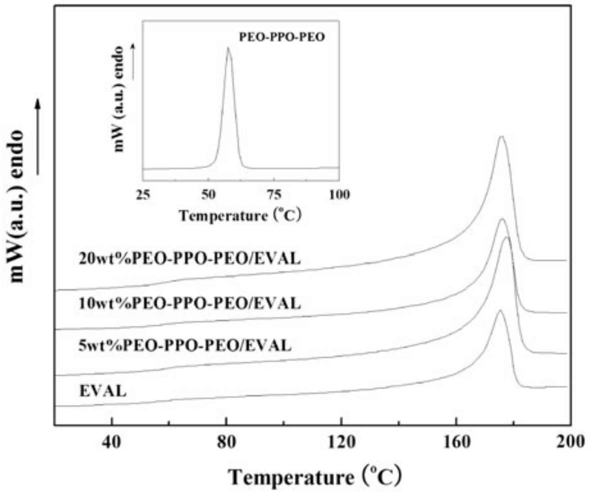

Fig. 4. DSC curves of PEO–PPO–PEO, EVAL, and EVAL/PEO–PPO–PEO blend.

placement on the surface. So, we measured the time dependence of the contact angle of a water drop on the surface of blend membranes with different PEO–PPO–PEO loadings. From Fig. 5, it can be clearly seen that the contact angle value of EVAL/PEO–PPO–PEO blend membranes drop much rapidly than that of pure EVAL membrane. And the higher PEO–PPO–PEO loadings, the faster the contact angle decreased. The decay of the contact angles has been viewed as a diffusion-controlled effect by some researchers, and models have been established to correlate the change of the contact angles during the aging processes [25]. For EVAL/PEO–PPO–PEO blend membranes, there were two major factors that promote the decay of the surface contact angles. The one is the increasing hydrophilic PEO–PPO–PEO content in the membrane, which was confirmed by FTIR–ATR and Table 1. PEO–PPO–PEO raised the polarity of blend membrane surfaces, which make a water drop spread on a membrane surface more easily. Secondly, the gradually higher porosity of EVAL/PEO–PPO–PEO blend membranes, seen from Fig. 1, contributes to the rapid decrease of the contact angles.

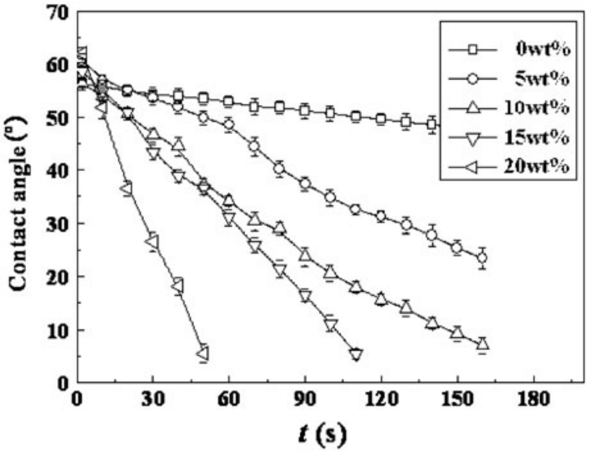

Fig. 5. Contact angle change with time of blend membranes with different PEO–PPO–PEO loading.

3.5. Mechanical properties of EVAL/PEO–PPO–PEO membranes

The influence of PEO–PPO–PEO loading on the tensile strength and break elongation of EVAL/PEO–PPO–PEO blend membranes are depicted in Fig. 6. It can be seen that both the tensile strength and break elongation ascend with increasing PEO–PPO–PEO loading in the membranes. The improvement of mechanical properties of EVAL/PEO–PPO–PEO blend membranes can be attributed to the formation of microstructure in EVAL/PEO–PPO–PEO blend membranes. Compared with EVAL membrane with a honeycomb like pore structure, a more sponge-like microstructure of the EVAL/PEO–PPO–PEO blend membrane with higher PEO–PPO–PEO loadings would possess the higher mechanical properties [26].

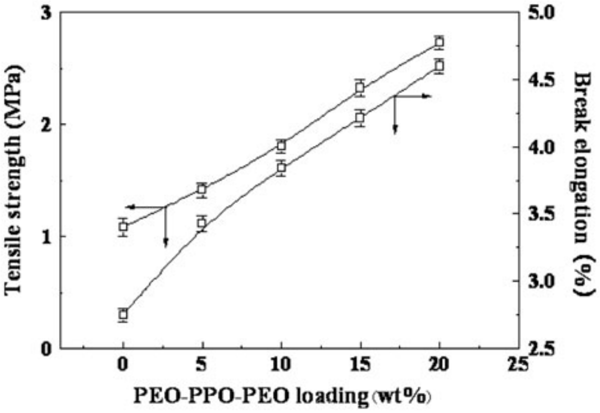

Fig. 6. Mechanical properties of EVAL/PEO–PPO–PEO blend membranes.

3.5. Membrane separation performance for oil/water emulsion

The oil/water emulsion separation performance of EVAL/PEO–PPO–PEO blend membranes was evaluated through filtration experiments. The permeation fluxes and oil rejection ratio through the EVAL/PEO–PPO–PEO blend membranes are shown in Figs. 7 and 8, respectively. It is noticed that the oil/water flux increased dramatically, while the oil rejection ratio decreases slightly with the increase of PEO–PPO–PEO loading. As seen from the surface and cross-section SEM images of the prepared membranes (Fig. 1), the increase of the PEO–PPO–PEO loading results in the slightly increase of porosity and pore size of the membrane surfaces, leading to the substantial increase in the flux and the reduction in oil rejection ratio.

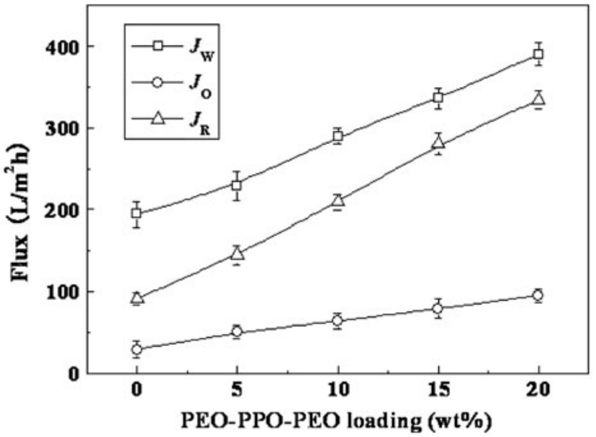

Fig. 7. Permeation fluxes of pure water and oil/water emulsion through the EVAL/PEO–PPO–PEO blend membranes.

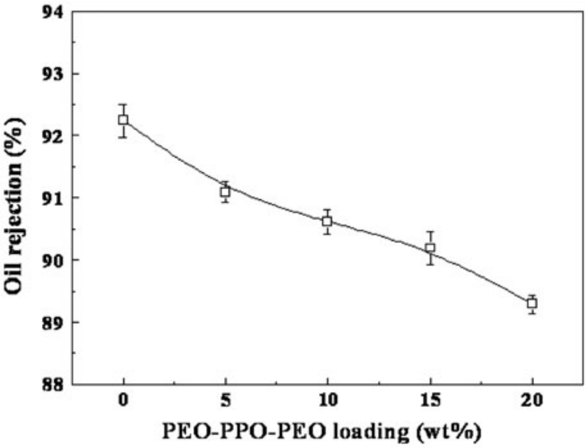

Fig. 8. Effect of PEO–PPO–PEO loading on the oil rejection of the EVAL/PEO–PPO–PEO blend membranes.

Table 2
Anti-fouling properties of the studied membranes

Membrane	PEO–PPO–PEO loading (wt.%)	FDR (%)	FRR (%)
M-0	0	85.05	46.91
M-5	5	78.16	63.32
M-10	10	77.93	72.07
M-15	15	76.49	83.33
M-20	20	75.64	85.64

In order to evaluate the antifouling property of the membranes, oil/water FDR and FRR were calculated using equations (2) and (3), respectively. The lower FDR and higher FRR values meant the better antifouling property of the membrane in oil/water separation performance. It can be seen from Table 2, oil fouling of the pure EVAL membrane results in a dramatic loss of the flux (FDR = 85.05%) after the permeation experiment of oil/water emulsion, suggesting a large amount of soybean oil depositing and/or adsorbing on the membrane surfaces. However, the oil/water flux reduction can be effectively alleviated by the introduction of PEO–PPO–PEO, and the recovery flux increases significantly with the increase of PEO–PPO–PEO loading.

The improved antifouling performance of the blend membranes were analyzed as given blew. When the membranes were exposed to the oil/water emulsion, the oil droplets tend to deposit directly on the membrane surface and gradually reorganize themselves, coalesce with each other due to the hydrophobic interactions. In our cases, there were strong hydrophobic interactions between the oil

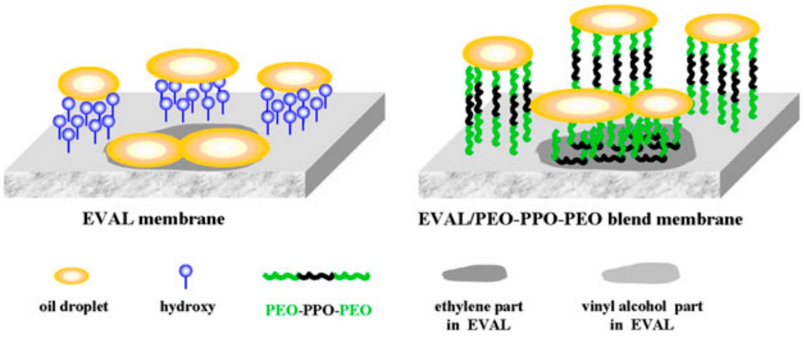

Fig. 9. Schematic illustration of fouling behavior for the membranes during the oil/water emulsion filtration period.

droplets and ethylene hydrophobic part in the EVAL membrane. Considerable amount of the oil droplets could directly deposit onto the membrane surface, leading to a serious membrane irreversible fouling. In contrast, when amphiphilic PEO–PPO–PEO was used as additives, the hydrophilic PEO chains were prone to migrate to the EVAL membrane surface to minimize the interfacial free energy at the water-EVAL interface during immersion precipitation process. The hydrophilic PEO chain stretching out of the membranes [20], weakened the hydrophobic interactions between the oil droplets and the EVAL blend membrane surface, which substantially reduced the deposition of the oil droplets. Furthermore, most of the oil droplets having deposited on the membrane surface could also be easily removed off by water washing, and the water flux can be recovered significantly. Fig. 9 is depicted to help better understanding the fouling behavior for the membranes during the oil/water emulsion filtration period.

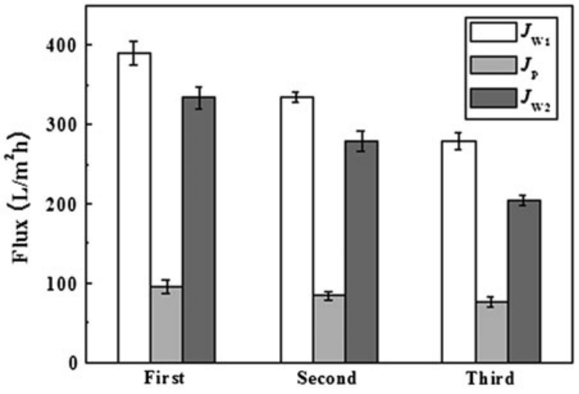

Fig. 10. Changes of the flux for the EVAL/PEO–PPO–PEO membranes after different times of filtration experiment. J_w, J_O, and J_R are the flux of pure water, the flux of oil/water emulsion, and the flux of pure water for cleaned membranes after filtration of oil/water emulsion respectively.

3.6. Recycling of the EVAL/PEO–PPO–PEO blend membrane

In the treatment of oily wastewater using membrane systems, the regeneration or reutilization of the membranes was always an important issue. Therefore, a filtration experiments with three runs were carried out to investigate the recycling property of the EVAL/PEO–PPO–PEO blend membranes with 20 wt.% PEO–PPO–PEO loadings (M-20). It could be seen from Fig. 10 that the oil/water flux of the EVAL/PEO–PPO–PEO blend membrane retained as 76 L/m^2 h, while the pure water flux could retain as 204 L/m^2 h after three runs. It can be thus concluded that blending PEO–PPO–PEO into EVAL matrix was an appropriate method to fabricate novel efficient membranes for oil–water separation. Nevertheless, the stability of EVAL/PEO–PPO–PEO blend membranes is still need to be assessed after filtration of an aqueous solution for a longer time. We will provide the relative data in our prospective work.

4. Conclusions

Amphiphilic PEO–PPO–PEO was introduced into EVAL membranes to fabricate novel EVAL/PEO–PPO–PEO blend membranes with desirable oil droplets fouling resistance by immersion precipitation method. Morphology of the membranes clearly showed that the addition of PEO–PPO–PEO was favorable for the formation of spongy like pores and higher porosity surface, resulting in the larger oil/water flux and higher oil rejection rate through the membrane. FTIR spectroscopic and DSC analysis confirmed the retention of PEO–PPO–PEO in the EVAL/PEO–PPO–PEO blend membranes, which consequently brought about an improved hydrophilic membrane surface, excellent fouling resistance, and desirable reuse property of the membranes. Finally, compared with the pure EVAL membrane, the EVAL/PEO–PPO–PEO blend membranes had the better mechanical strength due to the formation of sponge-like pore structure of EVAL/PEO–PPO–PEO blend membranes.

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