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Fabrication of Hydrophilic and Sponge-like PVDF/Brush-like Copolymer Blend Membranes Using Triethylphosphate as Solvent*

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Abstract Porous PVDF blend membranes with good hydrophilicity and a symmetric structure were prepared by the phase inversion method using amphiphilic brush-like copolymers, P(MMA-*r*-PEGMA), as hydrophilic additive and triethylphosphate (TEP) as solvent. P(MMA-*r*-PEGMA) was synthesized by radical polymerization in TEP. Then the obtained amphiphilic copolymer solution was mixed with PVDF and TEP to prepare the dope solution. The effects of P(MMA-*r*-PEGMA) content and coagulation composition on membrane morphologies were investigated using scanning electron microscopy (SEM). The results demonstrated that, even blended with amphiphilic copolymers, a symmetric structure can be formed. Hollow fiber membranes with a mainly symmetric structure were also fabricated. The dry hollow fiber membranes showed good hydrophilicity, high flux and good rejection performance because of their hydrophilic surface and pores wall.

Keywords: Poly(vinylidene fluoride); Membrane; Triethylphosphate; Hydrophilicity; Amphiphilic copolymer.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is an important membrane material due to its excellent chemical resistance, thermal stability and mechanical properties. Microfiltration and ultrafiltration PVDF membranes were widely investigated and applied in water purification. Much previous research indicated that improving hydrophilicity of PVDF membranes can enhance the properties of these membranes, such as fouling-resistant and water flux[1–10]. Lots of methods have been studied to improve the hydrophilicity, such as coating[11, 12], surface grafting[13–18] and blending[19–24]. In recent years, incorporating the membrane with amphiphilic copolymers has been proposed because a variety of amphiphilic copolymers can effectively provide the membrane with excellent hydrophilicity through a one-step preparation process[19, 25, 26].

PVDF can be easily dissolved in polar organic solvents, such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP) and triethylphosphate (TEP). Therefore, a non-solvent induced phase separation (NIPS) method is mainly used in preparation of PVDF membranes. However, blending amphiphilic copolymers often leads to forming asymmetric structures, especially the large finger-like voids, in cross-section due to the instantaneous demixing while DMF, DMAc or NMP is used as solvents. Such finger-like void structures will decrease the rejection stability and stretching/pressing resistance of membranes.

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Exploring the methods of fabricating symmetric structures, sponge-like voids or lace morphology, should be the main task for preparing high performance PVDF/amphiphilic copolymer blend membranes. Among the solvents of PVDF, TEP based dope solution tends to form sponge-like void membranes due to the delayed phase separation in water coagulation bath[27–29]. So far, no successful and applicable preparation method for hydrophilic PVDF/amphiphilic copolymer blend membranes using TEP as solvent has been reported. In this work, a brush-like poly(methyl methacrylate-*co*-poly(ethylene glycol) methyl ether methacrylate) (P(MMA-*r*-PEGMA)) was synthesized as the amphiphilic copolymer for blend PVDF membranes. The effects of amphiphilic copolymer content and coagulation compositions on the structures and properties of membranes have been investigated. These results provide a novel and simplified method for preparing PVDF/P(MMA-*r*-PEGMA) blend membranes with great application potential and a lower cost.

EXPERIMENTAL

Materials and Reagents

PVDF (FR-904, M_n = 380000) was obtained from Shanghai 3F New Materials Co. Ltd. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, M_n = 1200, industrial grade) was purchased from Shanghai Taijie Chem. Co. Ltd. Methyl methacrylate (MMA), TEP and AIBN were obtained from Shanghai Chemical Reagent Company, China. All chemicals and materials were used without further purification. The aqueous carbon black suspension was purchased from Ninghai Xingguang Stationery Co.

Synthesis of P(MMA-r-PEGMA)

The composition of P(MMA-*r*-PEGMA) copolymer can be controlled by the feed monomer ratio as described in our previous paper[30]. In this study, the weight ratio of MMA/PEGMA was chosen as 5:4. MMA and PEGMA monomers were mixed in TEP in a glass autoclave equipped with a mechanical stirrer at room temperature. The weight content of the total monomers was 40%. After N_2 was bubbled through the mixture to remove O_2 for 30 min, the reaction solution was heated to 65 °C and a desired amount of AIBN (mole ratio of total monomer, 1/200) was added and started to copolymerize for 24 h. Because the obtained copolymer can not be dissolved in water, water was used as precipitant to remove the unreacted PEGMA. At the end of the reaction, a small amount of the copolymer solution (5 g) was reprecipitated from TEP solution into water and then dissolved in TEP, and reprecipitated in water. This procedure was repeated three times. The obtained copolymer was dried in vacuum at 60 °C for 24 h before weighing and characterization. It was found that copolymer concentration in solution is 39.5%, indicating a very high conversion degree of two monomers.

Preparation of the Blend Membranes

P(MMA-*r*-PEGMA)/PVDF blend membranes were prepared *via* a typical NIPS process. PVDF was first dissolved in TEP at 80 °C, and then a amount of copolymer solution, which was directly used as synthesized without further separation, was added into the PVDF solution. The mixture was continuously stirred for 24 h to yield a clear solution. The compositions of the dope solutions are shown in Table 1 and Table 2. The bubbles were released under reduced pressure before flat and hollow fiber membrane preparation. The membrane fabrication conditions are also shown in Table 1. In preparation of flat membranes, the dope solutions were spread to 300 μm thick film on glass plate and then immediately immersed into a 25 °C coagulation bath. In preparation of hollow fiber membranes, water or TEP/water mixture was used as an internal bath. The dope solution was pressurized through a spinneret and immersed into an external coagulation bath of water at 25 °C using a 5 cm air gap. The nascent hollow fiber was taken up by a roller at 2 m/min. The obtained flat and hollow fiber membranes were washed with 40–60 °C water and changing water frequently for 24 h to completely remove the residual solvent. The membranes were dried in air for 48 h before structure and property characterization.

Table 1. Compositions of the flat membrane dope solutions and coagulation baths (weight)

	Sample No.	PVDF	P(MMA-*r*-PEGMA)	TEP	Coagulation bath
Flat membranes	M0	18	0	100	H_2O
	M1	16.2	1.8	100	H_2O
	M2/M2-0	14.4	3.6	100	H_2O
	M2-20	14.4	3.6	100	TEP/H_2O = 20/80
	M2-40	14.4	3.6	100	TEP/H_2O = 40/60
	M2-60	14.4	3.6	100	TEP/H_2O = 60/40
	M2-P	14.4	3.6 (Purified)	100	H_2O

Table 2. Compositions of the hollow fiber membrane dope solutions and coagulation baths (weight)

	Sample No.	PVDF	P(MMA-*r*-PEGMA)	TEP	Internal bath	External bath
Hollow fiber membranes	M2-H	14.4	3.6	100	H_2O	H_2O
	M2-H-40	14.4	3.6	100	TEP/H_2O = 40/60	H_2O

Characterization of the Blend Membranes

Scanning electron microscopy (SEM, Hitachi S-4800) was used to characterize the membrane morphologies. The hydrophilicity of the membrane surfaces were characterized on the basis of a water contact angle system (OCA20, Dataphysics, Germany) equipped with video capture at 25 °C. Pure water flux was measured *via* the standard end filtration process at 25 °C under the pressure of 0.1 MPa. The efficient pore size of membranes was investigated by the retention of black ink particle in aqueous solution, a dynamic light scattering device (90Plus, USA) was used to monitoring the particle size in permeate. For hollow fiber membranes, the flux and particle rejection properties were measured *via* a shell process.

RESULTS AND DISCUSSION

Effects of the P(MMA-r-PEGMA) Copolymer on the Flat Membrane Morphology

Amphiphilic copolymers serve the key role for applicable preparation of blend membranes. Although many methods have been reported on amphiphilic copolymers, low synthesis efficiency and high cost limit the application of most amphiphilic copolymers. Radical copolymerization in solution is an easy and economical method. Adopting this method, the copolymerization of MMA and PEGMA was successfully realized. The concentration of P(MMA-*r*-PEGMA) in the obtained solution is 39.5 wt%, which is very closed to the added monomer concentration (40 wt%) before copolymerization. The proportion of the residue monomers or homopolymer of PEGMA in the dope solutions is very small which has little effect on the composition and morphologies of the blend membranes, as shown in Fig. 1, there are nearly the same pore structure in M2 and M2-P membranes. So the copolymer solution can be directly used to prepare the casting solution of blend membranes without further separation and purification. The residue monomers or homopolymer of PEGMA can be removed in the membrane formation process. By changing the amount of copolymer solution mixed with PVDF and TEP, the ratio of copolymer/PVDF could be controlled efficiently.

Many studies indicated that the addition of amphiphilic copolymers often led to the generation of macrovoids in PVDF blend membranes[19, 20, 31]. Hence the morphologies of PVDF/P(MMA-*r*-PEGMA) blend membranes were investigated first, and the results are shown in Fig. 1. As the content of P(MMA-*r*-PEGMA) increased, the macrovoids in matrix and pore size on surface increased. The reason of this phenomenon lies in the fact that P(MMA-*r*-PEGMA) increases the affinity of the casting solution and the precipitant, which enhances the exchange rate between the casting solution and the non-solvent. The instantaneous demixing generated the macrovoid formation in the membranes. In this system, the low affinity between TEP[28] and water decreased the demixing rate, and the macrovoids, typical finger-like voids, were effectively depressed by using TEP as solvent.

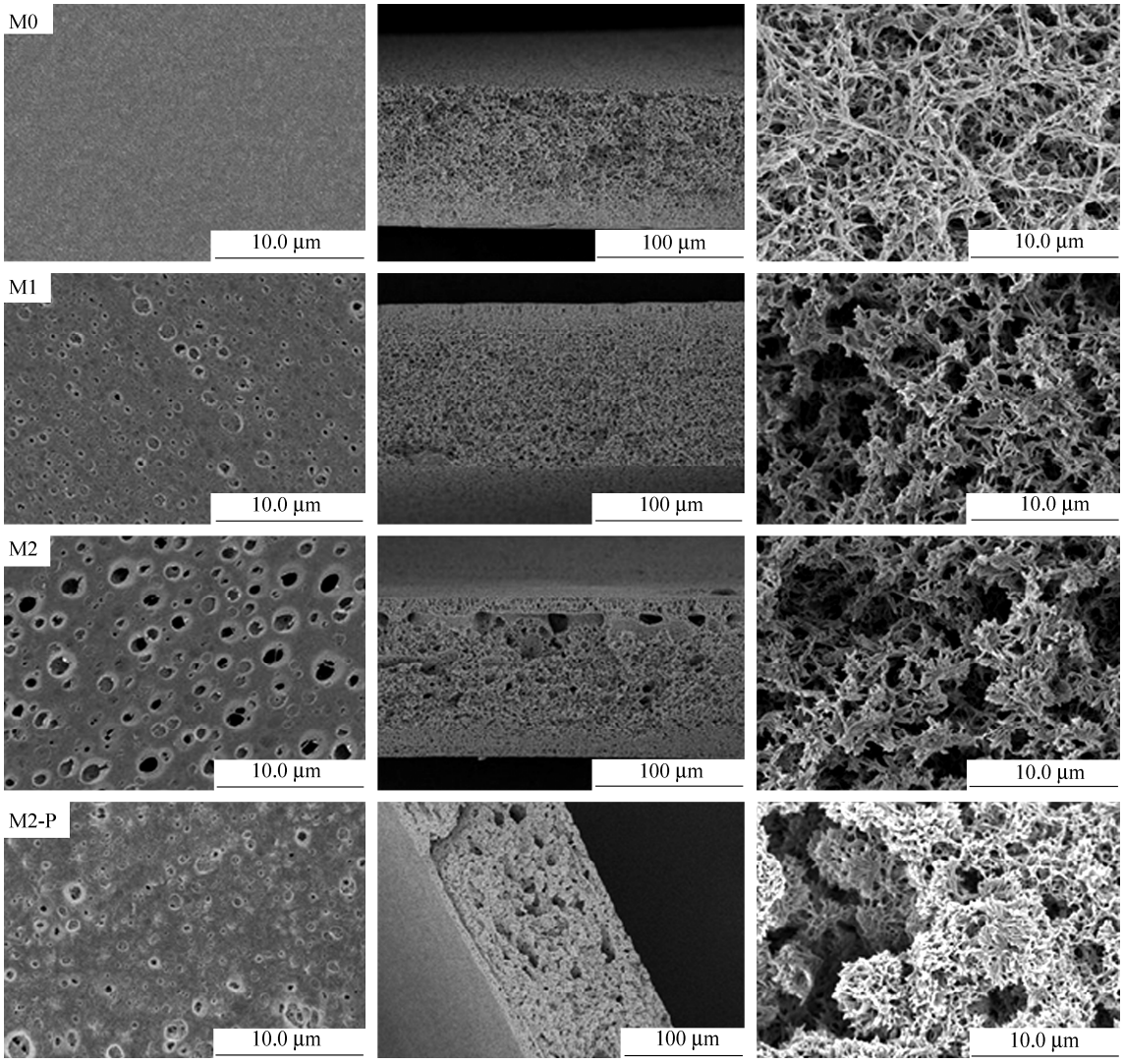


Fig. 1 SEM images of M0, M1, M2 and M2-P membranes formed in a coagulation bath of water (left: top surface, middle: cross section, right: high-magnification images of cross section)

Effects of Coagulation Compositions on the Flat Membrane Morphology

In the NIPS process, the morphologies of the membrane's surface and cross section were greatly influenced by coagulation compositions. By adding TEP into the coagulation water bath, the morphologies of the blend membranes are illustrated in Fig. 2. The surface porosity increases with the increase of TEP contents in baths. With increasing the content of TEP in the coagulation bath, the large finger-like voids were depressed in the membrane matrix. When the content of TEP in the coagulation bath is higher than 40 wt%, the finger like macrovoids disappear in cross section. In principle, the presence of TEP in coagulation decreases the non-solvent/solvent exchange rate, which often leads to the delayed-type demixing and a symmetric porous membrane[27]. Considering the porous surface together, it was found that the addition of TEP in the coagulation bath could efficiently control the PVDF/P(MMA-*r*-PEGMA) blend membranes with porous surface and sponge-like symmetric structures. Such observations form the basis of the technology for preparation of blend PVDF membranes with improved hydrophilicity. To validate this conclusion, the structure and properties of prepared PVDF/P(MMA-*r*-PEGMA) hollow fiber blend membranes were investigated and reported below.

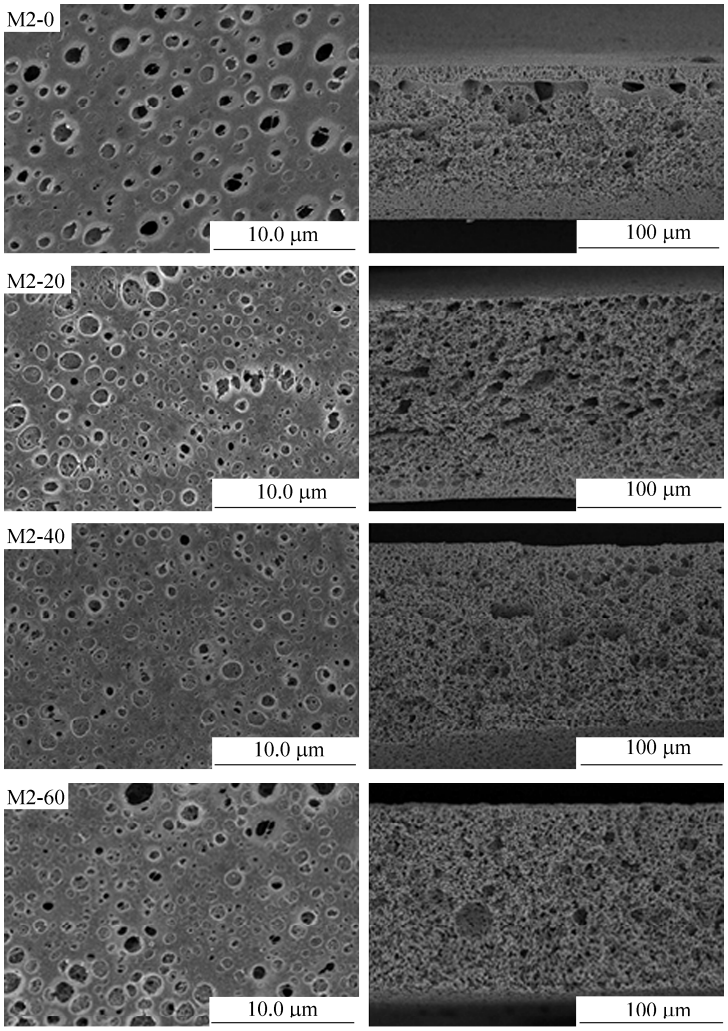


Fig. 2 SEM images of M2 membranes prepared in coagulation bath with different TEP/H_2O ratios by weight (M2-0:TEP/H_2O = 0/100, M2-20:TEP/H_2O = 20/80, M2-40:TEP/H_2O = 40/60 and M2-60:TEP/H_2O = 60/40)

Structures and Properties PVDF Hollow Fiber Blend Membranes

Based on the successful synthesis of P(MMA-*r*-PEGMA) and discussion on flat PVDF membrane preparation and structure, the P(MMA-*r*-PEGMA) solution was used directly to prepare the PVDF/P(MMA-*r*-PEGMA) hollow fiber blend membranes. The preparation conditions of the hollow fiber membranes are given in Table 1. The mass ratio of P(MMA-*r*-PEGMA)/PVDF in the dope solution was controlled in 1/4, which implies that the theoretical content of P(MMA-*r*-PEGMA) in the final membrane is 20 wt% with the full retention of this copolymer. By using water as the external coagulation bath, water or water-TEP mixture (TEP/water = 40/60, *W*/*W*) as the internal coagulant, two hollow fiber blend membranes (M2-H and M2-H-40) were prepared, respectively.

Morphologies and Structures

The morphologies of the hollow fiber membranes using water and water/TEP mixture as the internal coagulant are given in Fig. 3 and Fig. 4, respectively. Generally, the morphologies are in good agreement with those of the flat membranes. When 40% TEP/water solution was used as the internal coagulant, the cross-section showed more symmetric sponge-like structures, while the pore size decreased and the porosity increased due to instantaneous demixing.

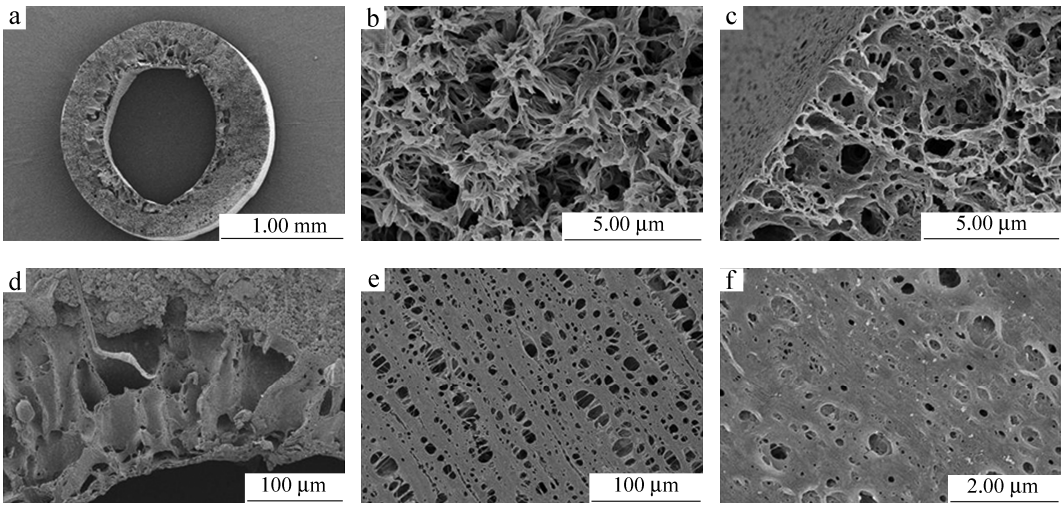


Fig. 3 The SME images of M2-H (a and b: cross-section, c: external, d: internal skin, e: inner surface, f: outer surface)

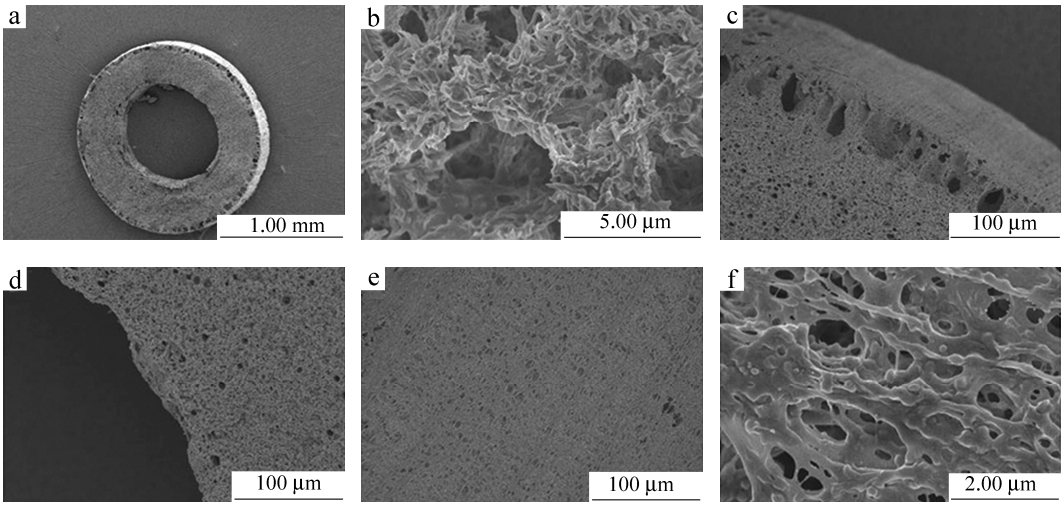


Fig. 4 The SME images of membrane M2-H-40 (a and b: cross-section, c: external skin, d: internal skin, e: inner surface, f: outer surface)

Hydrophilicity

Hydrophilicity is one of the most important characteristics of membranes. Good hydrophilicity leads to high flux and good fouling-resistance. The prepared hollow fiber membranes M2-H-40 in fully dried state were evaluated by water contact angle. As shown in Fig. 5, the contact angle of membrane M2-H-40 declined dramatically over time, and the angle dropped to 0° in 100 s. It is clear that water can permeate into the pores and cross the membrane very easily. The results indicated that the dry PVDF/P(MMA-*r*-PEGMA) blend membrane has good hydrophilicity both on the membrane surface and pores wall inside the membrane. In principle, the good hydrophilicity of the blend PVDF/P(MMA-*r*-PEGMA) membrane could be generated from the PEG side chains of MMA-*r*-PEGMA copolymer enriching.

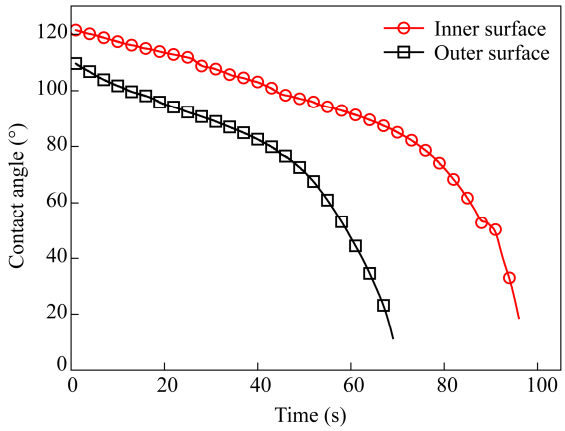


Fig. 5 Changes of water contact angles of membrane M2-H-40

Permeation Flux and Rejection

SEM images, shown in Fig. 3 and Fig. 4, indicated that the prepared hollow fiber blend membranes are microfiltration membranes. Meanwhile the pore size of the outer surface is much smaller than those of the inner surface. Therefore, the membranes are suitable to be used as outside to inside membranes. The outside to inside water flux of hollow fiber blend membranes M2-H and M2-H-40 was 300 L/m^2·h and 460 L/m^2·h, respectively, under 0.1 MPa. The high water flux should be attributed to the good hydrophilicity and porous surface.

Using the black carbon particle containing aqueous suspension as feed, the particle size analysis method was used to characterize the rejection property. As shown in Fig. 6, the largest particle size in permeate is 130 nm, revealing that the largest pore size lies in the corresponding range. All the particles with size larger than 130 nm can be thoroughly filtrated by M2-H-40. Such a value is smaller than the pore size, nearly 200 nm, found in the SEM (Figs. 4 and 5). This phenomenon can be explained by the formation of hydrogel layers on the membrane surface and pores wall[30, 32–34]. The enriched PEG side chains of P(MMA-*r*-PEGMA) copolymer on pores wall can absorb water, thus the stretching effect of hydrated tangling chains may generate a pore-size-reduction effect.

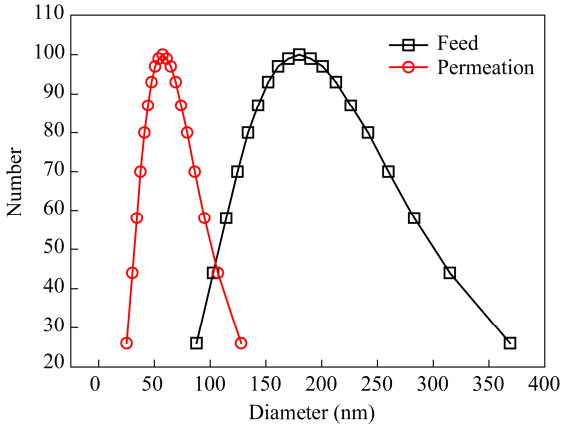


Fig. 6 Black carbon particle size distribution in feed and permeate for membrane M2-H-40

CONCLUSIONS

P(MMA-*r*-PEGMA) copolymer was successfully synthesized *via* radical polymerization. PVDF/P(MMA-*r*-PEGMA) blend membranes were prepared using TEP as solvent *via* a typical NIPS method. The symmetric PVDF/P(MMA-*r*-PEGMA) blend membranes in flat shape were realized by adding copolymer solution directly into the dope solution. Based on the delayed-type demixing mechanism, the hollow fiber blend membranes with

symmetric structures and good hydrophilicity were successfully prepared. For preparing hollow fiber blend membranes containing 20 wt% P(MMA-*r*-PEGMA) copolymer, water was used as an external coagulant and TEP/water mixture (40/60 by weight) as an internal coagulant. The largest pore size of the membranes was controlled in 130 nm. The pure water flux of this hollow fiber membrane reached 460 $L/m^2 \cdot h$ under 0.1 MPa. These results provide a novel and simplified method for preparing PVDF/P(MMA-*r*-PEGMA) blend membranes with great application potential and a relatively low cost.

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