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Original Article

Improved permeation performance and fouling-resistance of Poly(vinyl chloride)/Polycarbonate blend membrane with added Pluronic F127

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Abstract

The aim of this work was to prepare and characterize poly(vinyl chloride) (PVC)/polycarbonate (PC) blend membranes for use in ultrafiltration. Pluronic F127 was used as an additive to modify the membrane surface of the PVC/PC blended membranes. The PVC/PC blend membrane was first prepared using the phase inversion method from a casting solution of PVC with small amount of PC in N-methylpyrrolidone (NMP) and water as the non-solvent. The morphologies structure and properties, such as tensile strength, water flux, and bovine serum albumin (BSA) rejection of the blend membrane were studied. Increased amounts of PC resulted in an increase in the water flux and ability to reject protein. A concentration of 0.75 wt% PC provided the best improvement in tensile strength of blend membrane. Addition of different amounts of pluronic F127 to the casting solution of PVC/PC with a PC concentration of 0.75 wt% resulted in a decrease in the water contact angle that demonstrated the improvement of hydrophilicity of blend membrane. Scanning electron microscopy photographs showed that the modified PVC/PC membranes had a bigger pore volume in the porous sub-layer compared to the PVC/PC control membrane. The PVC/PC membrane with added Pluronic F127 exhibited a much higher flux and rejection of BSA in a protein filtration experiment than the PVC/PC membrane. An increase in flux recovery ratio of PVC/PC/pluronic 127 blend membrane indicated that the modified membranes could reduce membrane fouling useful for ultrafiltration.

Keywords: poly(vinyl chloride), polycarbonate, blend membrane, pluronic F127, ultrafiltration

1. Introduction

Phase inversion is the most commercially available method for preparing microporous polymeric membranes (Strathman and Kock, 1977; Bottino *et al.*, 1991). In this method, a homogeneous polymer solution is cast onto a suitable support and immersed in a coagulation bath containing a non-solvent, usually water. The exchange of solvent and non-solvent induces the separation of the system into two phases: a polymer-lean and a polymer-rich phase. The polymer-lean phase disperses into the concentrated polymer-rich phase resulting in the formation of a porous structure (Machado *et al.*, 1999). Many polymers such as poly (vinylidene fluoride) (PVDF), polysulfone (PSf), poly (ether imide) (PEI), polyacrylonitrile (PAN), and cellulose acetate (CA) can form microporous membranes using this method due to their thermal stability and chemical resistance (Kesting, 1971). However, these materials are expensive to prepare.

Poly(vinyl chloride) (PVC) makes an interesting polymer used to fabricate microporous membrane due to its stiffness, its excellent resistance to abrasion, acids, alkaline and microbial corrosion, and it is a low cost product. Some research has focused on the preparation of flat PVC ultrafiltration and microfiltration membranes using phase inversion (Hirose *et al.*,1979; Hirose and Yasukawa, 1981; Bodzek and Konieczny, 1991; Hiroshi *et al.*, 1993; Peng and Sui, 2006;

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Chinpa, 2008). PVC membranes for use in the ultrafiltration and microfiltration PVC for water treatment systems have been prepared by Gao *et al.* (1988). However, the drawback of pure PVC is its brittleness and liability to fracture. A new material formed by blending PVC with other polymers may have more desirable properties. A suitable polymer for blending with PVC as the major component might be polycarbonate (PC) because it has a rigid backbone with good mechanical strength and is suitable for producing a thermally resistant membrane (Vijayalakshmi *et al.*, 2008).

Due to the hydrophobic nature of PVC and PC, fouling on the membrane surface could occur during filtration of solutions containing substances like protein. A blend with a hydrophilic polymer material that has both hydrophilic and hydrophobic polymer segments might have the advantage of providing opportunities for easy surface modifications. Polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) triblock copolymers have been introduced to blend with polyethersulfone (PES) (Wang *et al.*, 2006; Zhao *et al.*, 2008) and cellulose acetate (CA) (Lv *et al.*, 2007) to reduce protein adsorption. The hydrophilic unit (PEO) not only improves permeation properties and fouling resistance, but the hydrophobic part (PPO) could anchor with the polymer membrane matrix (Wang *et al.*, 2006; Zhao *et al.*, 2008). Therefore, this additive will remain with the membrane matrix during the filtration process (Ma *et al.*, 2004).

The aim of this work was to prepare a PVC membrane with a high hydrophilicity, high water flux and good mechanical strength. In this work, the PVC/PC blend membranes were first prepared using the phase inversion technique by adding a small amount of PC into the PVC casting solution. The effects of the PC content on membrane morphology, pure water flux, BSA rejection, and tensile properties were studied. Secondly, Pluronic F127 was used as an additive to the casting solution to increase the hydrophilicity of the PVC/PC membrane. The effects of the Pluronic F127 content on membrane performance, morphologies, hydrophilicity, and fouling were studied in detail and discussed.

2. Experimental Details

2.1 Materials

PVC with a molecular weight of 48,000 g/mol was purchased from Fluka. PC is a commercial product (PC hollow profile sheet) with a molecular weight of about 55,500 g/ mol analyzed by GPC using a PS standard running with THF at 40°C. The PC was dissolved in chloroform and then precipitated in methanol in order to remove substances added during its manufacturing process. Pluronic F127 (ethylene oxide/propylene oxide block copolymer) from Sigma-Aldrich was used as a hydrophilic additive. Anhydrous NMP was also purchased from Aldrich. NMP was used as a solvent without any further purification. BSA with an average molecular weight of 67,000 Da was supplied from Fluka.

2.2 Preparation of blend solution

The blended solutions based on PVC, PC, and Pluronic F127, were prepared by dissolving the three polymers in NMP in different proportions (Table 1) at 60-65°C. The homogeneous solutions obtained were used within a week.

2.3 Preparation of membranes

The membranes were prepared by the classical phase inversion method using water as the coagulant. PVC/PC or PVC/PC/Pluronic F127 blended solutions were cast on a glass plate with a casting rod of 250 mm thickness. The cast films were pre-evaporated for 30 s in air (27±2°C, RH 75±2%) then immersed in a water bath for complete precipitation. The membranes were removed from the glass plate and washed thoroughly with a large amount of distilled water. The membranes were stored in distilled water until used.

2.4 Hydrophilicity of membrane surface

The hydrophilic property of the membrane surfaces was characterized by measuring the water contact angle (WCA). A water droplet of a constant volume was placed on

Table 1. Casting solution composition for preparing blend membrane.

Membrane	Casting solution composition				PC (wt%)	Pluronic F127 (wt%)
	PVC (g)	PC (g)	Pluronic F127 (g)	NMP (g)		
PVC	3.00	-	-	17	-	-
PVC-PC1	2.85	0.15	-	17	0.75	-
PVC-PC2	2.70	0.30	-	17	1.5	-
PVC-PC3	2.40	0.60	-	17	3.0	-
PVC-PC1-Plu3	2.85	0.15	0.6	16.4	0.75	3
PVC-PC1-Plu6	2.85	0.15	1.2	15.8	0.75	6
PVC-PC1-Plu9	2.85	0.15	1.8	15.2	0.75	9

the surface of the membrane using an automatic interfacial tensiometer (Data physic).

2.5 Water absorbance

The water absorbance was also studied as reported by Zhu *et al.* (2007). The water absorbance ratio (WA) was calculated according to

$$WA = [(w_{wet}-w_{dry})/w_{wet}] \times 100 \qquad (1)$$

Where w_{wet} and w_{dry} represent the weights of dried membrane and membrane soaked in water at room temperature for 24 hrs, respectively. Both measurements were carried out three times and the average values have been reported.

2.6 Membrane morphology observations

The cross-sectional morphologies of the obtained membranes were characterized by SEM (JSM 5200). The membranes were cut into pieces of various sizes. These pieces were immersed for 30-60 seconds in liquid nitrogen and then broken. The fractured membranes were coated with gold for initiating electrical conductivity before analysis.

2.7 Tensile properties of blend membrane

The tensile strength and elongation at break for various membranes were tested by the Universal Testing Machine (LLOYD). The measurement was carried out at room temperature and a pull rate of 5 mm/min.

2.8 Transport properties of the blend membrane

In order to measure the transport and separation properties of the blend membranes, the UF experiments were carried out using a stirred dead-end filtration cell. All experiments were conducted at room temperature using an operating pressure of 1 bar. The pure water flux was calculated as follow:

$$J_w = Q/A\Delta T \qquad (2)$$

where J_w is the pure water flux ($Lm^{-2}h^{-1}$), Q is the quantity of collected permeate (L), at the sampling time (hour) and A is the membrane area (m^2).

The solute rejection (R) of the blend membranes was tested with 0.1 g/dL of BSA. The protein concentration was measured by spectrophotometer (UV-model Lamda 25, Perkin Elmer) at a wavelength of 280 nm. The rejection of BSA was calculated using the following equation:

$$R = (1-C_p/C_f)\times 100 \qquad (3)$$

where C_p and C_f are the concentrations in the permeate and the feed, respectively.

The anti-fouling properties of the membrane were investigated as described elsewhere (Zhu *et al.*, 2007; Ma *et al.*, 2007; Zhao *et al.*, 2008; Arthanareeswaran *et al.*, 2009). The steady state pure water flux (J_{w1}) of the prepared membranes was first measured. Then the feed solution of 1 g/L of BSA solution (in phosphate buffer saline with pH = 7.4) was introduced and the filtrate was collected at 0.1 MPa until a steady state of flux (J_p) was attained. Subsequently, the membrane was washed with distilled water on a vibrator for 2hrs, and then the water flux was reevaluated and the steady-state value was defined as J_{w2}. The flux recovery ratio (FRR) was calculated according to the following equation (Ma *et al.*, 2007; Zhao *et al.*, 2008; Zhu *et al.*, 2008):

$$FRR\,(\%) = (J_{w2}/J_{w1}) \times 100 \qquad (4)$$

3. Results and Discussions

3.1 Effect of the PC concentration on the morphologies, pure water flux, and BSA rejection of PVC/PC blend membranes

PVC/PC asymmetrical membranes with different blend compositions were prepared by phase inversion, immersion method. The SEM images of cross-sections of PVC and the PVC/PC blend membranes (Figure 1) showed that the pure PVC and the PVC/PC blend membrane have an asymmetrical structure consisting of two skin layers (top and bottom skin layer) and a finger-like support layer or macrovoid. Generally, this structure is obtained when the casting solution is immersed directly into a non-solvent bath (van de Witte *et al.*, 1996). As shown in Figure 1(a), for a pure PVC membrane, a thick wall of finger-like pores is formed. As shown in Figure 1(b)-(d), finger-like pores with the thinner wall formed when

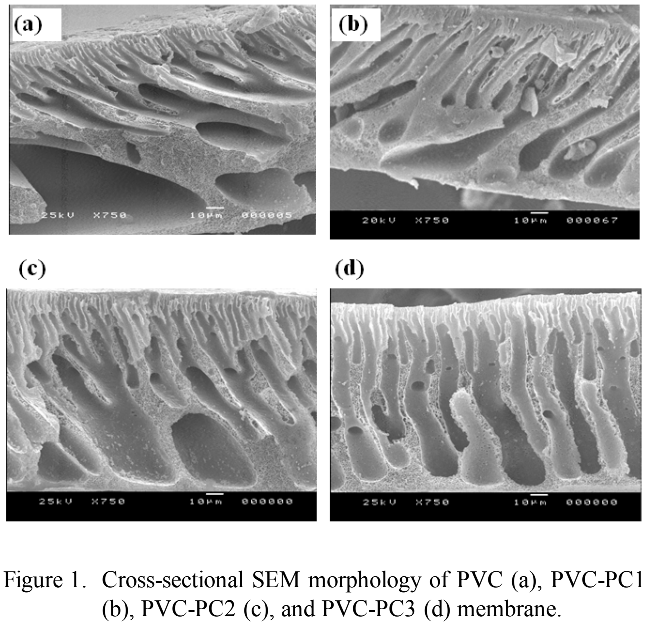

Figure 1. Cross-sectional SEM morphology of PVC (a), PVC-PC1 (b), PVC-PC2 (c), and PVC-PC3 (d) membrane.

PC was added to the PVC casting solution. Membranes with this structure might result in a higher pure water flux. In the case of the membrane blended with 3 wt% PC, most of the finger-like pores extended to the bottom of the membranes. It can be deduced that with an immiscible system such as PVC/PC (Neill and Karasz, 2000) a decrease in the interfacial adhesion could take place because of an increase in the dispersed phase content (Wu *et al.*, 2006). Following Wu *et al.* (2006) it could be explained that when the PC content is higher than 1.5 wt%, the larger volume of the PC dispersed phase would form leading to a wider distance between the PVC and PC phases. The finger-like pores would be formed under the skin layer and grow towards the bottom of the membrane.

The flux of pure water and rejection of BSA by membranes prepared from the casting solution with different composition are shown in Figure 2. The addition of PC to the PVC greatly improves the water flux of PVC. The pure water flux of the PVC/PC blend membrane increased from 9.7 to 147 L/m^2-h with the increase of the PC concentration from 0 to 3 wt%. The increase in the water flux is consistent with the structures observed in the SEM photographs.

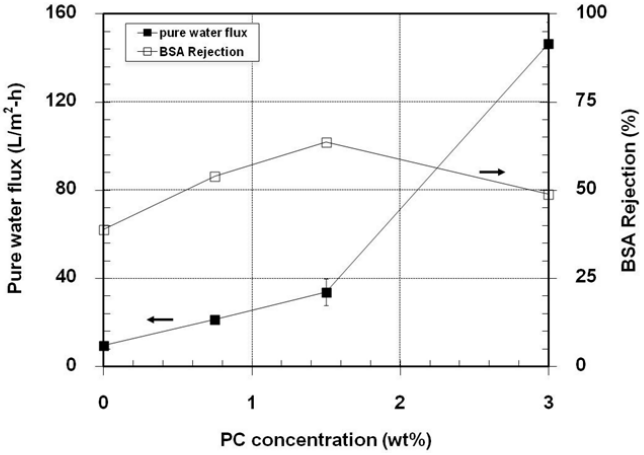

Figure 2. Pure water flux and BSA rejection of PVC/PC membrane as a function of PC content.

3.2 Effect of PC concentration on tensile properties

During the filtration process, an operating pressure is necessary to force the filtration substance through the porous membrane. The mechanical properties (tensile strengths and elongation at break of the membranes) were then studied and results are shown in Figure 3. The tensile strength (TS) slightly increased when PC was added to the PVC casting solution at a concentration of 0.75 wt%, and then TS decreased with the further increase of PC amount. The elongation of membranes was lower as an increase in amount of PC. A decrease in tensile properties might be due to the lack of interaction between the PVC and PC.

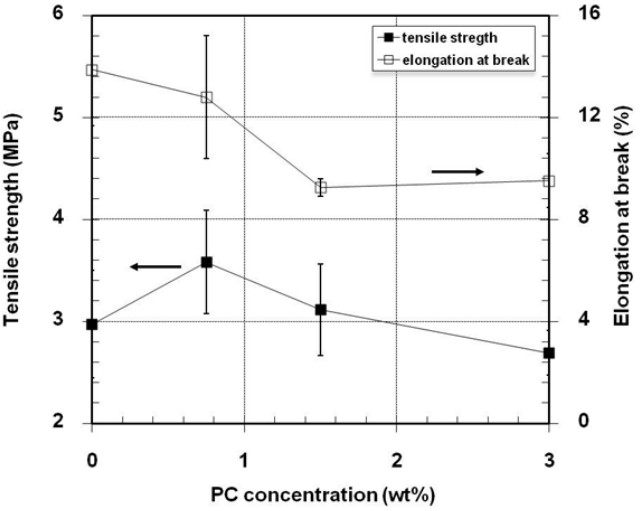

Figure 3. Mechanical properties of PVC/PC membrane as a function of PC content.

Membranes prepared from a casting solution with a PC content of 0.75 wt% had the highest mechanical strength, a higher pure water flux and BSA rejection compared with pure PVC membrane, the effects of adding different amounts of Pluronic F127 to this casting solution on the membrane performance were investigated .

3.3 Effect of Pluronic F127 on the hydrophilicity of a PVC/PC blend membranes

It is known that in the ultrafiltration process adsorption and deposition of protein on the membrane surface or in pores causes fouling (Huiman *et al.*, 2000; Ma *et al.*, 2000; Feng *et al.*, 2005). An increase in the membrane surface hydrophilicity can reduce membrane fouling. Several workers have used the water contact angle (WCA) measurement to study the hydrophilicity of membranes (Peng and Sui, 2006; Wang *et al.*, 2006; Zhao *et al.*, 2008).

Figure 4 shows the WCA as a function of the Pluronic F127 content. The hydrophobic character of the PVC/PC membrane (PC concentration of 0.75 wt %) is demonstrated by the high WCA (ca. 84°). Adding Pluronic F127 causes a decrease in the WCA to about 63°. These results indicated that the hydrophilicity of PVC membrane was greatly improved. The improvement of hydrophilicity could be attributed to the segregation of hydrophilic PEO units of Pluronic F127 on the membrane during membrane forming process, while hydrophobic PPO segments were trapped into PVC/PC membrane matrix (Wang *et al.*, 2006; Zhao *et al.*, 2008; Chen, *et al.*, 2009). This improvement of hydrophilicity implied that these membranes would have a higher permeability in the filtration process (Yu *et al.*, 2009).

3.4 Efect of Pluronic F127 on morphology, water content and transport properties of the blend membranes

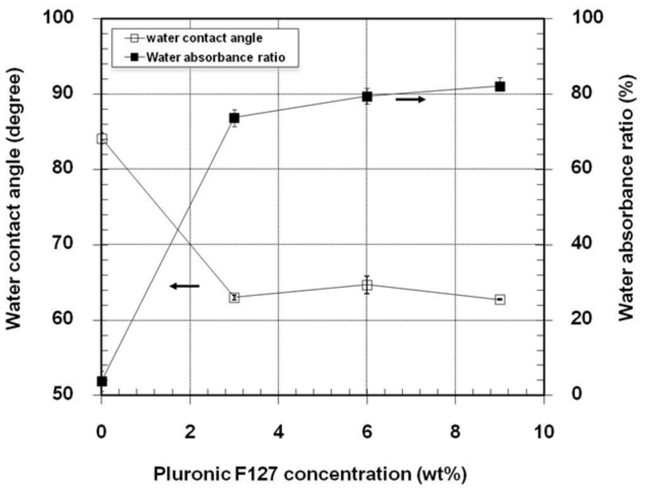

Figure 4. Water contact angle and water absorbance ratio of PVC/PC membrane as a function of Pluronic F127 content.

Figure 5 shows the SEM photographs of membranes prepared from the casting solution with different amounts of Pluronic F127. The blend membrane from casting the solution without pluronic F127 had a thick skin layer with a small size of the marcovoid wall (Figure 5(a)). In the presence of Pluronic F127 as shown in Figure 5(b)-(d), membranes had a thinner skin layer and larger macrovoid size. Membrane with this structure might provide a smaller resistance resulting in a higher pure water flux (Wu *et al.*, 2006). A similar finding was reported for CA/Pluronic F127 membranes (Lv *et al.*, 2007). The addition of Pluronic F127 into the casting solution results in a bigger volume of the marcovoid sub-layer due to leaching out of Pluronic F127 to the coagulant.

Measurements of the water content of the PVC control and PVC blend membranes showed that adding Pluronic F127 produced drastic changes in the water content of the blend membranes (Figure 4). WA increased from ca 4% to ca 82%. This can be explained by Pluronic F127 increasing the pore volume under the skin layer of the membrane (Figure 5). These pores could then fill with water (Lv *et al.*, 2007).

The variations in the pure water flux and rejection of BSA by the casting solution based on PVC/PC polymer at a PC concentration of 0.75 wt% containing Pluronic F127 at concentrations of 0, 3, 6 and 9 wt% are shown in Figure 6. Adding Pluroic F127 to the casting solution produced a much higher pure water flux and rejection of BSA rejection compared with PVC/PC membrane. The water flux value was only 21.5 L/m^{2}h for PVC/PC membrane and increased significantly to 506 L/m^{2}h with a Pluronic F127 content of 3 wt%. The increase in pure water flux could be explained by considering the SEM photographs. However, it was found that at a concentration of Pluronic F127 of 9 wt%, the pure water flux dramatically decreased. It was deduced that an increase in Pluronic F127 content to 9% might increase the viscosity of the casting solution and lead to thicker skin layer of the membrane formed by delayed phase inversion; see Figure 5 (e)-(f).

3.5 The effect of Pluronic F127 on anti-fouling properties of blend membrane

In order to study anti-fouling properties of the blended membranes, FRR was evaluated by using BSA as the protein model. The higher the FRR values the better are the anti-fouling properties of the membrane (Wang *et al.*, 2006). The values of FRR for all blend membranes increased with the presence of Pluronic F127 (Figure 7). This was due to the introduction of a hydrophilic PEO layer at the membrane surface, which agrees with water contact angle data. These results implied that casting a solution with Pluronic F127 provides for a reduction of the fouling and an improved flux recovery.

4. Conclusion

PC/PVC blend membranes were prepared simply by the immersion precipitation method. The blend membrane with a PC concentration of 0.75 wt% offered a higher pure water flux and higher mechanical strength when compared with a pure PVC membrane. By adding pluronic F127 to the PVC/PC based casting solution, the hydrophilicity of the

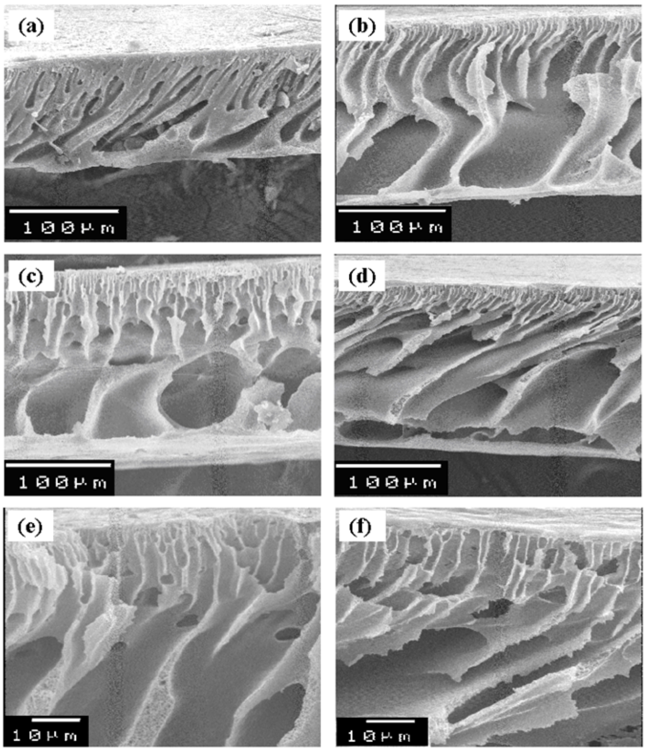

Figure 5. Cross-sectional SEM morphology of PVC-PC1 (a), PVC-PC1-Plu3 (b), PVC-PC1-Plu6 (c), and PVC-PC1-Plu9 (d) membrane. Magnification of upper layer of PVC-PC1-Plu3 (e), and PVC-PC1-Plu9 (f).

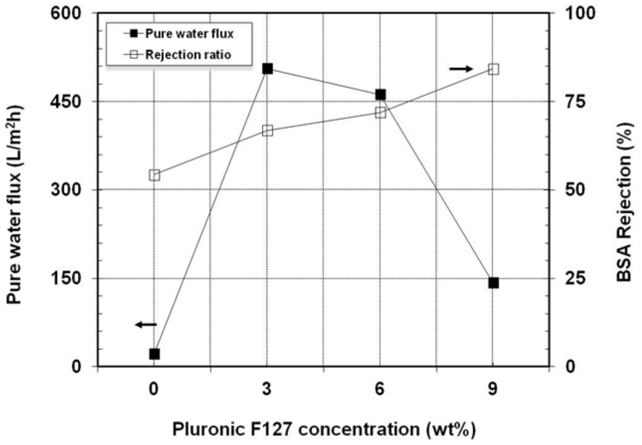

Figure 6. Pure water flux and BSA rejection of PVC/PC/Pluronic F127 membrane as a function of Pluronic F127 content.

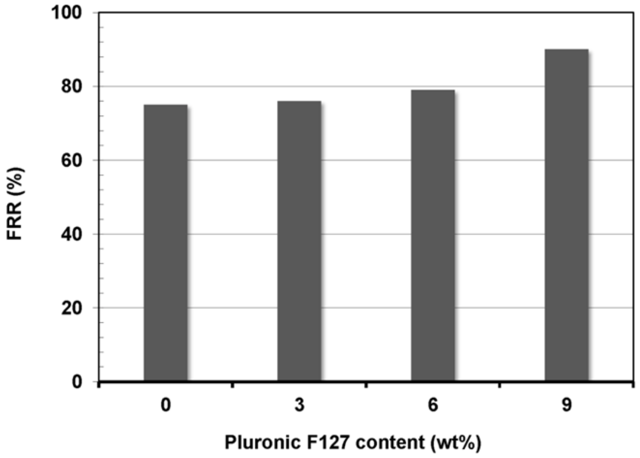

Figure 7. Flux recovery ratio as a function of Pluronic F127.

membranes was significantly increased. In addition, membranes with a larger macrovoid and a thinner skin layer were obtained that resulted in an enhancement of the pure water flux. An increase in the FRR of the membrane indicated that the PVC/PC based membranes containing Pluronic F127 could reduce the membrane fouling and improve their usefulness for applications for ultrafiltration.

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