Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20799

76 (2017) 148–154
May

Characterization of antioxidant incorporated polymeric blend membrane through *in situ* incorporation along with surface modification

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ABSTRACT

The 2,2′-methylenebis(6-tert-butyl-4-ethylphenol) (MBEP) is incorporated through *in situ* into a polymeric blend membranes of polysulfone (PSU) and waste polyethylene terephthalate (PET). These membranes are surface treated with 2,2′-ethylidenebis(4,6-di-tert-butylphenol) (EBBP). This study is carried out to evaluate the improvement in anti-fouling properties of membrane surface. Study on stability is carried along with different molecular weight cut-off (MWCO) polymer blends. The surface wettability of blend polymeric membranes with antioxidants was significantly improved. Further, flux studies and fouling experiments were carried out with effluent from textile industry. The stability of modified membranes was evaluated by immersion tests. The effluent was used as a model foulant to investigate the anti-biofouling performance of modified membranes. The results of stability tests showed that modified membranes had better mechanical and chemical stability.

Keywords: Waste polyethylene terephthalate; 2,2′-ethylidenebis(4,6-di-tert-butylphenol); 2,2′-methylenebis (6-tert-butyl-4-ethylphenol)

1. Introduction

In ultrafiltration (UF), membranes with pore size 0.1–0.001 µm are used for separation process. Phase separation is a common method for polymeric membrane preparation [1,2]. For developing new materials with preferable properties, blending of two different polymers can help [3]. Creating a membrane with fouling resistance characteristics is always a challenge to researchers working in separation techniques. The aim of all researchers is to synthesize a fouling resistant membrane through cost and energy effective method [4]. The foulants always exhibit hydrophobicity and they react strongly with membrane surfaces having hydrophobic in nature. During all studies, concentration was on making the membrane surface more hydrophilic and hence achieves reduction in fouling. Constant research in this area proved that the wettability can be improved by thin coating or incorporation of additive materials [5,6]. To keep the hydrophilicity of the resultant membrane, different methods like grafting, substitution, coating, etc are used. Using these methods chemical bonding of polymer chains of functional groups having hydrophilic nature was done on the surface of the membrane [2,7]. Polysulfone (PSU), being a polymer with good thermal and chemical properties, is widely used as a major base material for ultrafiltration membranes [8,9]. Polysulfone surface is hydrophobic and hence shows strong fouling characteristics [10]. This demands a modification in membrane process to improve its structure, hydrophilicity and cross section morphology [11]. None of these methods proved a permanent solution for introducing hydrophilic surface for longer duration. This was because of their low resistance to various chemicals and weak bonding with membrane structure. Blending of polymers of hydrophobic nature with various additives of hydrophilic nature will result in to membranes with high flux and good fouling resistance [12,13]. Such findings motivate researchers again and again to work in this area to achieve more hydrophilic surface for each and every membrane [14].

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1944-3994 / 1944-3986

The most important and critical problem in membrane science is fouling and hence reduction in flux as time moves during filtration. A catastrophic flux decline occurs on the membrane surface due to concentration polarization in early operation stage itself. Due to the deposition of protein particles or colloids on the surface of membrane or on the pores of the membrane an immediate decrease in flux occurs. Normally frequent membrane cleaning and shear rate control are the routine practices to remove the foulants [15]. But sometimes there may be adsorbed foulants, which are irreversible in nature, results internal fouling. Internal fouling is hard to be removed by either chemical or physical process. Because of these reasons materials and structures for preparation of membrane and membrane modifications are selected based on their resistance to fouling. But in practical it is very difficult and challenging to find out a fouling resistant membrane with high energy efficiency and value for money concept [3,4]. The blend of two different polymers imparts required characteristics to the resultant membranes and during this process, if some suitable additives were added; it will further enhance the desired properties [16–18]. Recently, different types of nanomaterials are being incorporated in the synthetic membranes to overcome the problem of fouling and to improve the performance of the membranes [19–23].

The present study is aimed to develop a fouling-tolerant hydrophilic membrane surface by incorporating antioxidant 2,2′-methylenebis(6-tert-butyl-4-ethylphenol) (MBEP) in polysulfone (PSU) and waste polyethylene terephthalate (PET) blend membranes. These membranes are surface treated with 2,2′-ethylidenebis(4,6-di-tert-butylphenol) (EBBP). The resultant membranes with best suitable molecular weight cut-off (MWCO) are expected to exhibit good fouling resistance and surface wettability. Further, to establish the use of waste polymer for preparing membranes with substantially good qualities.

2. Experimental

2.1. Membrane preparation

All the chemicals were procured from Sigma-Aldrich unless otherwise specified. The polysulfone (PSU)/ polyethylene terephthalate (PET) ultrafiltration membranes are prepared by phase inversion process. During membrane preparation process, antioxidant 2,2′-methylenebis(6-tert-butyl-4-ethylphenol) (MBEP) is incorporated *in situ* and 2,2′-ethylidenebis(4,6-di-tert-butylphenol) (EBBP) through surface modification. Continuous stirring is required for making the casting solution homogeneous. This homogenous casting solution is stored in refrigerator for 24 h [13]. Casting solutions with MBEP were cast into thin films of approximately 150 µm thick on Teflon sheets, and then the films were put into a water bath for gelation. Immediately after the gelation is complete, surface modification with EBBP is done by dipping the membrane in EBBP solution for 24 h. The membranes formed were again immersed in distilled water for 24 h to make sure of total phase separation and to remove water soluble components. Later the membranes were dried at room temperature and used for further characterization.

2.2. Membrane characterization

2.2.1. Stability of modified membranes and UV–Vis absorption spectra

Strong hydraulic back flushing is used to measure physical stability of membranes modified with antioxidants. Textile effluent is used to fill the cell. The membranes were kept upside down in the cell and the experiment is conducted at a pressure of 50 psi for approximately 10 min. Same experiment was repeated with pure water to measure the pure water flux [24,25]. In order to test the chemical stability of the surface coated antioxidant, chemicals like sodium hydroxide and hydrochloric acid were used. Membrane samples with and without antioxidant coating are treated with NaOH and HCl solution of pH between 12–14, and 1–4, respectively. Membrane samples were taken out once in 72 h and used for flux determination. The samples were again dipped into the chemical solution. Approximately two week is required for chemical stability studies. In order to evaluate the stability of the polymeric blend membrane with surface modification, immediately after *in situ* incorporation of antioxidant into the membrane UV-Vis absorption studies were done using Lambda 35 UV-Vis spectrophotometer (Perkin-Elmer, USA). Diffuser reflection helps to detect the absorption of antioxidant EBBP in to already modified membranes.

2.2.2. Contact angle

Optical instrument Pheonix 300 is used to measure the membrane surface contact angle. This study was carried out for understanding the hydrophilicity of membrane surface. Membrane samples, after proper drying, were kept on a planar plate. A syringe was used to drop drops of water [26]. Proper care has been taken to avoid spreading of water. A distance of 0.5 cm between tip-to-plate is kept fixed. Images from 5 different locations were taken and average of these values was used as final to assess the hydrophilic nature of the membrane.

2.2.3. Protein adsorption analysis

High fat content milk was used as a foulant to measure the fouling by protein adsorption. Protein absorbance is measured using a microscope (TE-2000, Nikon, Tokyo, Japan) [27]. Pieces of membrane were kept in such way that it will not get exposed to light and hence no chances of any decomposition. All images were taken in same environment with a maximum exposure time of 0.2 s.

2.2.4. Filtration experiments with emulsified oil

In order to study the flux variations due to oil content in effluent and oily water fouling, emulsified oil was used. Cross flow filtration system was used to perform filtration test. Membranes were stabilized by feeding deionized water on membranes mounted on the cell. Once the flux becomes constant, oil emulsion is used as feed solution. The entire experiment was conducted at 1 bar pressure and at room temperature for 1 h. The flux is defined by Eq. (1) and rejection by Eq. (2) [28]:

$$J_w = \frac{\Delta m}{\rho \cdot A \cdot \Delta t \cdot \Delta p} \tag{1}$$

where Δm, Δt, ρ, A and Δp are the permeate weight, filtration time, density of water, membrane area and applied pressure, respectively.

Oil rejection coefficient R was calculated using below equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_f and C_p are the oil concentration in feed and in the permeate.

2.2.5. MWCO calculation and pure water flux

The MWCO and pure water flux of the blend membranes were measured using the conventional cross flow apparatus [13]. Before experiments, the samples were kept in deionized water. Pure water flux details were measured at ambient temperature and at 1 bar pressure.

2.2.6. Scanning electron microscopic studies

Using Philips scanning electron microscope (SEM), morphology of membranes was studied. Small membrane pieces were cleaned and subjected to nitrogen environment, until it gets frozen [28]. Samples were dried and gold sputtered for producing electric conductivity. Images were taken at high vacuum conditions.

2.2.7. Pore statistics

Using milk water of different molecular weights, pore statistics of membrane was calculated. Below equation is used to calculate average pore size of the resultant membrane [29–31]:

$$\bar{R} = 100\left(\frac{\alpha}{\%R}\right) \tag{3}$$

where $\bar{R}$ is average radius of pore and α is average radius of solute. Using Eq. (2) solute rejection (R) can be calculated keeping C_p as permeate concentration and C_f as the feed concentration. Solute radius$_{\text{avg}}$ (Stokes radii) can be calculated by plotting molecular weight of solute to radius of solute [29]. Normally the membrane skin layer takes part in separation process effectively. Based on this concept, the surface porosity, ε, is calculated as below [29]:

$$\varepsilon = \frac{3\pi\mu J_w}{\Delta P \bar{R}} \tag{4}$$

where μ is viscosity of permeate water (Pa s), J_w is flux (m^3/m^2 s), ΔP is trans-membrane pressure (Pa) and $\bar{R}$ is the average radius of membrane pore (Å).

2.2.8. Equilibrium water content

Extent of hydrophobicity or hydrophilicity of a membrane can be predicted from equilibrium water content (EWC) values. The EWC also have a direct linkage with membrane porosity. Because of this, equilibrium water content is considered as a major parameter for membrane characterization [30]. For this, the wet membrane surface was cleaned and then weighed. The wet membrane is weighed after drying in an oven at about 60°C for 24 h. The EWC at ambient conditions is defined as [31–34]:

$$EWC(\%) = \frac{\text{Wet membrane weight} - \text{Dry membrane weight}}{\text{Wet membrane weight}} \times 100 \tag{5}$$

2.2.9. Chemical oxygen demand

Chemical oxygen demand (COD) was evaluated by standard method 5220D used for determining COD of water and effluent. UV-Vis spectroscopy based on different wavelengths was used for COD estimation.

3. Results and discussion

3.1. Stability of modified membranes

In order to assess the life and strength of incorporation or coating, stability test was conducted. To test the mechanical strength of the modified membranes, hydraulic washing in reverse direction, was carried out at a pressure of 50 psi for 10 min. The specific flux value before and after back flush were compiled in Table 1. No significant change is observed in specific flux even after 10 min back flush for antioxidant incorporated membranes. The antioxidant molecules are covalently immobilized on the membrane surface and inside the pore structure through a possible reaction between the nucleuses of the material. The synthesized membranes are found to be stable to resist the hydraulic pressure in back-flushing experiments. It is observed that antioxidant incorporated membranes are capable to block the hydraulic pressure even at 50 psi.

Further the chemical stability was also studied by soaking in different chemicals like sodium hydroxide and hydrochloric acid solutions. Specific flux values with time are shown in Table 2. The more the contact with the chemicals, the more the fluxes of antioxidant added membrane samples. The relation with soaking time is more evident

Table 1
Specific flux values of membranes before and after back flush

Membrane	Specific flux (L/m^2 h bar) before back-flush	Specific flux (L/m^2 h bar) after back-flush
PSU/PET	240	215
PSU/PET:EBBP	52	50
PSU/PET:EBBP/MBEP	18	16.8

Table 2
Contact angle – with and without antioxidant incorporated membranes

Membrane	Contact angle (°)
PSU/PET	52.8
PSU/PET/MBEP	21.2
PSU/PET/MBEP:EBBP	16.6

with hydrochloric acid and sodium hydroxide. Membrane samples soaked in sodium hydroxide solution shows an increase in flux value for membranes modified with antioxidants. Further, UV-Vis absorbance of membrane with and without antioxidant is carried out. Fig. 1 shows that the stability increases on addition of antioxidants to the membrane. The increase clearly indicates that polymer blend membrane with both the antioxidants is mechanically and thermally more stable. Initial results of OIT tests also support the brilliant thermal stability of these membranes [13].

3.2. Contact angle

From Table 2, it is evident that contact angle of doubly modified membranes are much lower than that of unmodified membranes establishing the fact that presence of antioxidants in membrane can reduce the contact angle. The contact angle value of PSU/PET membrane is 52.8 and when MBEP is introduced it falls to 21.2 and further on the addition of EBBP to it, the value reaches to 16.6. Antioxidants chains are distributed on the blend membrane surface and hence the contact angle will decrease on the addition of antioxidants. It is observed that contact angle decreases on increase of antioxidant content in it and hence results to a membrane with higher hydrophilicity. Contact angle is related with surface energy in such a way that surface energy is higher if the contact angle values are less.

3.3. Specific flux

Table 3 presents the specific flux values of unmodified and modified membranes for pure water. It can be clearly seen that, although PSU/PET membranes have slightly larger pore size than the PSU/PET membrane modified with antioxidants, the flux reduction of modified membrane was highly remarkable. The PSU/PET membrane modified with *in situ* MBEP has a relative flux reduction of approximately 80–85% for membrane modified via *in situ* and surface is having approximately 90–95%, while membrane without any modification is having very low, i.e. approximately 20%–25%. Incorporation of antioxidant into membrane increases relative flux reduction marginally. Same trend was observed in earlier studies also [13,35,36]. It may be because of the presence of antioxidants in the pore structure of membrane. This leads to high membrane resistance. Due to *in situ* addition of MBEP, the MBEP particles have been deposited on the pore structure of the membrane and due to the surface treatment, EBBP get deposited on the membrane surface or the pore entrances.

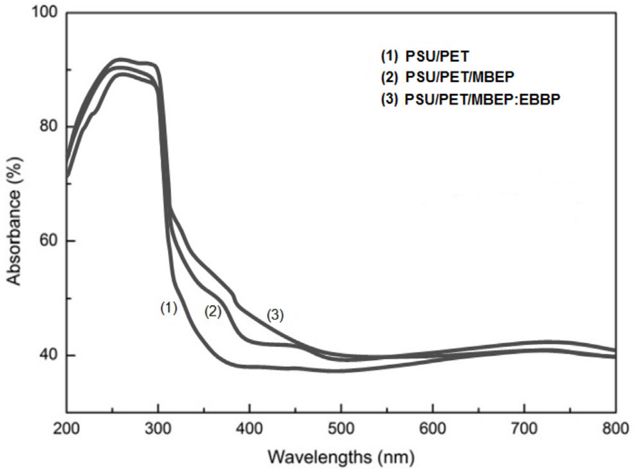

Fig. 1. The UV-VIS absorbance of: 1) PSU/PET membrane, 2) PSU/PET/MBEP membrane and 3) PSU/PET/MBEP:EBBP membrane.

Table 3
Chemical stability test – specific flux with time for with and without antioxidant incorporated membranes

Membrane	Solution	Time (d)	Specific flux (L/m^2 h bar)
PSU/PET/MBEP:EBBP	Sodium hydroxide	0	56
		3	58
		6	60
		9	66
		12	61
	Hydrochloric acid	0	56
		3	60
		6	63
		9	63
		12	61
PSU/PET/MBEP	Sodium hydroxide	0	53
		3	55
		6	56
		9	57
		12	55
	Hydrochloric acid	0	53
		3	49
		6	51
		9	50
		12	51
PSU/PET	Sodium hydroxide	0	25
		3	39
		6	40
		9	43
		12	41
	Hydrochloric acid	0	23
		3	22
		6	21
		9	21
		12	21

3.4. Emulsified oil filtration

The major hurdle in all industry is separation of oily water and the methodologies used for it. The membrane fouling is the main constraint for economically feasible membrane separation process for waste water with oil. Emulsified oil is a common foulant that reduces the separation efficiency of membrane. It forms a dense oily layer on the surface of the membrane during filtration. Fouling can be reduced to some extent by creating and maintaining a hydrophilic surface. The fouling tolerance and rejection properties of synthesized membranes were calculated using emulsified oil. The oil rejections in antioxidants incorporated membranes were found to be higher when compared with PSU/PET membrane. Oil rejection data are mentioned in Table 4. Oil content coefficient increases from 94.4% of PSU/PET membrane without antioxidant to 96.6% with MBEP as antioxidant and to 97.1% with MBEP and EBBP in system. These values clearly indicate that oil content rejection is higher for antioxidant incorporated membranes.

Table 4
Oil rejection values of PSU/PET membranes with and without antioxidants

Membrane	PWF (L/m^2 h bar)	Oil rejection R (%)
PSU/PET	8	94.5
PSU/PET/MBEP	114	96.6
PSU/PET/MBEP:EBBP	152	97.1

3.5. Morphological studies

The surface and cross sectional SEM images given in Fig. 2. Fig. 2a,b,c indicate surface morphology and Fig. 2d,e,f indicate the cross sectional morphology. The surface

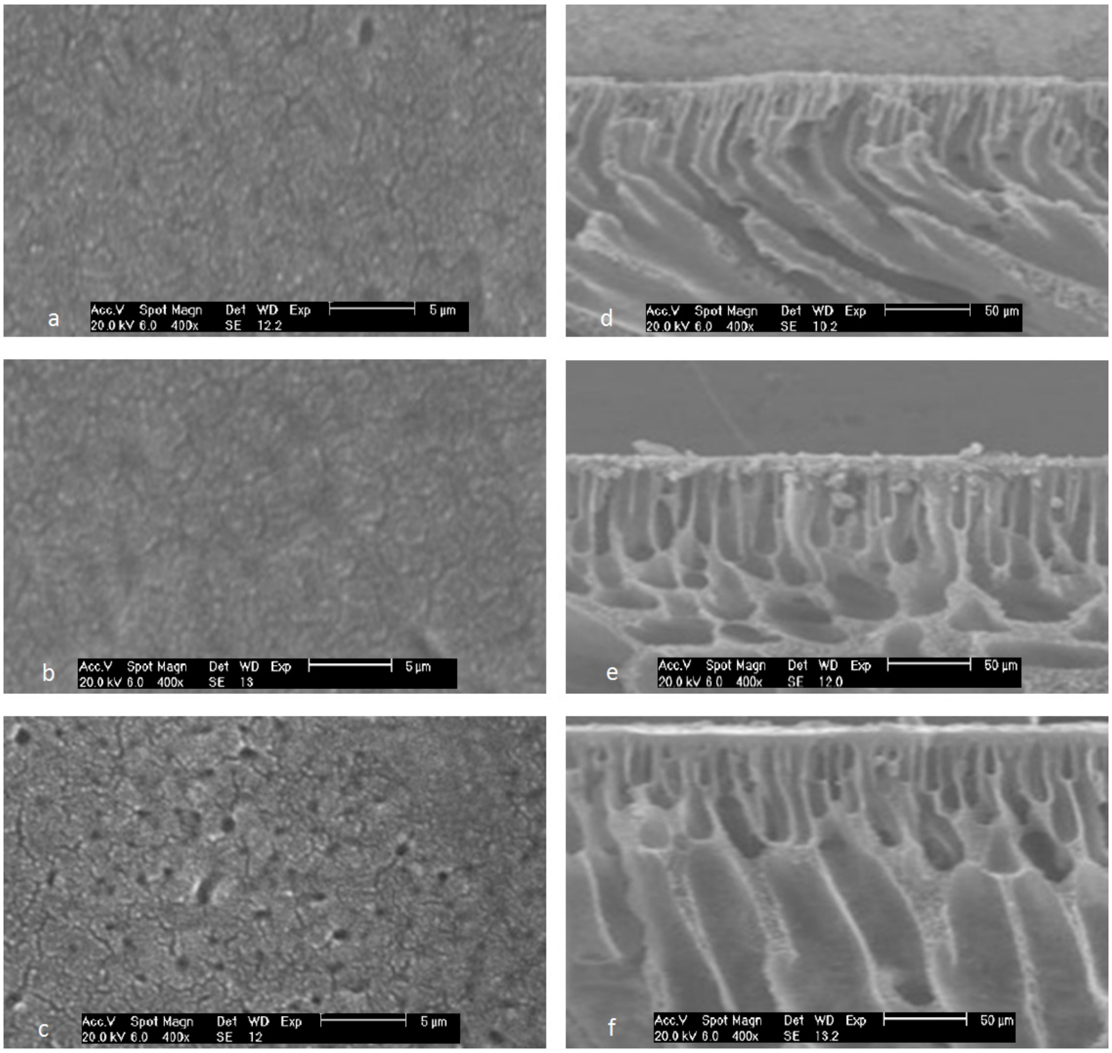

Fig. 2. SEM images of surfaces and cross sections: 2(a,b,c) surface morphology of (a) PSU/PET membrane, (b) PSU/PET/MBEP membrane and (c) PSU/PET/MBEP:EBBP membrane and 2(d,e,f) Cross sectional morphology of (d) PSU/PET membrane, (e) PSU/PET/MBEP membrane and (f) PSU/PET/MBEP:EBBP membrane.

morphology changed more due to surface modification with antioxidant EBBP than *in situ* incorporation of antioxidant. PSU/PET/MBEP membranes show a skin layer and a porous sublayer. Basically, it exhibits asymmetric structure. These structures consist of a skin and highly porous sublayer. Thickness of skin layer reduces and becomes further thinner on incorporation of antioxidants in to the membranes. Macrovoid size in porous sublayer exhibits same trend. Finger-like structures formed due to *in situ* incorporation of MBEP in the membrane. Changed membrane morphology resulted into high water flux.

3.6. Average pore size

The average pore sizes were calculated and compiled in Table 5. The results indicate that the membrane without antioxidant in it shows smaller pore size. The PSU/PET membrane without any antioxidant had an average pore size of 40 Å. The average pore size increases from 40 to 52 Å on *in situ* incorporation of MBEP. The values of average pore size further increases to 66 Å, due to the introduction of EBBP to the already MBEP added membrane structure.

3.7. Porosity

The values compiled in Table 5 show that the membrane without any antioxidant is having low porosity value, i.e., 0.8×10^{-4} and the porosity increases to 1.3×10^{-4} on incorporation of MBEP antioxidant into it. The values of porosity further increase to 2×10^{-4} on surface treatment with EBBP to the MBEP pre-treated membrane structure.

The introduction of antioxidants into the membranes may favour in the formation of pores with increased size. Increased pore size and porosity ultimately lead to increase in permeate flux. This is because large pore size always helps to increase permeate flux and reduce rejection of solute. Practically speaking membranes with large number of pores are preferred for all applications. This is because small sized pores help to increase retention and more pores will support better flux for permeate.

3.8. Equilibrium water content

To get an idea of hydrophilicity and flux pattern of membrane equilibrium water content (EWC) is estimated. The values of equilibrium water content are compiled in Table 6. The values indicate that there is marginal increase occurs due to the addition of antioxidants to the membrane. The PSU/PET membrane without any antioxidant is having equilibrium water content as 78% while it is noted as 85% for MBEP added membrane and 92% for MBEP added and EBBP coated membrane.

This clearly indicated the effect of leachability of water soluble antioxidants incorporation in larger pores formation. These values give an indication of water molecules fraction present in the membrane pores. And increased water content results more porous membrane.

Table 5
Average pore size and porosity of PSU/PET membranes with and without antioxidants

Membrane	Average pore size (Å)	Porosity × 10^4 (%)
PSU/PET	40	0.8
PSU/PET:EBBP	52	1.3
PSU/PET:EBBP/MBEP	66	2.0

3.9. Chemical oxygen demand of permeate

Oil rejection coefficient and COD data are compiled in Table 7. The COD values reduce from 85.5 to 67.8 ppm on addition of MBEP and further reduce to 55.5 ppm on the introduction of EBBP to the system. All the values are less than 100 ppm, preferred and prescribed by the law.

4. Conclusions

PSU/PET blended asymmetric ultrafiltration membranes were subjected to modification with *in situ* antioxidant MBEP incorporation as well as surface modification with antioxidant EBBP. The hydrophilicity, stability and anti-fouling of modified membranes were investigated. The membrane surface roughness significantly increased in membranes which show presence of antioxidant at the surface of the membrane. The results of stability tests indicated that PSU/PET membrane with both antioxidants is exhibiting more mechanical stability through intensive hydraulic back-flushing. The modified membranes exhibited much better chemical stability to acid and alkali solution. The membrane modifications of *in situ* incorporation and surface modification substantially improved the hydrophilicity of membranes. COD values and oil rejection of permeate clearly indicate that the membranes perform well even after incorporation of antioxidants to it. These clearly indicate that incorporation of antioxidant resulted membranes samples with more applica-

Table 6
Equilibrium water content of PSU/PET membranes with and without antioxidants

Membrane	Equilibrium water content (%)
PSU/PET	78
PSU/PET:EBBP	85
PSU/PET:EBBP/MBEP	92

Table 7
Permeate quality of PSU/PET membranes with and without antioxidants

Membrane	COD (ppm)
PSU/PET	85.5
PSU/PET:EBBP	67.8
PSU/PET:EBBP/MBEP	55.5

tions in industrial operations. Water flux was significantly improved. Further it is obvious from the results that the water flux is inversely proportional to solute rejection. The PSU/PET/MBEP:EBBP blend membranes are having excellent resistance to fouling especially to oil containing water. This clearly gives hope to a promising energy efficient material with excellent separation characteristics for purifying industrial effluent. Such membrane synthesis methodology needs to be studied thoroughly with more characterization to come up with more feasible and viable materials and process.

References

[1] R.W. Baker, Membrane Technology and Applications, McGraw-Hill, New York, 2000.

[2] Y.H. Cho, H.W. Kim, S.Y. Nam, H.B. Park, Fouling-tolerant polysulfone–poly (ethylene oxide) random copolymer ultrafiltration membranes, J. Membr. Sci., 379 (2011) 296–306.

[3] M. Zeng, Z. Fang, C. Xu, Effect of compatibility on the structure of the microporous membrane prepared by selective dissolution of chitosan/synthetic polymer blend membrane, J. Membr. Sci., 230 (2004) 175–181.

[4] A.D. Marshall, P.A. Munro, G. Tragardh, The effect of protein fouling in microfiltration and ultrafiltration on permeate flux, protein retention and selectivity: a literature review, Desalination, 91 (1993) 65–108.

[5] M. Ahmad, F.A.A. Aleem, A. Mutiri, A. Ubaisy, Biofouling in RO membrane systems part 1: fundamentals and control, Desalination, 132 (2000) 173–179.

[6] J. Weia, G.S. Helma, N. Corner-Walkera, X. Houb, Characterization of a nonfouling ultrafiltration membrane, Desalination, 192 (2006) 252–261.

[7] H. Ju, B.D. McCloskey, A.C. Sagle, V.A. Kusuma, B.D. Freeman, Preparation and characterization of crosslinked poly(ethylene glycol) diacrylatehydrogels as fouling-resistant membrane coating materials, J. Membr. Sci., 330 (2009) 180–188.

[8] S. Wu, Polymer Interface and Adhesion, Chapman and Hall, London, 1987.

[9] Y.H. Cho, H.W. Kim, S.Y. Nam, H.B. Park, Fouling-tolerant polysulfone–poly (ethylene oxide) random copolymer ultrafiltration membranes, J. Membr. Sci., 379 (2011) 296–306.

[10] A. Urkiaga, D. Iturbe, J. Etxebarria, Effect of different additives on the fabrication of hydrophilic polysulfone ultrafiltration membranes, Desal. Water Treat., 56 (2015) 3415–3426.

[11] S. Mok, D.J. Worsfold, A. Fouda, T. Matsuura, Surface modification of polyethersulfone hollow fiber membranes by γ-ray irradiation, J. Appl. Polym. Sci., 51 (1994) 193–199.

[12] H. Ju, B.D. McCloskey, A.C. Sagle, V.A. Kusuma, B.D. Freeman, Preparation and characterization of crosslinked poly(ethylene glycol) diacrylatehydrogels as fouling-resistant membrane coating materials, J. Membr. Sci., 330 (2009) 180–188.

[13] S. Rajesh, Z.V.P. Murthy, In situ synthesis and characterization of 2,2′-methylenebis (6-tert-butyl-4-ethylphenol) incorporated polymeric membranes, Adv. Polym. Technol., 33 (2014) 21392.

[14] A.K. Nair, P.M. Shalin, P.E. JagadeeshBabu, Performance enhancement of polysulfone ultrafiltration membrane using TiO$_2$ nanofibers, Desal. Water Treat., 57 (2016) 10506–10514.

[15] K. Ruengruehan, P. Fagkaew, G. Ahn, S. Kang, S.O. Ko, Relating membrane surface properties and flux recovery during the chemical cleaning of forward osmosis membrane, Desal. Water Treat., 57 (2016) 26621–26628.

[16] Y. Zhang, R. Lin, M. Yuan, X. Yue, Effects of pore-forming additives on structures and properties of PVDF/Fe^{3+}/Cu^{2+} hollow fiber membranes, Desal. Water Treat., 51 (2013) 3903–3908.

[17] F. Ma, H. Ye, Y.Z. Zhang, X.L. Ding, L.G. Lin, L. Zhao, H. Li, The effect of polymer concentration and additives of cast solution on performance of polyethersulfone/sulfonated polysulfone blend nanofiltration membranes, Desal. Water Treat., 54 (2014) 618–625.

[18] V. Ghaffarian, S.M. Mousavi, M. Bahreini, H. Chamani, Poly (butylene succinate)/polyethersulfone/poly (ethylene glycol) membrane: influence of additive molecular weight and concentration on morphology, properties, and performance of the membrane, Desal. Water Treat., 57 (2016) 16800–16809.

[19] S.A. Aani, C.J. Wright, M.A. Atieh, N. Hilal, Engineering nanocomposite membranes: Addressing current challenges and future opportunities, Desalination, 401 (2017) 1–15.

[20] J.H. Jhaveri, Z.V.P. Murthy, A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes, Desalination, 379 (2016) 137–154.

[21] J.H. Jhaveri, Z.V.P. Murthy, Nanocomposite membranes, Desal. Water Treat., 57 (2016) 26803–26819.

[22] Y. Manawi, V. Kochkodan, M.A. Hussein, M.A. Khaleel, M. Khraisheh, N. Hilal, Can carbon-based nanomaterials revolutionize membrane fabrication for water treatment and desalination?, Desalination, 391 (2016) 69–88.

[23] J.H. Jhaveri, C.M. Patel, Z.V.P. Murthy, Preparation, characterization and application of GO-TiO$_2$/PVC mixed matrix membranes for improvement in performance, J. Ind. Eng. Chem., DOI: 10.1016/j.jiec.2017.03.035 (Available Online).

[24] S.S. Madaeni, A. Rahimpour, J. Barzin, Preparation of polysulphone ultrafiltration membranes for milk concentration: effect of additives on morphology and performance, Iran. Polym. J., 14 (2005) 421–428.

[25] D. Rana, T. Matsuura, Surface modifications for antifouling membranes, Chem. Rev., 110 (2010) 2448–2471.

[26] F. Li, J. Meng, J. Ye, B. Yang, Q. Tian, C. Deng, Surface modification of PES ultrafiltration membrane by polydopamine coating and poly(ethylene glycol) grafting: Morphology, stability and anti-fouling, Desalination, 344 (2014) 422–430.

[27] M.M. Bradford, A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding, Anal. Biochem., 72 (1976) 248–254.

[28] P.T.P. Aryanti, Khoiruddin, I.G. Wenten, Influence of additives on polysulfone-based ultrafiltration membrane performance during peat water filtration, J. Water Sustain., 3 (2013) 85–96.

[29] A. Nabe, E. Staude, G. Belfort, Surface modification of polysulfone ultrafiltration membranes and fouling by BSA solutions, J. Membr. Sci., 133 (1997) 57–72.

[30] J.A. Raguime, G. Arthanareeswaran, P. Thanikaivelan, D. Mohan, M. Raajenthiren, Performance characterization of cellulose acetate and poly(vinylpyrrolidone) blend membranes, J. Appl. Polym. Sci., 104 (2007) 3042–3049.

[31] M.N. Sarbolouki, A general diagram for estimating pore size of ultrafiltration and reverse osmosis membranes, Sep. Sci. Technol., 17 (1982) 381–386.

[32] G. Arthanareeswaran, D. Mohan, M. Raajenthiren, Preparation, characterization and performance studies of ultrafiltration membranes with polymeric additive, J. Membr. Sci., 350 (2010) 130–138.

[33] B. Chakrabarty, A.K. Ghoshal, M.K. Purkait, Effect of molecular weight of PEG on membrane morphology and transport properties, J. Membr. Sci., 309 (2008) 209–221.

[34] Y. Su, X. Jian, S. Zhang, C. Yan, Preparation of novel PPES-B UF membrane with good thermal stability: the effect of additives on membrane performance and cross-section morphology, J. Membr. Sci., 271 (2006) 205–214.

[35] S. Rajesh, Z.V.P. Murthy, Ultrafiltration membranes from waste polyethylene terephthalate and additives: synthesis and characterization, Quím. Nova, 37 (2014) 653–657.

[36] S. Rajesh, Z.V.P. Murthy, PSU/PET copolymer based asymmetric polymeric membranes: influence of antioxidant, Desal. Water Treat., 57 (2016) 26820–26829.