Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1084597

57 (2016) 16800–16809
August

Taylor & Francis
Taylor & Francis Group

Poly (butylene succinate)/polyethersulfone/poly (ethylene glycol) membrane: influence of additive molecular weight and concentration on morphology, properties, and performance of the membrane

Vahideh Ghaffarian[a,b,*], Seyed Mahmoud Mousavi[a], Masoumeh Bahreini[c], Hooman Chamani[a,b]

[a]*Faculty of Engineering, Department of Chemical Engineering, Ferdowsi University of Mashhad, Mashhad, Iran, Tel./Fax: +98 511 8942504; emails: va.ghafarian.87@alumni.um.ac.ir (V. Ghaffarian), mmousavi@um.ac.ir (S.M. Mousavi), hooman.chamani@alumni.um.ac.ir (H. Chamani)*
[b]*Research Center of Membrane Processes and Membrane, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran*
[c]*Faculty of Science, Department of Microbiology, Ferdowsi University of Mashhad, Mashhad, Iran, email: mbahreini@um.ac.ir*

Received 19 January 2015; Accepted 12 August 2015

ABSTRACT

In the present study, characteristics of poly (butylene succinate) (PBS)/polyethersulfone (PES)/poly (ethylene glycol) (PEG) membrane were described in terms of the presence of hydrophilic and biodegradable additive of PEG in two different levels for concentration and molecular weight. The membranes were prepared using immersion precipitation technique at two coagulation bath temperatures (CBT) of 0 and 25°C. Experiments showed that the examined levels for PEGs changed the membrane morphology in both surface and cross-sectional structures. Moreover, the presence of PEGs improved the final membrane wettability, tensile strength, and biodegradability. According to Fourier transform infrared analysis, no chemical bond was formed between PEG and PBS/PES. The variations of the membrane morphology affected the fluxes for both pure water and wastewater. As a result, the highest fluxes were obtained for the membrane with 7 wt.% of PEG400 prepared at CBT of 25°C.

Keywords: Blend; Membrane; Biodegradable; Morphology; Hydrophilicity

1. Introduction

The preparation of partially biodegradable materials by the addition of a biodegradable component to synthetic polymers was recommended by Griffin [1]. Generally, the blends of biodegradable polymers and non-biodegradable ones are of particular significance as the blend can combine biodegradability with good processability and mechanical resistance [2].

Membrane technology is now considered as a promising separation tool in various industrial processes such as food, pharmaceutical and biotechnological industries; pure water production; and water and wastewater treatment [3]. The main materials for membrane preparation are still polymers due to their suitable properties [3]. Thus, the usage of biodegradable polymers in field of membrane seems to be necessary, as the biodegradable membranes can be well discarded to the environment after passing the service life. It can be expected that these types of novel

---

*Corresponding author.

1944-3994/1944-3986 © 2015 Balaban Desalination Publications. All rights reserved.

membranes can be an interesting alternative to the common membranes, such as cellulose acetate (CA), polysulfone (PSf), and polyethersulfone (PES), if the final membrane is suitably comparable in different specifications such as mechanical properties, permeability, and selectivity. There are some limited studies on using the biodegradable polymers for membrane preparation [4–7].

With the aim of applying the poly (butylene succinate) (PBS) as a biodegradable polymer for the preparation of environmentally friendly membranes, its blend membranes with CA and PES were prepared and characterized in our previous studies [8–10]. According to the poor mechanical properties of PBS [11], blending technique was suggested. Moreover, by changing the blend ratio, comparison between different characteristics of the blend membranes and membranes of CA and PES was done. The addition of these two amorphous polymers to semi-crystalline PBS reduced the final membrane crystallinity, increased the mixture solvency, facilitated the membrane formation, and noticeably enhanced the final membrane tensile strength. However, at a constant blend ratio, the above improvements, especially the tensile strength one, were more considerable for the PES blend membranes in comparison with the CA ones.

Desiring on further modification and obtaining a high-performance membrane, in the present study, poly (ethylene glycol) (PEG) was added to the PBS/PES blend. PEG, besides the other materials such as polyvinylpyrrolidone, lithium chloride, and glycerol has been commonly used as an additive in the membrane preparation [12]. However, due to PEG's biodegradability [13], it is expected that the final membrane biodegradation is retained or even improved. Thus, the effects of CBT and also concentration and molecular weight of PEG were evaluated on the final membrane cross-sectional and surface structure, tensile strength, hydrophilicity, biodegradablility, and performance.

2. Materials and methods

2.1. Materials

PBS extended with 1,6-diisocyanatohexane was purchased from Sigma-Aldrich. PES was supplied from BASF company. PEGs ($M_w = 400$ and 20,000) were obtained from Merck and used as additive for the casting solutions. 1-methyl-2-pyrrolidone (NMP) was supplied from Merck to use as a solvent. Distilled water was used as a coagulant and also for the permeation test. Furthermore, the food wastewater was sampled from a local factory for the treatment experiments.

2.2. Membrane preparation

For all prepared membranes, total polymer concentration of the PBS/PES blend and also the blend ratio were fixed at 17% and 70/30, respectively. For the membrane preparation, PES was initially dissolved in NMP. Then, PBS was added into the casting solution. Finally, PEG additive (400 or 20,000) was added to the PBS/PES solution and mixed completely using a mechanical stirrer. The casting solution was spread on a glass plate with the help of a film applicator. Then, the casted film was moved to the non-solvent bath of distilled water for immersion–precipitation. The prepared membranes were finally dried in a vacuum oven. The composition of the casting solutions besides the applied CBT for preparation of the membranes is presented in Table 1.

2.3. Membrane characterization

Cross-sectional and surface morphologies of the membranes were observed by scanning electron microscopy (SEM) using a KYKY-EM3200 scanning microscope. The membranes were frozen in liquid nitrogen, broken, and sputtered with gold before SEM analysis.

Fourier transform infrared (FTIR) spectra were collected by Thermo Nicolet Avatar 370 FTIR (USA). The analysis was performed at the wave number range of 400–4,000 cm^{-1} by scanning 32 times.

To examine the wetting characteristics of the membranes, the contact angle between deionized water and the membrane surface was determined using contact angle measuring instrument of G10, KRUSS (Germany). The contact angle was measured at least three random positions on each membrane sample and the mean value was reported.

Table 1
Membrane preparation conditions

Membrane	PEG (M_w)	PEG (wt.%)	CBT (℃)
M1	–	–	25
M2	400	7	25
M3	400	15	25
M4	400	7	0
M5	400	15	0
M6	20,000	7	0
M7	20,000	15	0

Tensile testing was conducted with Zwick tensile machine at a cross head speed of 1 mm/min. Each measurement was performed on three separate samples and the average value was reported.

The membrane biodegradability was investigated by measuring its weight loss during the burial test in compost. Each specimen was buried in compost and incubated at temperature of 30°C. The compost was kept wet by supplying water every 3 d. Each sample was taken out of the compost after specified time, washed with water, dried at 37°C for 24 h in an oven, and then weighted. Digital pictures of the biodegraded membranes were taken by a digital camera (DSC-HX100V, Sony, Japan).

Performance of the prepared membranes was characterized by measuring pure water flux (PWF), wastewater flux, and rejection of pollution indices. The bread wastewater was used as feed. The experiments were conducted using a laboratory-scale flat sheet filtration system. The PWF and wastewater flux were evaluated at trans-membrane pressure of 3 bars and room temperature. Three pollution indices of turbidity, total dissolved solids, and chemical oxygen demand were determined in the feed and permeate streams for calculation of their rejections.

3. Results and discussion

3.1. SEM studies of the prepared membranes

Figs. 1 and 2 depict the cross-sectional and surface SEM images of the PBS/PES/PEG membranes, respectively. These figures show the effect of PEG concentration and molecular weight as well as CBT on morphology of the membranes. As observed from the SEM images:

(1) Increasing the PEG400 concentration from 0 to 7 wt.% caused the formation of a membrane with more open structure and higher thickness. Further increasing the PEG400 concentration from 7 to 15 wt.% decreased the membrane thickness.
(2) The addition of 7 wt.% PEG400 to the PBS/PES membrane reduced the size of the membrane surface pores while the pore number at the surface was increased. Although more increase in PEG400 concentration slightly reduced the membrane surface porosity, a number of large pores could be seen at the membrane surface.
(3) Reducing CBT and also increasing the molecular weight of PEG from 400 to 20,000 resulted in decreasing the membrane porosity.

3.1.1. Effect of PEG400 concentration

When a casting solution containing PBS, PES, and 7 wt.% PEG400 is immersed in the coagulation bath, phase separation process is started. PEG400 has almost low molecular chain length and consequently good mobility which results in its movement to the lean polymer phase of the membrane surface along with the solvent outflow. Therefore, the aggregated PEG molecules are uniformly dispersed on the membrane surface causing the formation of more porous surface [12]. In other words, the presence of PEG molecules at the surface facilitates the diffusion of water molecules to the casted film during the immersion step in the coagulation bath, which consequently becomes a point for pore formation [14].

It should be also mentioned that PEG is a hydrophilic additive with non-solvent properties which means to have high and low affinity to the solvent (NMP) and polymer (PBS and PES), respectively. Accordingly, the PEG presence increases thermodynamic instability of the casted film and thereupon improves the demixing rate or in other words, the precipitation rate of the membrane in the coagulation bath. The direct effect of acceleration of precipitation is the formation of a porous membrane with higher thickness [14].

From other point of view, the presence of PEG enhances the viscosity of the casting solution due to higher molecular weight of PEG than that of NMP and also the inter- and intra-molecular aggregation or entanglements of the polymer chains in the presence of PEG [15]. For more viscose casting solutions, the diffusional exchange rate between the solvent and non-solvent is reduced during the solidification process which is followed by reducing the membrane porosity and thickness [15].

As a result, the addition of PEG can have the dual effect on the membrane morphology. It can increase the membrane porosity due to intensification of thermodynamic instability of the casting solution. On the other hand, its presence may lead to the formation of denser structure because of increasing the casting solution viscosity. The parameters that can govern the final structure by dominating one of the above effects are the molecular weight and also the concentration of PEG in the casting solution.

With respect to Figs. 1 and 2, for the membranes prepared at CBT of 25°C, the addition of 7 wt.% PEG400 increased the membrane porosity which refers to increasing the thermodynamic instability of the casting solution and also the movement of PEG400 molecules toward the film surface during the immersion step. However, as the PEG400 concentration was

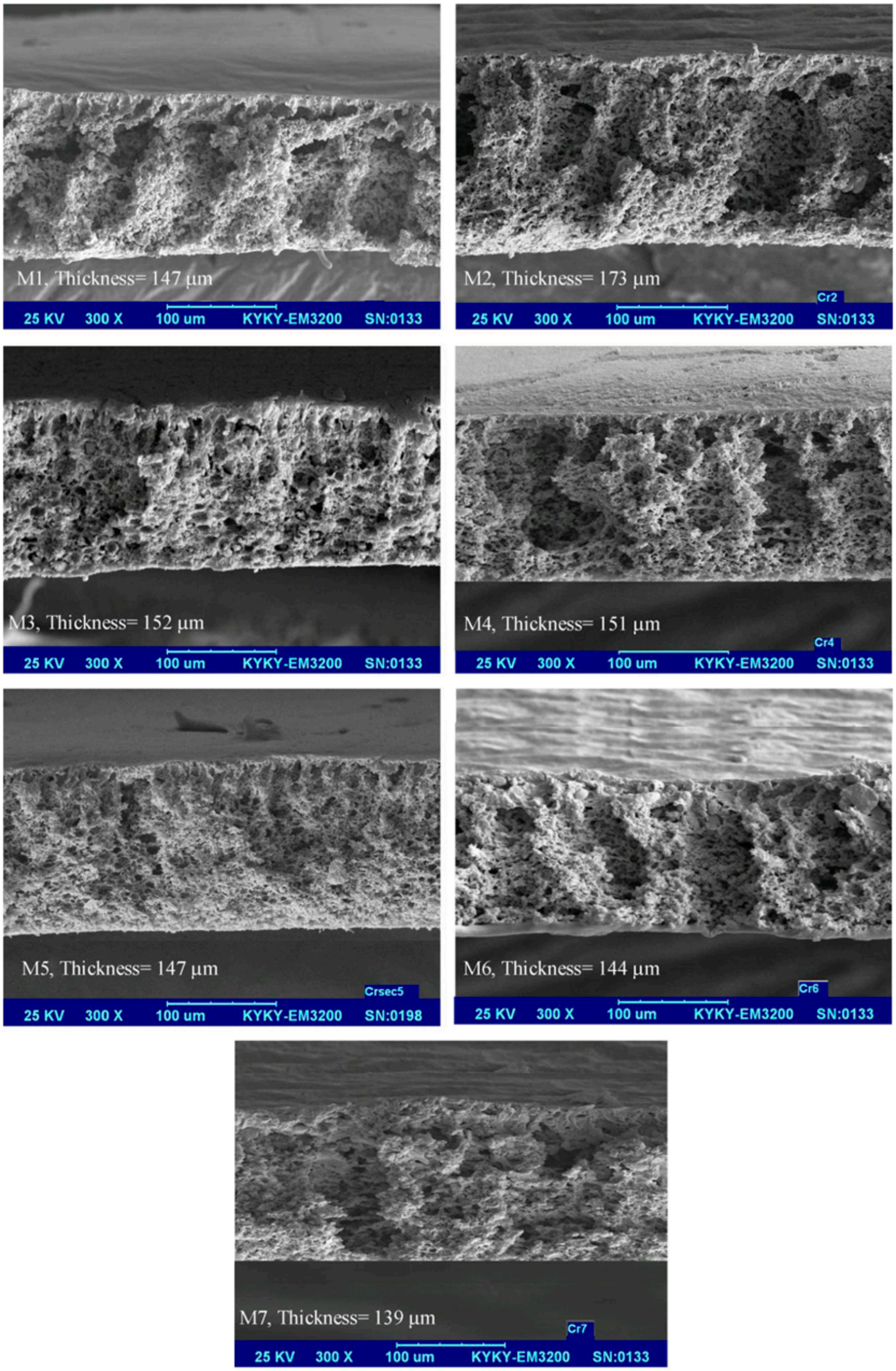

Fig. 1. SEM cross-sectional images of the PBS/PES/PEG membranes.

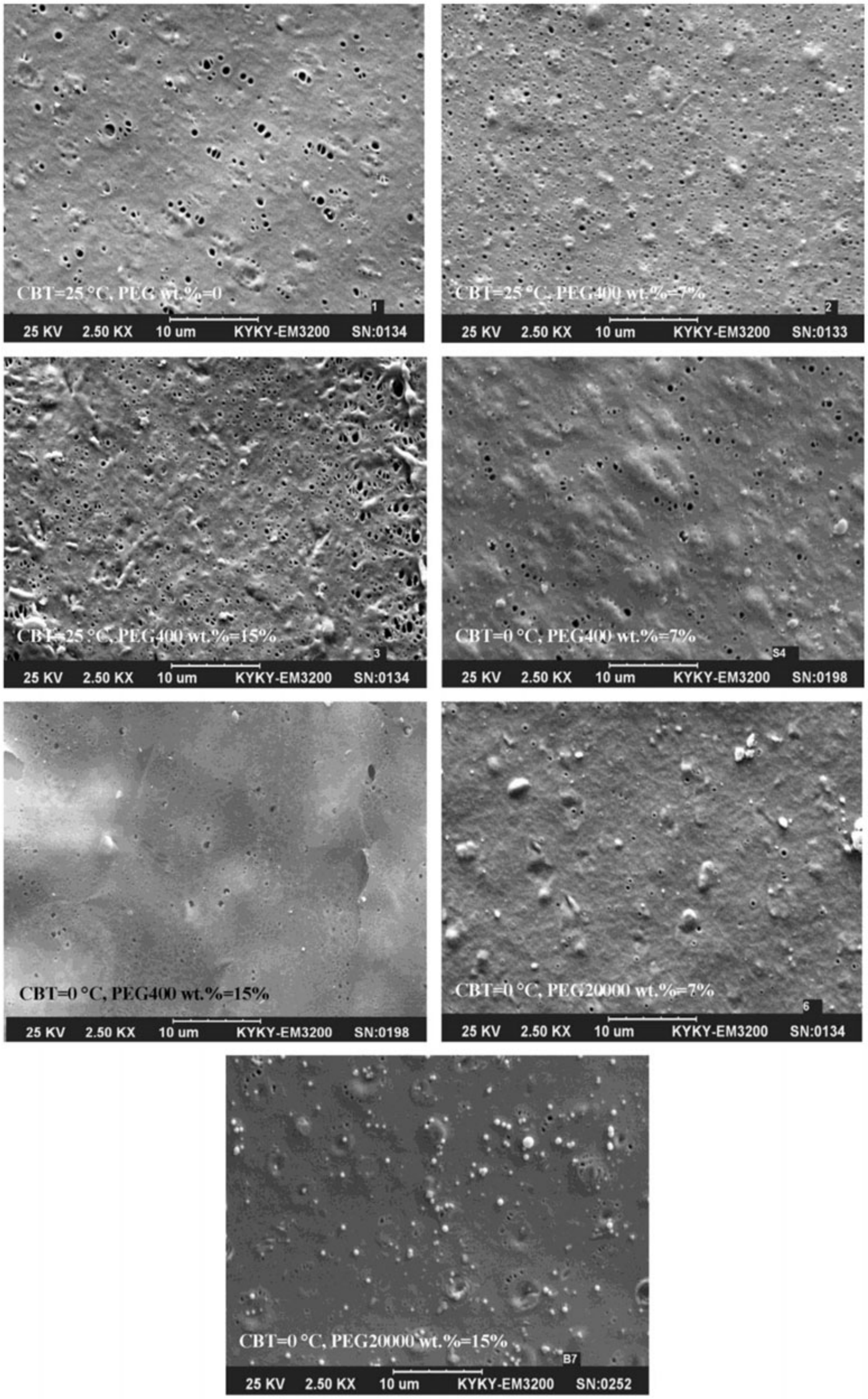

Fig. 2. SEM surface images of the PBS/PES/PEG membranes.

increased from 7 to 15 wt.%, the effect of viscosity governed the membrane formation process and as a result, the membrane thickness was reduced. In this case, it was expected that the movement of PEG400 molecules to the surface was relatively inhibited because of reducing the exchange rate of the solvent/non-solvent. However, at higher PEG400 concentration, the number of molecules that tried to reach the surface was increased. Thus, the aggregation of PEG molecules at the surface was intensified and also some pores were connected to each other, forming a number of pores with higher diameters as shown in Fig. 2.

3.1.2. Effect of CBT

To investigate the CBT effect on the membrane structure, it is noted that the membrane precipitation is certainly slowed down at lower CBT. This delay in the membrane formation refers to reducing the mutual diffusivities between the solvent (NMP) and non-solvent (water) in the casting solution during the solidification process in the coagulation bath. Similar to the previous studies [16,17], the membranes prepared at lower CBT had denser structure with lower thickness with respect to Figs. 1 and 2.

3.1.3. Effect of PEG molecular weight

The effect of PEG molecular weight and also the increasing concentration of high molecular weight PEG on the membrane morphology can be seen in Figs. 1 and 2. At higher PEG molecular weight, viscosity of the casting solution is certainly increased. Furthermore, the higher the PEG molecular weight, the longer the PEG molecules' chain length and also the poorer the mobility of PEG molecules [12]. In fact, the presence of PEG20000 enhances the entanglement of polymer chains, consequently reduces the polymers' mobility and also surely increases the solution viscosity. As a result, the precipitation rate of the cast film in the coagulation bath was obviously decreased which caused the formation of a membrane with lower porosity [12]. In this case, the membrane thickness was declined.

3.2. FTIR analysis

In Fig. 3, the FTIR spectra of the membranes are shown. The peaks of the PBS/PES blend membrane were described elsewhere [9]. Adding PEG to the blend membrane, no additional peak was observed, as there is no chemical reaction between PBS/PES and PEG. Moreover, due to the existence of similarities between PEG bands and bands of PES and PBS, the peaks are overlapped. However, adding 15 wt.% of PEG400 and PEG2000 to the blend membrane, the carbonyl band (1,717 cm^{-1}) from PBS was shifted to 1,719 and 1,722 cm^{-1}, respectively. Furthermore, the asymmetric stretching of O=S=O at 1,329 cm^{-1} from PES in the PBS/PES membrane was shifted to a higher wave number by 2 and 3 cm^{-1}, according to the addition of 15 wt.% of PEG400 and PEG2000, respectively. These show the existence of an intermolecular interaction between the polymers and PEG, as suggested by He et al. for blending chitosan with PEG [18].

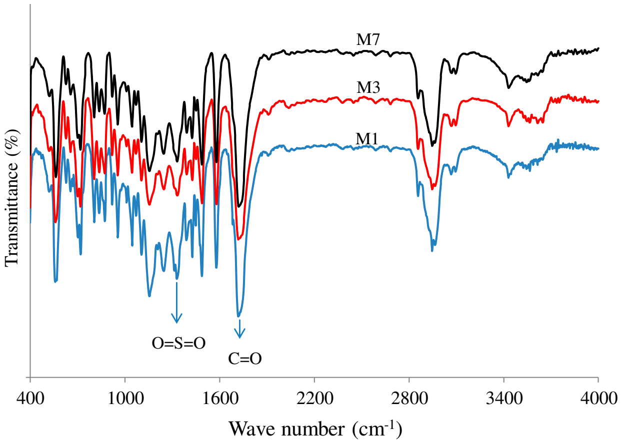

Fig. 3. FTIR spectra of the PBS/PES/PEG membranes.

3.3. Contact angle

Fig. 4 shows the effects of PEG concentration, PEG molecular weight, and CBT on hydrophilicity of the

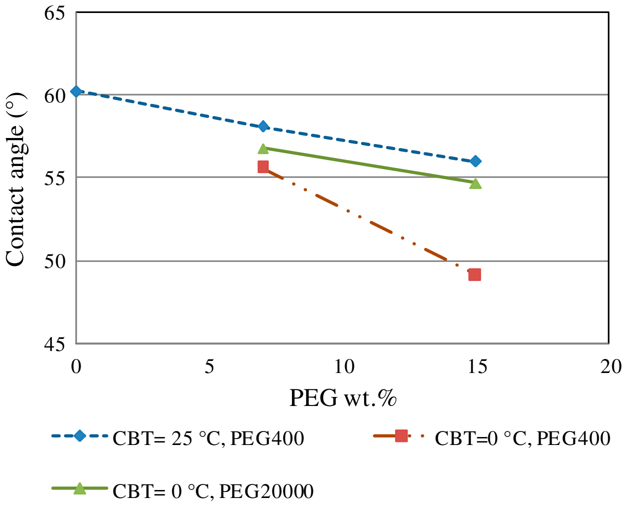

Fig. 4. Contact angle of the PBS/PES/PEG membranes.

prepared membranes. The highest contact angle or in other words, the lowermost hydrophilicity was obtained for the PBS/PES membrane without the addition of PEG. Increasing the PEG concentration, the membrane contact angle was decreased, indicating an increase in the surface hydrophilicity by the addition of PEG to the casting solution. Similar results were reported for hydrophilicity of different membranes, when PEG [14] or other hydrophilic additives [3,16,17] were added with various concentrations.

With respect to Fig. 4, more hydrophilic surfaces were obtained for the membranes containing PEG400, when CBT was decreased. For the PEGs with low molecular weights, PEG leaching is much more noticeable [19]. For the membrane prepared at higher CBT, PEG400 can be easily washed out during the membrane formation process due to its higher solubility and diffusivity [14]. Thus, at low CBT of 0°C, the quantity of PEG remained in the membrane structure was higher which resulted in lower contact angle. Moreover, hydrophilicity of the membrane was lower when higher molecular weight of PEG was used for the membrane preparation. This observation refers to the fact that the PEG molecules with higher molecular weight have lower mobility and thus, lower amount of them reaches the film surface during the membrane formation in the coagulation bath. Accordingly, wettability of the final membrane surface was lower.

3.4. Tensile strength

Tensile strength of the PBS/PES/PEG membranes is depicted in Fig. 5. The results show that:

(1) The addition of PEG400 to the PBS/PES membranes prepared at CBT = 25°C slightly reduced the membrane tensile strength.

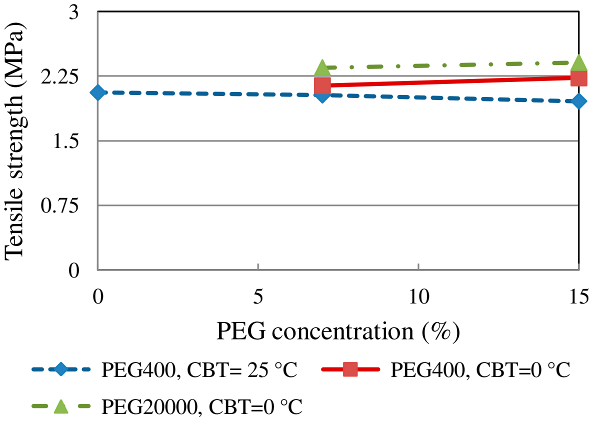

Fig. 5. Tensile strength of the prepared membranes.

(2) Decreasing CBT, higher tensile strength was achieved for the PBS/PES/PEG400 membranes.

(3) At CBT = 0°C, the addition of PEG20000 was more effective in comparison with the addition of PEG400 to improve the membrane tensile strength.

For the membranes prepared at CBT = 25°C, the addition of 7 wt.% PEG400 increased the membrane cross-sectional porosity. At higher PEG400 concentration, some undesired big pores were formed at the surface. It was known that high porosity and large cavities in the membrane structure reduced the tensile strength [9]. Thus, tensile strength of the M1–M3 membranes was slowly decreased.

Decreasing CBT, the precipitation process in the coagulation bath was slowed down. Moreover, the casting solution viscosity was increased for the solution containing 15 wt.% PEG400. Effects of low CBT and high viscosity resulted in the formation of the membranes with lower porosities which directly enhanced the membrane tensile strength.

The differences in molecular weight and consequently chain length of PEG400 and PEG20000 significantly affected the entanglements of the polymer chains. In other words, the incorporation of PEG20000 caused a stronger interaction between the membrane components, leading to the enhancement of tensile strength. Furthermore, it should be mentioned that the porosity of M6 and M7 membranes was noticeably decreased.

3.5. Biodegradability

Weight loss of the membranes is presented in Fig. 6, as a function of burial time. Moreover, the appearance of the membranes at the end of the burial test is shown in Fig. 7. The PBS/PES membrane (M1) is semi-biodegradable, because just 70% of the polymeric blend can be degraded (PBS content). Accordingly, the difference in biodegradation rates of the PBS/PES/PEG membranes is attributed to the presence of PEG and the membrane surface porosity.

Morphology, hydrophilicity, and molecular weight are all known as the factors affecting biodegradability [20–22]. Moreover, PEG is a biodegradable polymer and its addition to the casting solution can enhance the rate of membrane biodegradability due to its biodegradation and also increase in the film surface area created after its consumption by micro-organisms. A similar result was previously reported, when rice-husk flour was added to PBS [23].

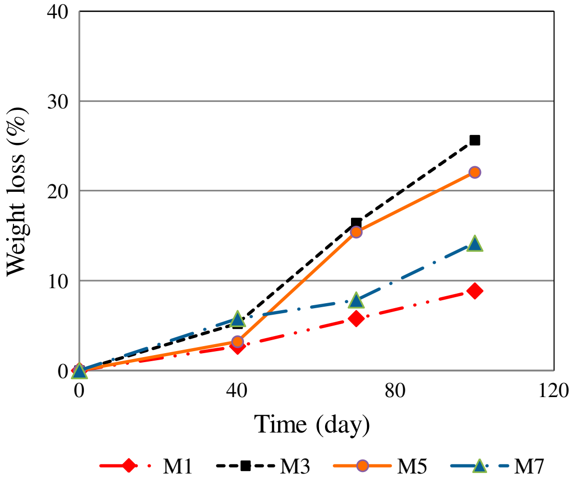

Fig. 6. Weight loss of the prepared membranes during the burial test.

With regard to Fig. 6, weight losses of all buried membranes were almost close to each other up to 40 d of the test. After that, weight losses of M3 and M5 were considerably improved in comparison with those of the other membranes. As discussed in Section 3.1.1, during the membrane formation, PEG400 easily moves to the membrane surface. For M3 and M5, effective surface area of the buried membrane was increased due to PEG400 degradation which was present at the membrane surface. As a result, weight losses of these membranes were improved extensively. Decreasing CBT slightly reduced the degradation rate by reducing the membrane surface porosity.

Increasing the PEG molecular weight from 400 to 20,000 decreased the membrane degradation rate noticeably referring to lower porosity.

3.6. Permeation and rejection

In Fig. 8(a), the permeation of pure water and wastewater for the prepared membranes is illustrated. Moreover, the ability of the membranes for reducing the pollution indices of the wastewater is indicated in Fig. 8(b).

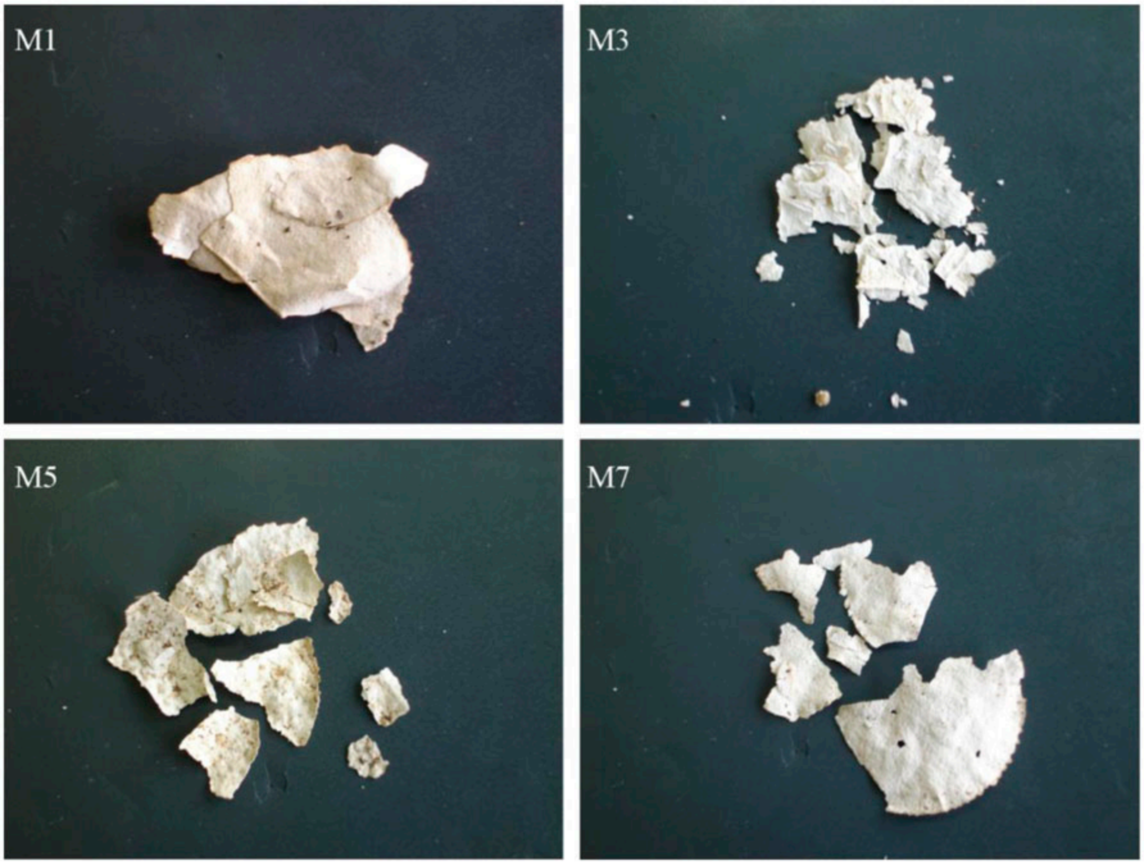

Fig. 7. Appearance of the membranes buried in compost for 100 d.

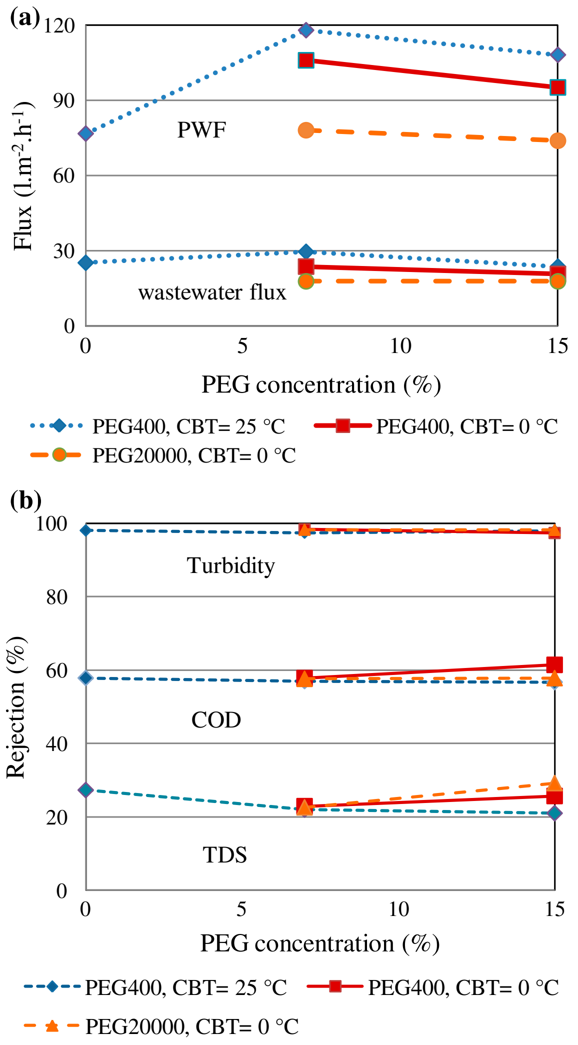

Fig. 8. (a) Pure water and wastewater flux and (b) pollution indices' rejection of the prepared membranes.

The changes in permeation quantity of the membranes in terms of the preparation conditions issue from the combined effects of morphology and hydrophilicity. As observed, the addition of PEG400 to the casting solution initially increased both the membrane porosity and hydrophilicity, which reduced the main resistance against the permeation. Thus, the highest fluxes of pure water and the wastewater were obtained for M2. Simultaneously, increasing the membrane porosity resulted in reducing the rejection of the pollution indices.

Reducing CBT and increasing PEG molecular weight decreased the membrane porosity in both surface and cross-sectional structures. As a result, permeation of pure water and the wastewater was decreased. Moreover, in treating the wastewater, rejection of the pollution indices was improved.

4. Conclusion

The effects of PEG additive and CBT on the PES/PBS/PEG blend membrane prepared via immersion precipitation were studied. For this purpose, different levels of PEG concentration (7 and 15 wt.%), PEG molecular weight (400 and 20,000), and CBT (0 and 25˚C) were examined and the final membranes were characterized using the tests of SEM, FTIR, contact angle, tensile strength, biodegradability, PWF, and the wastewater treatment.

For the membrane prepared at CBT = 25˚C, increasing the PEG400 concentration in the casting solution firstly increased the membrane porosity and then decreased it due to the dual effects of PEG on the membrane morphology. Furthermore, the membranes prepared at lower CBT of 0˚C or ones prepared with PEG20000 were found to have denser structure according to reducing the precipitation rate during the immersion process. Hydrophilicity of the membranes was improved at higher PEG concentration, lower CBT, and lower PEG molecular weight. Accordingly, M5 showed the highest hydrophilicity. Increasing PEG molecular weight and reducing CBT increased the membrane tensile strength. Moreover, the other membrane specifications including biodegradability and performance were influenced by the mentioned factors with respect to especially the variations of the membrane morphology.

References

[1] S.M. Lomakin, S.Z. Rogovina, A.V. Grachev, E.V. Prut, Ch.V. Alexanyan, Thermal degradation of biodegradable blends of polyethylene with cellulose and ethylcellulose, Thermochim. Acta 521 (2011) 66–73.

[2] I.E. Raschip, C. Vasile, D. Macocinschi, Compatibility and biocompatibility study of new HPC/PU blends, Polym. Int. 58 (2009) 4–16.

[3] S.M. Mousavi, E. Saljoughi, Z. Ghasemipour, S.A. Hosseini, Preparation and characterization of modified polysulfone membranes with high hydrophilic property using variation in coagulation bath temperature and addition of surfactant, Polym. Eng. Sci. 52 (2012) 2196–2205.

[4] A. Zarei, V. Ghaffarian, Preparation and characterization of biodegradable cellulose Acetate-starch membrane, Polym. Plast. Technol. Eng. 52 (2013) 387–392.

[5] Z. Mao, Y. Cao, X. Jie, G. Kang, M. Zhou, Q. Yuan, Dehydration of isopropanol–water mixtures using a novel cellulose membrane prepared from cellulose/N-methylmorpholine-N-oxide/H_2O solution, Sep. Purif. Technol. 72 (2010) 28–33.

[6] S.S. Shenvi, S.A. Rashid, A.F. Ismail, M.A. Kassim, A.M. Isloor, Preparation and characterization of PPEES/chitosan composite nanofiltration membrane, Desalination 315 (2013) 135–141.

[7] A. Moriya, P. Shen, Y. Ohmukai, T. Maruyama, H. Matsuyama, Reduction of fouling on poly(lactic acid) hollow fiber membranes by blending with poly(lactic

acid)–polyethylene glycol–poly(lactic acid) triblock copolymers, J. Membr. Sci. 415–416 (2012) 712–717.

[8] V. Ghaffarian, S.M. Mousavi, M. Bahreini, M. Afifi, Preparation and characterization of biodegradable blend membranes of PBS/CA, J. Polym. Environ. 21 (2013) 1150–1157.

[9] V. Ghaffarian, S.M. Mousavi, M. Bahreini, H. Jalaei, Polyethersulfone/poly (butylene succinate) membrane: Effect of preparation conditions on properties and performance, J. Ind. Eng. Chem. 20 (2014) 1359–1366.

[10] V. Ghaffarian, S.M. Mousavi, M. Bahreini, Effect of blend ratio and coagulation bath temperature on the morphology, tensile strength and performance of cellulose acetate/poly(butylene succinate) membranes, Desalin. Water Treat. 54 (2015) 473–480.

[11] S.Y. Hwang, E.S. Yoo, S.S. Im, The synthesis of copolymers, blends and composites based on poly (butylene succinate), Polym. J. 44 (2012) 1179–1190.

[12] D.-Y. Zuo, Y.-Y. Xu, W.-L. Xu, H.-T. Zou, The influence of PEG molecular weight on morphologies and properties of PVDF asymmetric membranes, Chin. J. Polym. Sci. 26 (2008) 405–414.

[13] H.U. Zaman, J.M.M. Islam, M.A. Khan, R.A. Khan, Physico-mechanical properties of wound dressing material and its biomedical application, J. Mech. Behav. Biomed. 4 (2011) 1369–1375.

[14] E. Saljoughi, S.M. Mousavi, Development of high performance nanofiltration membranes with hydrophilic surface for the removal of cadmium from contaminated water, Sep. Sci. Technol. 47 (2012) 2305–2310.

[15] E. Saljoughi, M. Sadrzadeh, T. Mohammadi, Effect of preparation variables on morphology and pure water permeation flux through asymmetric cellulose acetate membranes, J. Membr. Sci. 326 (2009) 627–634.

[16] S.M. Mousavi, F. Dehghan, E. Saljoughi, S.A. Hosseini, Preparation of modified polyethersulfone membranes using variation in coagulation bath temperature and addition of hydrophilic surfactant, J. Polym. Res. 19 (2012) 9861–9872.

[17] S.M. Mousavi, E. Saljoughi, M.R. Sheikhi-Kouhsar, Preparation and characterization of nanoporous polysulfone membranes with high hydrophilic property using variation in CBT and addition of tetronic-1107 surfactant, J. Appl. Polym. Sci. 127 (2013) 4177–4185.

[18] L.-H. He, R. Xue, D.-B. Yang, Y. Liu, R. Song, Effects of blending chitosan with PEG on surface morphology, crystallization and thermal properties, Chin. J. Polym. Sci. 27 (2009) 501–510.

[19] A.K. Hołda, I.F.J. Vankelecom, Integrally skinned PSf-based SRNF-membranes prepared via phase inversion-Part A: Influence of high molecular weight additives, J. Membr. Sci. 450 (2014) 512–521.

[20] V. Tserki, P. Matzinos, E. Pavlidou, D. Vachliotis, C. Panayiotou, Biodegradable aliphatic polyesters. Part I. Properties and biodegradation of poly(butylene succinate-co-butylene adipate), Polym. Degrad. Stab. 91 (2006) 367–376.

[21] A. Lindström, A.-C. Albertsson, M. Hakkarainen, Quantitative determination of degradation products an effective means to study early stages of degradation in linear and branched poly(butylene adipate) and poly(butylene succinate), Polym. Degrad. Stab. 83 (2004) 487–493.

[22] B.D. Ahn, S.H. Kim, Y.H. Kim, J.S. Yang, Synthesis and characterization of the biodegradable copolymers from succinic acid and adipic acid with 1,4-butanediol, J. Appl. Polym. Sci. 82 (2001) 2808–2826.

[23] H.-S. Kim, H.-J. Kim, J.-W. Lee, I.-G. Choi, Biodegradability of bio-flour filled biodegradable poly(butylene succinate) bio-composites in natural and compost soil, Polym. Degrad. Stab. 91 (2006) 1117–1127.