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Effect of blend ratio and coagulation bath temperature on the morphology, tensile strength and performance of cellulose acetate/poly(butylene succinate) membranes

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ABSTRACT

In the present study, blend membranes of cellulose acetate (CA)/poly(butylene succinate) (PBS) were prepared. The membrane morphology, tensile strength and performance in bread wastewater treatment were evaluated in terms of the membrane preparation conditions. According to the results, presence of PBS varied the membrane structure by reducing the extension of macro pores in the membrane sublayer. CA could effectively improve tensile strength of the membranes. Reducing coagulation bath temperature resulted in obtaining the membranes with denser structure and also higher tensile strength. Considering differences in surface and cross-sectional structures, the membranes with PBS content of 85 and 100% were found to have the highest separation ability, whereas the highest flux belonged to the membrane with 50% PBS.

Keywords: Membrane; Blend ratio; Morphology; Wastewater treatment

1. Introduction

Gaining special attentions, membranes are extensively used in different separation processes of various industries such as water treatment and agro-food industries [1]. Today, the membranes that prevail commercially are asymmetric ones made from synthetic polymers, copolymers or blends using phase inversion method [2]. The films prepared by blending polymers usually result in modified physical and mechanical properties in comparison with films prepared of the individual components [3]. Furthermore, the membrane technology using blended polymer membranes offers high potential for the complete management of separation than using individual polymers [4].

Poly(butylene succinate) (PBS) is a biodegradable polyester which was invented by Showa Highpolymer in Japan at the early 1990s [5]. It has good processability and thermal properties. However, as compared with conventional polyesters such as poly(ethylene terephthalate) and poly(butylenes terephthalate), poorer mechanical properties and higher price of PBS prevent its widespread application [6]. Thus, blending PBS with cellulose acetate (CA) may reduce these problems.

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It should be noted that PBS is a semi-crystalline polymer [7] and its crystallization capability can lead to a variety of morphologies when amorphous polymers such as CA [8] are blended with it. Although a number of researches investigated preparation of membrane using semi-crystalline polymers by means of immersion precipitation technique, most of these researches devoted on poly(vinylidene fluoride) [9,10].

In the previous study, PBS was blended with CA in order to prepare a biodegradable membrane using phase inversion method induced by immersion precipitation technique [11]. In the present study, the CA/PBS membrane morphology and tensile strength were investigated in detail as a function of the preparation conditions including the blend ratio and coagulation bath temperature (CBT). Moreover, effects of the aforementioned variables were studied on applicability of the membranes for bread wastewater treatment.

2. Materials and methods

2.1. Materials

Membrane-forming polymers of CA (39.8 wt.% acetyl content, Mn = 30,000 and density = 1.3 g/ml) and PBS (Tm = 120˚C and density = 1.3 g/ml) were prepared from Sigma-Aldrich. The solvent used was 1-methyl-2-pyrrolidone (NMP) which was supplied from Merck. Distilled water was applied as non-solvent. Wastewater used in the present study was sampled from a local bread factory. The values of turbidity, chemical oxygen demand (COD) and total dissolved solid in the wastewater sample were 1,079 (NTU), 11,500 (mg/l) and 2,584 (mg/l), respectively.

2.2. Membrane preparation

CA/PBS membranes were prepared by phase inversion process as a well-known technique for preparing a variety of membranes. The blend solutions based on CA and PBS were prepared by dissolving two polymers at different compositions in NMP as solvent. The homogeneous solution was cast on a glass plate by a film applicator and moved toward water bath for immersion precipitation. The prepared membranes were dried in vacuum oven.

For preparation of all membranes, total polymer concentration was fixed at 17%. It should be noted that PBS solubility in NMP is temperature dependent. Accordingly, the membranes that are rich in PBS (with PBS content higher than 50%) are not formed when CBT is lower than 50˚C. To evaluate the effect of the blend ratios and also CBT, 12 membranes are prepared as presented in Table 1.

Table 1
Compositions and CBTs for the prepared membranes

Membrane	CA/PBS blend ratio	CBT (˚C)
M1	100/0	25
M2, M3	85/15	0, 25
M4, M5	70/30	0, 25
M6, M7, M8	60/40	0, 25, 50
M9	50/50	50
M10	30/70	50
M11	15/85	50
M12	0/100	50

2.3. Membrane characterization

2.3.1. Morphological test

The surface and cross-sectional views of the membranes were examined using scanning electron microscopy (SEM, KYKY-EM3200). To observe cross-section of the membranes, the dried specimens were frozen and then fractured in liquid nitrogen. Prior to the examination, all samples were coated with gold in order to provide electrical conductivity to the membranes.

2.3.2. Mechanical properties

Drying the samples completely, their mechanical properties were tested using Zwick tensile test machine. All tests were performed at a cross-head speed of 1 mm/min. For each test, three samples were used and the average values for tensile strength were reported.

2.3.3. Membrane performance

The performance of the prepared membranes was characterized using a cross-flow system. This experimental set-up consists of a reservoir, a pump, valves, pressure gauges, a heat exchanger, temperature indicators and a flat sheet membrane module. The details of the set-up can be found elsewhere [12]. Bread wastewater was used as test feed for wastewater treatment process. The permeate flux of the prepared membranes was measured at transmembrane pressure of 3 bar. Furthermore, the membrane separation ability was investigated in terms of the rejection percentage of turbidity and COD. The apparatuses used for measurement of these pollution indices were turbidity meter of Lutron TU-2016 (Taiwan) and PCcheckit COD vario (Lovibond, Germany).

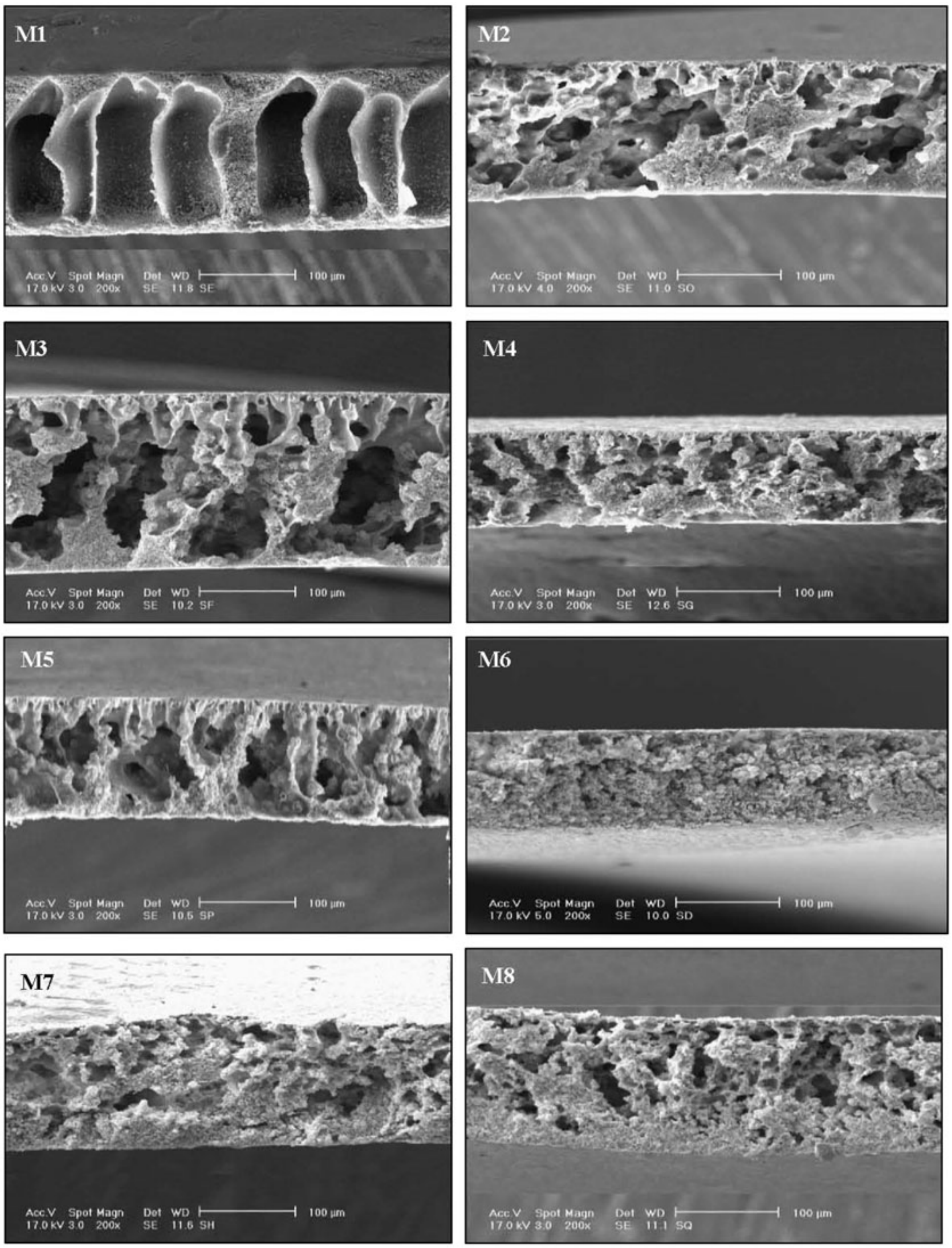

Fig. 1. SEM cross-sectional images of the CA-rich membranes prepared at different CBTs of 0, 25 and 50˚C (200× magnifications).

3. Results and discussion

3.1. Membrane morphology

3.1.1. CA-rich membranes

Fig. 1 presented the cross-sectional images of the CA/PBS membranes with high CA concentration at different CBTs. Evaluating the membrane general morphology, the membranes having asymmetric structure consists of a dense skin layer on a porous support layer. For pure CA casting solution, a porous sublayer with finger like pores was obtained. Addition of PBS gently changed the structure by suppression of macro pores in the sublayer. This observation refers to the membrane formation mechanism and accordingly demixing processes occurred at the coagulation bath.

For amorphous polymers such as CA, liquid–liquid demixing may occur during the membrane formation [13]. For the membrane prepared with a semi-crystalline polymer such as PBS, liquid–liquid demixing and solid–liquid demixing participate in formation of final

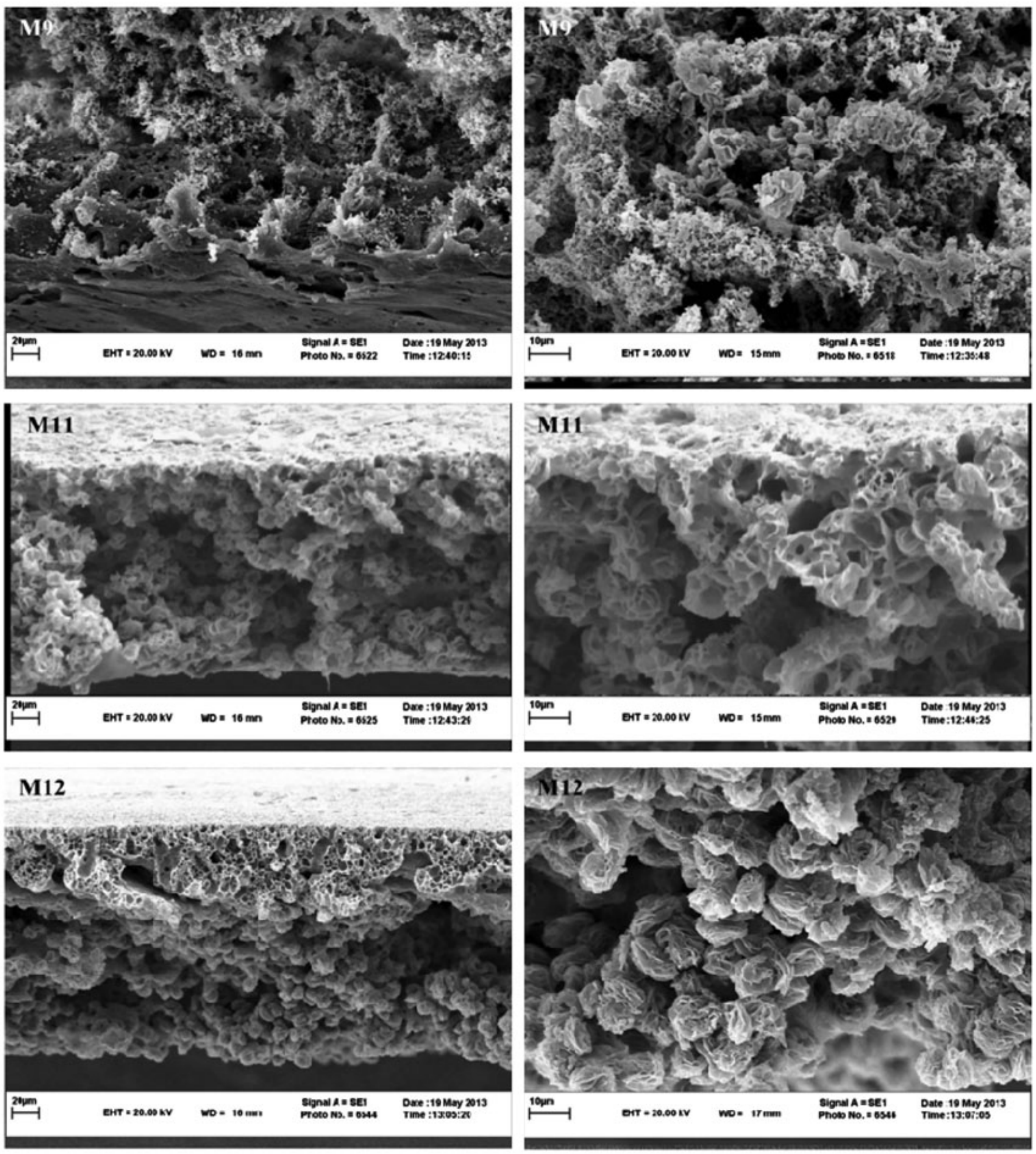

Fig. 2. SEM cross-sectional images of the PBS-rich membranes prepared at CBTs of 50˚C (left column: 1,000× magnification; and right column: 3,000× magnification).

structure of the membrane [14]. Thus, at constant CBTs, increasing PBS content in the casting solution would result in increasing probability of crystallization taking place (solid–liquid demixing) in addition to liquid–liquid demixing. In this case, blending gradually reduced the sublayer porosity. In other words, the slight growth of crystalline particle in the sublayer due to the presence of PBS gradually slowed down the precipitation process. The consequence of crystalline particle growth was limitation of the growth of polymer-lean phase in sublayer. Thus the macrovoids extension is inhibited.

According to the presence of macrovoids, it can be concluded that liquid–liquid demixing mainly governs the formation of the blend membranes with low PBS concentration (15–40%). However, the polymer crystallization can be seen only on the walls surrounded the pores, which refers to occurring crystallization sequentially after liquid–liquid demixing. In fact, the structure is initially driven from liquid–liquid demixing; then crystallization follows.

From Fig. 1, the effect of CBT on the membrane structure can also be evaluated. At constant blend ratio, reducing CBT decreased diffusional flow of the solvent (NMP) and nonsolvent (water) during solidification of the casting solution in the coagulation bath. Thus, the precipitation rate was reduced that would be resulted in the formation of denser structure in the sublayer. This observation is in agreement with the previous findings [15,16].

3.1.2. PBS-rich membranes

Cross-sectional structures of M9, M11 and M12 are presented in Fig. 2 at high magnifications. For the membranes prepared at high PBS concentrations (more than 50%), importance of crystallization is increased. Thus, macro pores suppression was intensified and more homogenous structure with respect to PBS crystallinity would be obtained.

Due to lower PBS concentration in M9, crystallization could not be developed in this structure as much as it in M11 and M12 membranes. On the other hand, presence of crystalline particles can be clearly seen in the sublayers of M11 and M12 indicating that crystallization is important. Thus, crystallization in M11 and M12 probably starts after liquid–liquid demixing sooner than that in the other CA/PBS membranes containing semi-crystalline units. For further clarification, SEM images of surfaces of pure PBS membrane

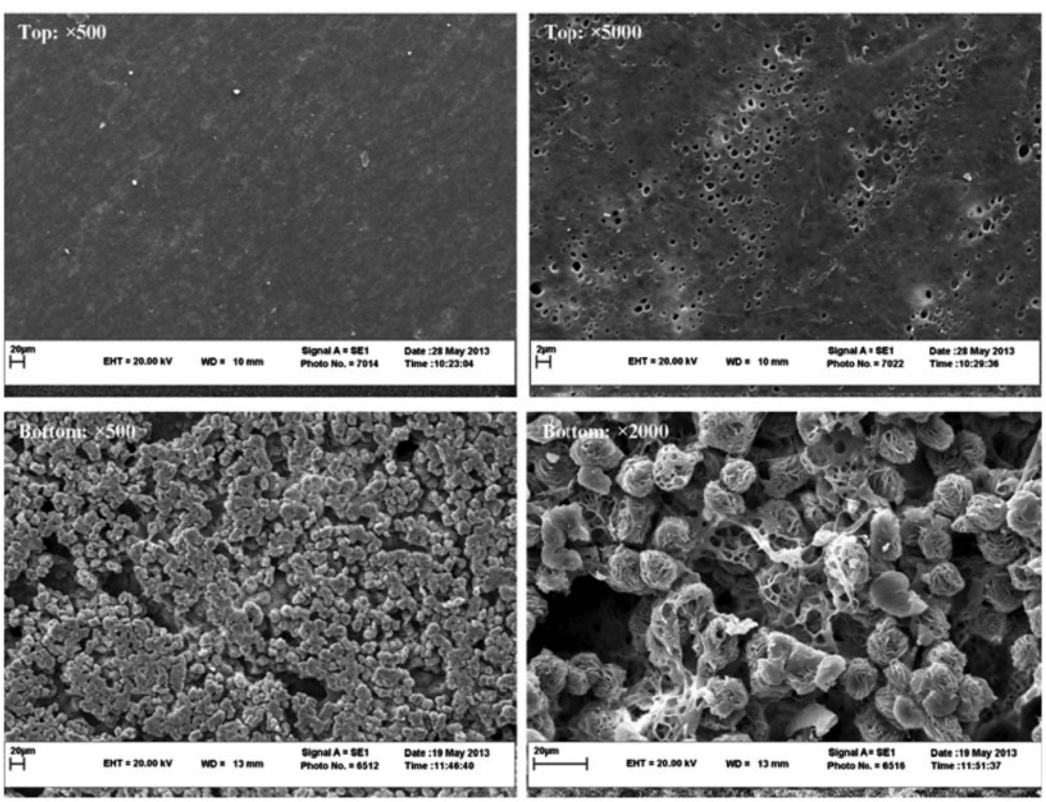

Fig. 3. SEM images of top and bottom surfaces of pure PBS membrane.

are shown in Fig. 3. Regarding Fig. 3, image of the membrane bottom is full of semi-crystalline units.

3.2. Tensile strength

Fig. 4 illustrated tensile strength of the CA/PBS membranes as a function of blend ratio and CBT. Tensile strength of pure CA membrane is 2.5 MPa that is almost close to what previously reported for almost similar membranes prepared by other researchers [17–19]. Regarding the aforementioned poorer mechanical properties of PBS, increasing its concentration in the casting solution results in reduction of the membrane strength. Therefore, pure PBS and CA membranes have the lowest and highest tensile strength, respectively.

As discussed in Section 3.1.1, decreasing CBT resulted in the formation of denser structure in the sublayer. Therefore, with respect to Fig. 4, the tensile strength of the membranes prepared at higher CBTs is lower than it of the other membranes. The literature confirms this result [20]. Moreover, the observed trend for tensile strength as a function of PBS concentration and CBT is similar to what observed for polyethersulfone/PBS blend membrane [21].

3.3. Membrane performance

The bread wastewater treatment experiments were carried out and the membranes permeation as well as their separation abilities was studied. Flux results are shown in Fig. 5.

It should be considered that the blend casting solution is not expected to be as homogenous as the pure CA or PBS casting solution. Therefore, increasing the blend ratio of CA/PBS membrane from 100/0 or 0/100 to 50/50 resulted in obtaining a membrane with a surface containing larger pores. The direct effect of the aforementioned variation was the gradual improvement in permeate flux by the addition of a polymer to another polymer and thus obtaining the maximum permeate flux for the membrane with blend ratio of 50/50.

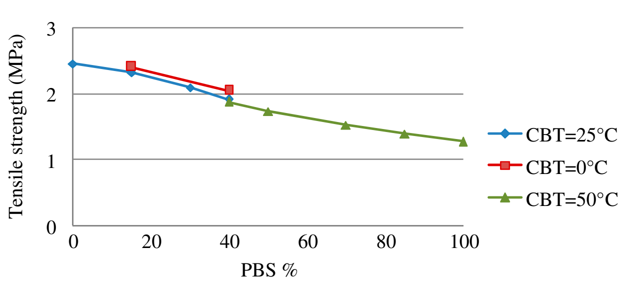

Fig. 4. Effect of membrane preparation conditions on the tensile strength.

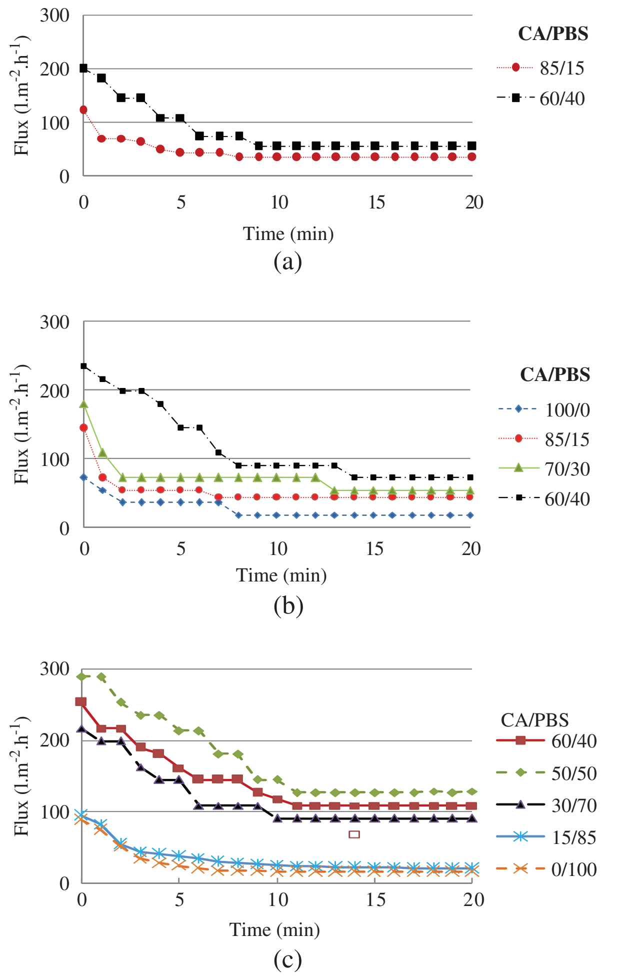

Fig. 5. Permeate flux through the CA/PBS membranes prepared at (a) CBT = 0°C, (b) CBT = 25°C and (c) CBT = 50°C.

At constant blend ratio, decreasing CBT reduced the mutual diffusivities between components during the film solidification in the coagulation bath. Thus, demixing process was slowed down and a denser structure was obtained. Consequently, the membranes prepared at lower CBT had lower permeate fluxes. Comparing the effect of CBT and blend ratio, the stable fluxes of permeate through the prepared membranes are illustrated in Fig. 6.

The membranes ability in reduction of the bread wastewater pollution indices is depicted in Fig. 7. Results show that increasing PBS concentration in the membrane from 0 to 50% reduces the rejections probably due to increasing the membrane surface porosity which has facilitated passage of the pollutants. Further increase in PBS concentration (higher than 50%) improved the rejections. This result refers to both surface and cross-sectional structures of the membranes.

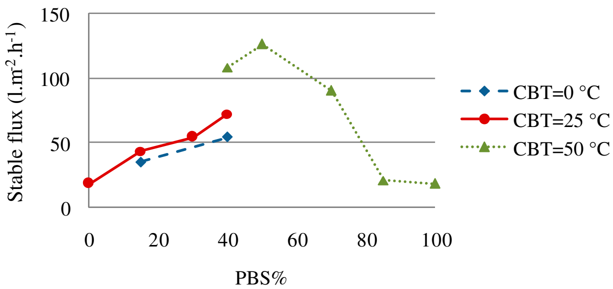

Fig. 6. Stable flux of permeate through the prepared membranes.

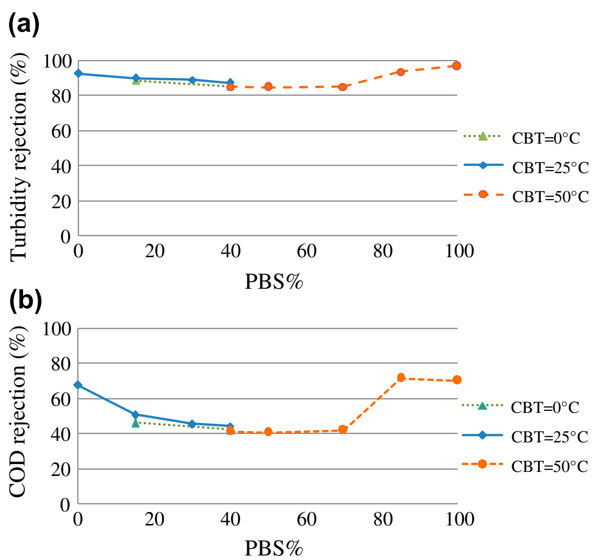

Fig. 7. Effect of PBS percent and CBT on the rejection of two pollution indices of turbidity and COD.

For rich PBS membranes, the surface porosity decreased which would inhibit the pollutants passage. Moreover, in cross-sectional structure of these membranes, macro pores were gradually decreased. These variations continued till the obtained structure for M11 and M12 became full of semi-crystalline units. Obviously, such structures are less permeable and consequently more selective than those structures dominated by macro pores. Thereupon, both reduced surface porosity and cross-sectional structure of PBS-rich membranes which would help for obtaining higher separation ability. With respect to Fig. 7, CBT's effect on performance of CA-rich membranes is almost negligible.

4. Conclusion

The effects of variation of CBT and blend ratio in CA/PBS casting solution were investigated on the morphology, tensile strength and bread wastewater treatment of the prepared membranes. It was shown that addition of PBS to CA noticeably affected the final structure by the suppression of macro pores in the membrane sublayer. Moreover, reducing CBT decreased rate of the membrane precipitation in the coagulation bath and thus resulted in formation of denser membrane. CA was found to enhance tensile strength of the blend membranes. Decreasing CBT, the tensile strength of the membranes was slightly improved.

Performance of CA/PBS blend membranes was considerably influenced by the blend ratio. The results for bread wastewater treatment showed that addition of PBS value up to 50% increased the permeate flux. This improvement resulted in decreasing the rejection of pollution indices. Moreover, at higher PBS concentrations, the permeate flux and rejection varied their trend in a reverse manner. Accordingly, the highest rejection for pollution indices of turbidity and COD was obtained for the rich PBS membranes.

References

[1] S. Srebnik, Polymer adsorption on multicomponent surfaces with relevance to membrane fouling, Chem. Eng. Sci. 58 (2003) 5291–5298.
[2] A. Idris, N. Mohd. Yusof, R. Rashid, I. Ahmed, High Performance Blended Membranes Using a Novel Preparation Technique, Project Report, Faculty of Chemical and Natural Resource Engineering, Malaysia, 2008.
[3] S. Zivanovic, J. Li, P.M. Davidson, K. Kit, Physical, mechanical, and antibacterial properties of chitosan/PEO blend films, Biomacromolecules 8 (2007) 1505–1510.
[4] M. Sivakumar, D. Mohan, R. Rangarajan, Preparation and performance of cellulose acetate-polyurethane blend membranes and their applications. Part 1, Polym. Int. 47 (1998) 311–316.
[5] Y.J. Phua, N.S. Lau, K. Sudesh, W.S. Chow, Z.A. Mohd Ishak, Biodegradability studies of poly(butylene succinate)/organo-montmorillonite nanocomposites under controlled compost soil conditions: Effects of clay loading and compatibiliser, Polym. Degrad. Stab. 97 (2012) 1345–1354.
[6] L. Zheng, C. Li, D. Zhang, G. Guan, Y. Xiao, D. Wang, Synthesis, characterization and properties of novel biodegradable multiblock copolymers comprising poly (butylene succinate) and poly(1,2-propylene terephthalate) with hexamethylene diisocyanate as a chain extender, Polym. Int. 60 (2011) 666–675.
[7] Z. Qiu, T. Ikehara, T. Nishi, Miscibility and crystallization in crystalline/crystalline blends of poly(butylene succinate)/poly(ethylene oxide), Polymer 44 (2003) 2799–2806.
[8] M. Flieger, M. Kantorová, A. Prell, T. Řezanka, J. Votruba, Biodegradable plastics from renewable sources, Folia Microbiol. 48 (2003) 27–44.

[9] A. Akbari, M. Hamadanian, V. Jabbari, A.Y. Lehi, M. Bojaran, Influence of PVDF concentration on the morphology, surface roughness, crystalline structure, and filtration separation properties of semicrystalline phase inversion polymeric membranes, Desalin. Water Treat. 46 (2012) 96–106.

[10] D.-J. Lin, H.-H. Chang, T.-C. Chen, Y.-C. Lee, L.-P. Cheng, Formation of porous poly(vinylidene fluoride) membranes with symmetric or asymmetric morphology by immersion precipitation in the water/TEP/PVDF system, Eur. Polym. J. 42 (2006) 1581–1594.

[11] 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.

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

[13] T.H. Young, L.P. Cheng, W.M. You, L.Y. Chen, Prediction of EVAL membrane morphologies using the phase diagram of water–DMSO–EVAL at different temperatures, Polymer 40 (1999) 2189–2195.

[14] I.M. Wienk, R.M. Boom, M.A.M. Beerlage, A.M.W. Bulte, C.A. Smolders, H. Strathmann, Recent advances in the formation of phase inversion membranes made from amorphous or semi-crystalline polymers, J. Membr. Sci. 113 (1996) 361–371.

[15] 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.

[16] 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.

[17] G. Arthanareeswaran, T.K. Sriyamunadevi, Effect of silica particles on cellulose acetate blend ultrafiltration membranes: Part I, Sep. Purif. Technol. 64 (2008) 38–47.

[18] G. Arthanareeswaran, P. Thanikaivelan, Fabrication of cellulose acetate–zirconia hybrid membranes for ultrafiltration applications: Performance, structure and fouling analysis, Sep. Purif. Technol. 74 (2010) 230–235.

[19] A.R. Moghadassi, Z. Rajabi, S.M. Hosseini, M. Mohammadi, Fabrication and modification of cellulose acetate based mixed matrix membrane: Gas separation and physical properties, J. Ind. Eng. Chem. (2013) in press.

[20] M. Amirilargani, E. Saljoughi, T. Mohammadi, M.R. Moghbeli, Effects of coagulation bath temperature and polyvinylpyrrolidone content on flat sheet asymmetric polyethersulfone membranes, Polym. Eng. Sci. 50 (2010) 885–893.

[21] 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. (2013) in press.