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Polyethersulfone/poly (butylene succinate) membrane: Effect of preparation conditions on properties and performance

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ABSTRACT

In this study, biodegradable polymer of poly (butylene succinate) (PBS) was blended with polyethersulfone (PES) to prepare a novel semi-biodegradable membrane. The effect of blend ratio and coagulation bath temperature (CBT) was investigated on membrane characteristics including membrane morphology, mechanical strength and also treatment ability. Moreover, Fourier transform infrared (FTIR) spectrum, thermal stability, biodegradation and contact angle of the membranes were studied. Results demonstrated that the wastewater permeation through the prepared membranes was increased by blending the polymers and reached to maximum at blend ratio of 50/50. The wastewater treatment of PES/PBS blend membranes was improved by increasing PBS content.

1. Introduction

The management of solid waste disposal is becoming very urgent in industrialized and developing countries. Among the various possible routes to eliminate the wastes, biodegradation and bio-recycling have attracted extensive interest. Biodegradable polymers can be produced with less overall energy consumption than their petrochemical counterparts and tend to be less toxic to the environment [1,2]. In recent years great attempts have been done in the development of biodegradable products in different fields of medical applications (mainly surgical sutures and drug delivery system), food packaging, etc. [3].

Membrane based separations have become one of the most promising technologies for the 21st century. As an advanced wastewater treatment technology, membrane technology has a key role in lower pollutant levels in purifying and/or concentrating a wide variety of fluids from water and wastewater to pharmaceutical and chemical products. Membrane processes have been considered as attractive alternatives compared to conventional wastewater treatment processes owing to their advantages such as selective separation, continuous and automatic operation, easy and well-arranged process conduction, purification without the addition of chemicals, easy scale-up and low space requirement [4]. According to increasing interest in applying polymeric membranes and at the same time increasing environmental concerns, it seems to be necessary to prepare and also introduce degradable or even semi-degradable membranes that can be discarded to the environment after passage of the membranes shelf life. Generally, this application was mentioned by some researchers just for a few number of biodegradable polymers such as cellulose [5], starch [6,7], chitosan [7,8] and poly (lactic acid) [9,10].

As one of the commercial and most representative biodegradable polymers, PBS presents interesting properties including melt processability and relatively proper thermal and chemical resistance. However, practical application of PBS has been limited because of its weak strength. Therefore, it is essential to find a suitable method to improve its mechanical strength especially for particular application of membrane preparation.

PES is the material of choice for numerous membrane applications due to its outstanding mechanical strength, thermal stability, and film-forming ability. It is a highly polar aromatic polymer with high resistance to aqueous acids and alkalis at elevated temperature [11]. Following different purposes, PES has been blended with various polymers to make a suitable membrane, e.g. Wilhelm et al. blended PES with poly (ether ether ketone) [12].

In present work, PES has been blended with PBS in different percentages varying in the range of 0–100%. The PES/PBS blend has

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been studied with a proper view for developing a novel and semi-biodegradable membrane in order to reduce the source of waste pollution. The effects of the blend ratio and coagulation bath temperature (CBT) have been investigated on the fundamental membrane characteristics including morphology, mechanical strength and treatment ability. Also, the pure and blend membranes properties were evaluated by the thermal stability, contact angle and biodegradation experiments.

2. Experimental

2.1. Materials

PES was obtained from BASF Company. PBS was supplied from Sigma-Aldrich. According to the supplier, the PBS was extended with 1, 6-diisocyanatohexane. Solvent of 1-methyl-2-pyrrolidone (NMP) with an analytical purity of 99.5% was supplied from Merck.

Wastewater sourced for this study was obtained from a local bread factory. The wastewater characteristics are presented in Table 1.

2.2. Membrane preparation

Membranes of PES/PBS were prepared using phase inversion method induced by immersion precipitation. For this aim, various PES/PBS/NMP solutions were prepared while concentration of total polymer was adjusted at 17%. The selected weight ratios of PES/PBS were 100/0, 85/15, 70/30, 50/50, 30/70, 15/85 and 0/100.

The blend solution was prepared by dissolving two polymers of PBS and PES at predefined compositions in NMP as the solvent. It should be noted that PBS was dissolved in NMP at darkness and temperature of 50 °C. The solution was stirred continuously till completely homogeneous mixture was obtained.

The solution was subsequently poured onto a glass plate, and spread with a film applicator to be as thin as 250 μm. Then, the glass plate was immediately immersed in non-solvent (distilled water) bath for immersion precipitation. After primarily phase separation and membrane formation, the prepared membrane was kept in distilled water for 24 h to ensure complete removal of residual NMP. Finally, the prepared membranes were dried using vacuum oven.

Considering effect of CBT, membranes with blend ratios of 70/30, 50/50 and 30/70 for PES/PBS were prepared at three different CBTs of 0, 25 and 50 °C. For pure PBS membrane, just coagulation bath temperature of 50 °C could be applied as PBS solubility in NMP is depended on temperature.

2.3. Characterization of PES/PBS membrane

2.3.1. FTIR spectroscopy

FTIR spectra were recorded using a Thermo Nicolet Avatar 370 FTIR (USA) applying KBr disk method. The analysis was carried out in the wave number range of 400–4000 cm^{-1} with scanning 32 times.

2.3.2. Scanning electron microscopy (SEM)

Scanning electron microscope (KYKY-EM3200) was used to elucidate the membranes surface and cross-sectional morphology. The dried membrane strips were immersed in liquid nitrogen and broken. The samples were gold sputtered before preparing the images.

2.3.3. Thermogravimetric analysis

The thermal stabilities of the membranes were determined through thermogravimetric analysis (TGA). The thermograms were recorded under air atmosphere using TGA-50 (Shimudza Company, Japan) at temperature range of 25–800 °C and a heating rate of 10 °C/min.

2.3.4. Test of mechanical property

After complete drying of the membranes, tensile strength of the prepared membranes was measured 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. The average values were reported for the tensile strength.

2.3.5. Biodegradability test

Compost burial test was carried out to examine the biodegradability of the prepared membranes. Buried membranes were incubated at constant temperature of 30 °C for about five months. Water was supplied at intervals of 3 day and the compost was kept not to be dried. The test specimens were periodically dug out of the compost and then were gently washed to remove attached compost and dust. Being completely dried in oven, the degradation extent was determined by the weight loss, appearance (taking the digital picture using Camera DSC-P200, Sony, Japan) and microscopic surface observation.

2.3.6. Contact angle

Hydrophobicity/hydrophilicity of the prepared membranes was determined by contact angle value of water drop deposited on the membrane surface using the contact angle measuring instrument of G10, KRUSS (Germany). The contact angle value of each membrane was measured at least at four various positions on the membrane sample and the mean value was reported.

2.3.7. Membrane performance evaluation

Performance of the prepared membranes was characterized using an experimental setup. The permeate flux and rejection of pollution indices were determined for all membranes using bread wastewater as feed. All the experiments were conducted at transmembrane pressure (TMP) of 3 bars and room temperature. Turbidity, total dissolved solids (TDS) and chemical oxygen demand (COD) were considered as the pollution indices of wastewater.

Table 1
Characteristics of bread wastewater.

Index	Value
Turbidity (NTU)	1079
TDS (mg/l)	2584
COD (mg/l)	11,500

3. Results and discussion

3.1. FTIR analysis

Fig. 1 shows the FTIR spectra of PES/PBS membranes with blend ratios of 100/0, 50/50 and 0/100. Generally, the spectra of incompatible polymers are simply the sum of the spectra of the pure polymer components. For miscible blends, frequency shifts usually indicate specific interactions between the characteristic groups of the pure polymers [13]. For PBS membrane, the peaks at 1716 cm^{-1} and 1156 cm^{-1} correspond on carbonyl and –C–O–C– stretching in ester linkage, respectively. Moreover, the band at 1046 cm^{-1} is due to –O–C–C– stretching vibrations in PBS. Similarly, several characteristic bands of PES membrane can be identified including aromatic C=C band at 1486 and 1578 cm^{-1}, asymmetric and symmetric stretching of O=S=O at 1319 and 1152 cm^{-1}, and also aromatic ether (–C–O–C–) at 1243 cm^{-1}. According to the spectrum of PES/PBS blend membrane, the shifts from 1716 to

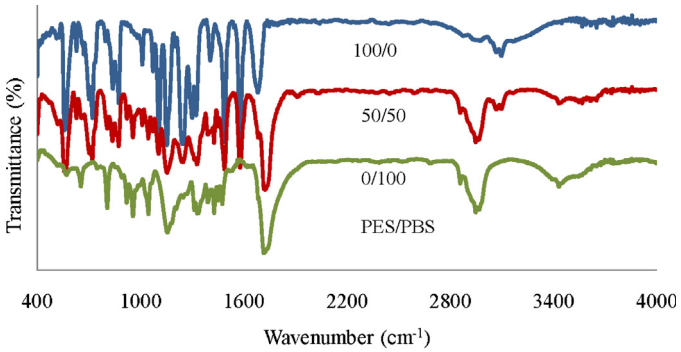

Fig. 1. FTIR spectra of the membranes of PES, PBS and their blend.

1723 cm^{-1} and 1046 to 1041 cm^{-1} are observed for the PBS characteristic bands. Furthermore, the shift from 1319 to 1327 cm^{-1} can be seen for the asymmetric stretching of O=S=O. These results confirm compatible nature of the PES/PBS blend membrane.

3.2. Morphological studies

Microscopic studies using SEM images were carried out to reveal qualitative information regarding cross sectional morphology of the prepared membranes. SEM cross sectional images of the blended membranes with different ratios of PES/PBS are depicted in Fig. 2. Asymmetric structure of all membranes comprises a dense top layer and a porous sublayer. As shown, pure PES membrane has fully developed macrovoids formed in sublayer. Addition of semi-crystalline polymer of PBS to the casting solution gradually changes the final membrane structure by suppression of the macrovoids.

To explain above observation, it is necessary to understand the membrane formation mechanism. When the cast film containing PES amorphous polymer is immersed into the coagulation bath (distilled water), liquid–liquid demixing process governs the membrane formation as illustrated in the previous study [14]. In brief, the membrane is formed based on the nucleation and growth of polymer-poor phase within the polymer-rich phase.

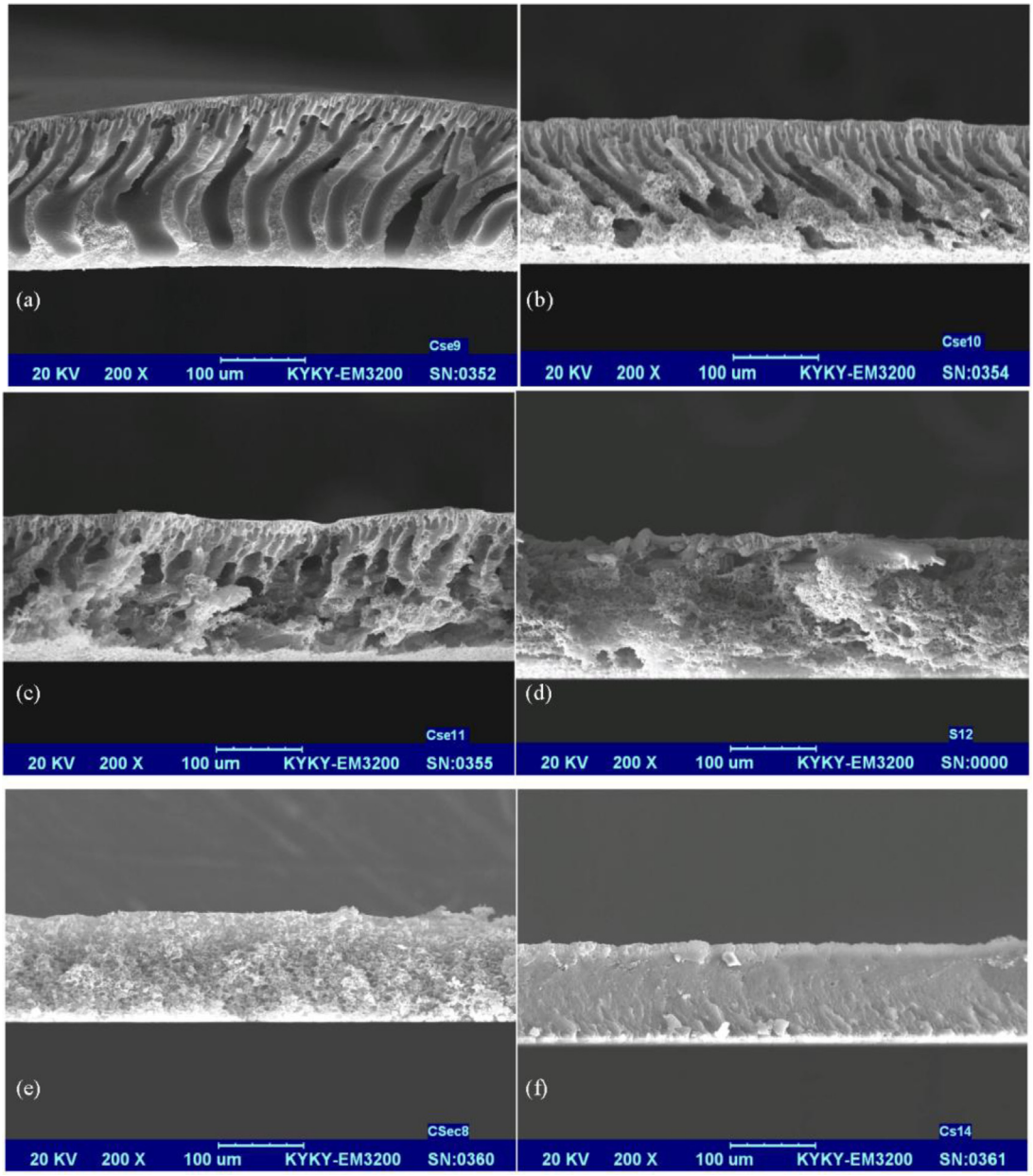

Fig. 2. SEM cross-sectional images of the membranes with PES/PBS blend ratios of: (a) 100/0; (b) 85/15; (c) 70/30; (d) 50/50; (e) 30/70 and (f) 15/85 prepared at CBT = 25 °C.

On the other hand, for the membranes prepared with semi-crystalline polymers using immersion precipitation technique, both liquid–liquid demixing and crystallization (solid–liquid demixing) processes are responsible for the final structure [15–17]. It should be considered that under ordinary precipitation conditions, crystallization is slower than liquid–liquid demixing due to the time needed for the polymer molecules orientation [17]. With respect to the semi-crystallinity of PBS, its addition to the PES membrane probably results in occurring the crystallization process.

Form Fig. 2, it can be clearly seen that the dominant process in PES-rich membranes is liquid–liquid demixing process due to the presence of macrovoids. For membranes with PBS concentration in the range of 30–50%, the macropores still were able to grow but their extension was limited. Indeed, the membrane structure was derived at first from liquid–liquid demixing then crystallization followed which resulted in presence of crystalline particles on the walls surrounding the pores.

Further increase in PBS concentration resulted in the more tendency of occurring crystallization process. In this case, the crystalline structure would be fixed in their location and suppressed further liquid–liquid phase separation which resulted in completely disappearing the macropores in the membrane sublayer.

The effect of CBT on the membrane structure is presented in Fig. 3. Raising CBT from 0 °C to 50 °C increases mutual diffusivities between the non-solvent and the solvent in the casting solution during phase inversion process. This directly enhances the rate of precipitation. In fact, at higher CBTs for constant polymer content, nucleuses of polymer-poor phase grow rapidly. Acceleration of demixing increases membrane thickness and thereupon the membrane porosity, because when the polymer content is constant and simultaneously the membrane thickness increases, total volume of a certain content of the polymer increases. This leads to formation of a rather more open structure or in other words, more porous structure [18].

3.3. TGA analysis

Aiming at investigation of the effect of blend ratio on the thermal stability of membranes, thermogravimetry analysis was performed. The typical TGA traces of weight loss as a function of temperature for the neat PBS and PES membranes and their blends are shown in Fig. 4.

With respect to Fig. 4, increasing PES content in the blend membrane, the thermograms are shifted to higher temperature ranges. In fact, the addition of PES improves the thermal stability of the PBS membrane.

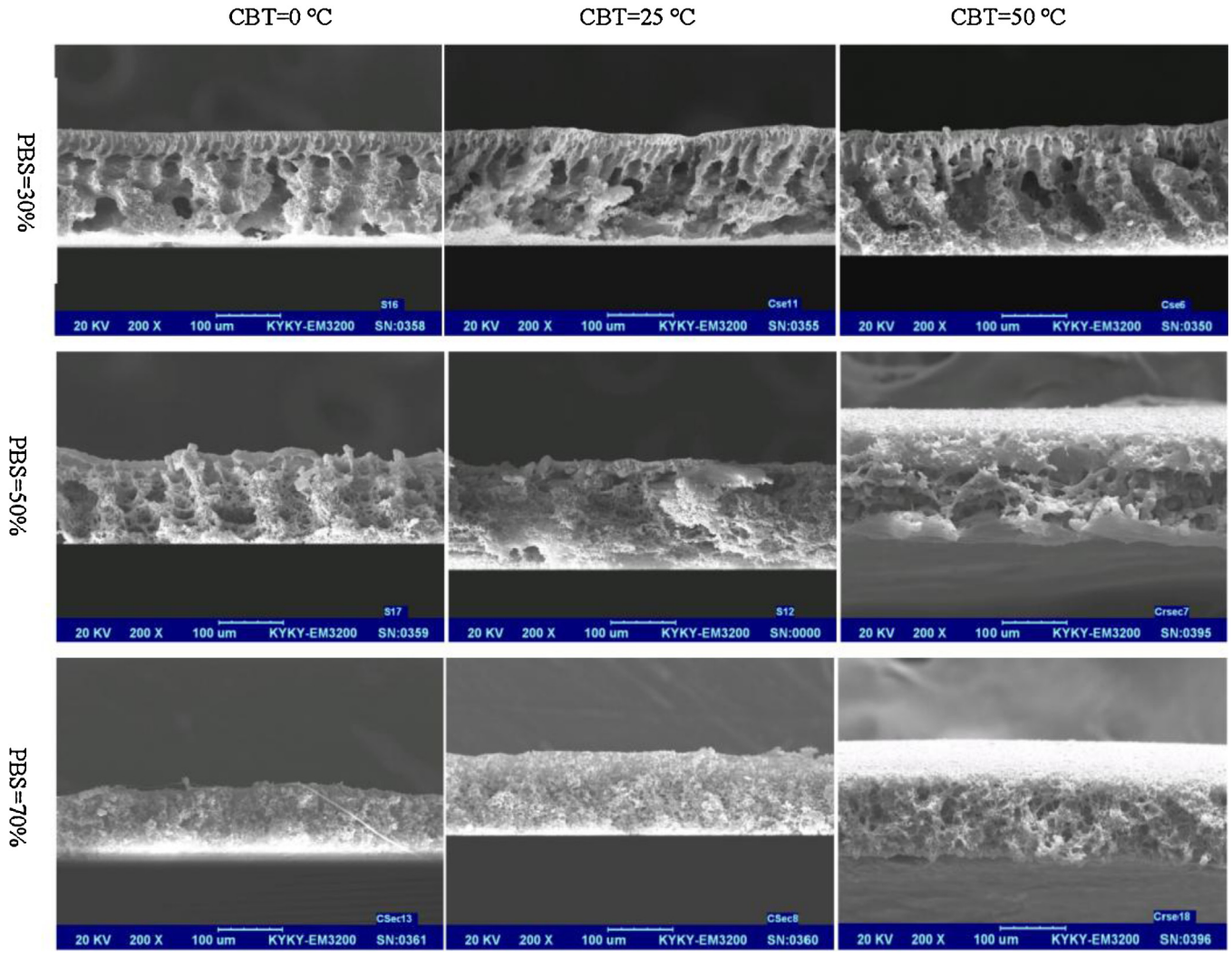

Fig. 3. SEM cross-sectional images of the membranes with PES/PBS blend ratios of 70/30, 50/50 and 30/70 prepared at different CBTs of 0 °C, 25 °C and 50 °C.

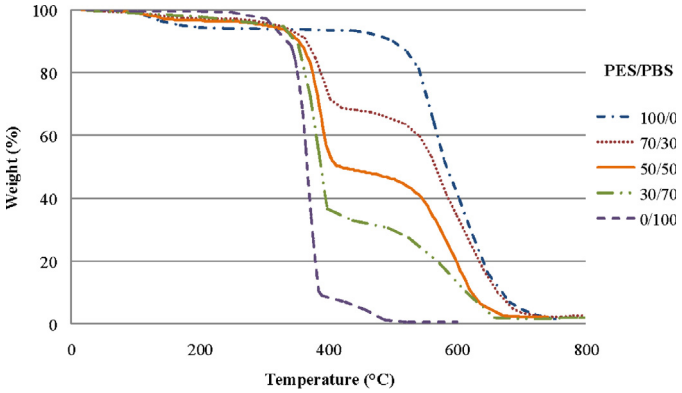

Fig. 4. TGA curves of the neat PES and PBS membranes and their blends.

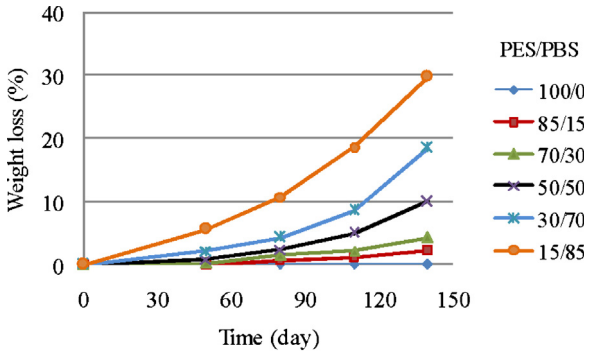

Fig. 6. Weight loss of neat PES and PBS membranes and their blends during the burial in compost.

3.4. Mechanical property

The tensile strength of PES/PBS membranes prepared at different CBT levels is presented in Fig. 5. As expected, the increase of PBS percent decreases the tensile strength of the membranes due to relatively poor mechanical properties of PBS. Thus, the pure PBS and PES membranes have the lowest and highest tensile strength, respectively.

Increasing CBT, the tensile strength of the membranes is slightly decreased, which is more observable for the membranes prepared at CBT of 50 °C. Regarding section 3.2, the membranes prepared at higher CBTs are more porous. The high porosity and large cavities in the membrane structure decrease the mechanical properties [19,20]. This result was also reported for PES/polyvinylpyrrolidone (PVP) membranes prepared at different CBTs [21].

3.5. Biodegradation

Fig. 6 shows the weight loss of the membranes during the burial test. The examined membranes were prepared at CBT of 25 °C. Presence of a biodegradable component (PBS), in membrane structure, facilitates the destruction of membrane under the influence of the microorganisms and environmental action. In fact, PBS macromolecules are subjected to degradation with formation of micro cracks on the surface of the membrane. Due to increase of the effective surface (as a result of the formation of micro cracks), membrane fragmentation then occurs more intensively. The neat PBS membrane buried for about 50 day could not be fully recovered because of a considerable fragmentation. Fig. 7 shows the photos and SEM micrographs of the same samples at first and also end of the degradation test. The test duration for all membranes was 140 days.

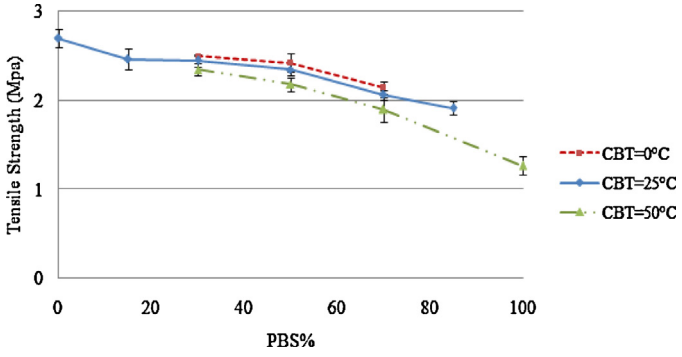

Fig. 5. Effect of PBS concentration and CBT on tensile strength of the membranes.

3.6. Contact angle measurement

Fig. 8 illustrated variations in the membrane contact angle due to increasing PBS concentration in the casting solution. Generally, the values of contact angle for PES and PBS membranes are almost close to each other. Accordingly, it is not expected that contact angle of the blend membranes changes a lot. However, besides type of polymer, membrane porosity can affect contact angle measurement. For more porous surfaces, the water droplet can be spread easier which results in obtaining lower contact angle [22]. Thus, as shown in Fig. 7 and what will be further discussed in section 3.7, addition of PBS from 0% to 50% gently improves the final membrane surface porosity. As a result, the values of contact angle for these membranes have descending trend.

3.7. Membrane performance

In Fig. 9, the wastewater permeation for the membranes prepared at different CBTs is presented as a function of operation time. The adjusted operating condition is 3 bar and 25 °C for TMP and temperature, respectively.

After immersion of the cast film including pure polymer and NMP into water bath, the precipitation starts due to the low miscibility between the polymer and water. Simultaneously, the high miscibility between NMP and water causes their diffusional flow (the exchange of NMP and water) in several points of the film which subsequently leads to formation of nucleuses of polymer-poor phase. Indeed, the low affinity between polymer chains and water molecules, at points that water molecules diffuse, results in repelling the polymer chains and consequently formation of the nucleuses. Growth of the nucleuses is continued until the membrane solidification happens [23].

Now, in PES/PBS blend, affinity between two polymers is relatively low and the casting solution is surely not as uniform as the pure polymer casting solution. Therefore, by addition of the second polymer to the casting solution, the surface pores get larger and reach to the maximum value at blend ratio of 50/50. As a result, the membrane surface porosity is gradually increased up to this ratio which can completely be confirmed by comparing the SEM surface images of PES/PBS membranes with blend ratio of 100/0, 50/50 and 15/85 in the second column of Fig. 7. Increasing the membrane porosity by addition of the second polymer improves the permeate flux directly which is shown in all three parts of Fig. 9.

At constant blend ratio, reduction of CBT reduces mutual diffusivities between components in the system during solidification of the casting solution. The precipitation process takes place slower which results in thinner membrane (Fig. 3). Moreover, the

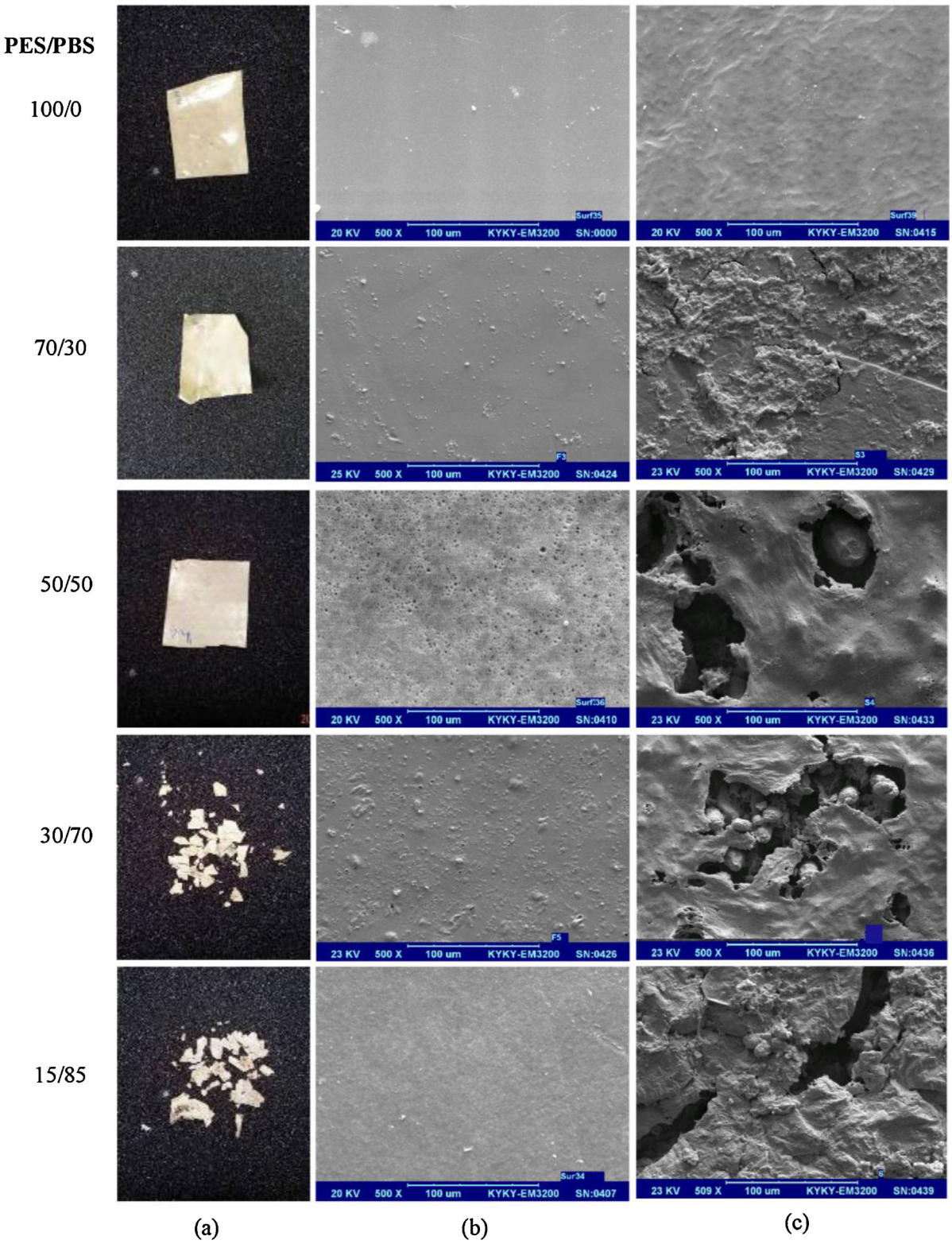

Fig. 7. Visual observation photograph of the membranes at the end of the burial test (a), SEM surface images of the membranes at 0 day (b) and the end of the burial test (c).

polymer concentration on the top layer and substrate of the membrane is increased and approximately a denser structure is obtained. Thus, the membranes prepared at lower CBT have lower fluxes (Fig. 9). Comparing the effect of CBT, stable fluxes of the prepared membranes is shown in Fig. 10 as a function of blend ratio.

Applying the same operating conditions (TMP = 3 bar and $T = 25\ ^{\circ}C$), the influences of the PES/PBS polymer composition and also CBT on the rejection of wastewater pollution indices are shown in Fig. 11. Increasing PBS concentration in the polymer mixture enhances the retentions of COD, turbidity and TDS. This enhancement reaches to optimum values at 85% and also 100% of

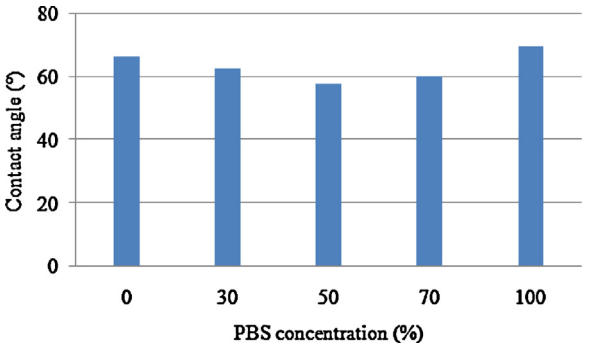

Fig. 8. Effect of PBS concentration on the membrane contact angle.

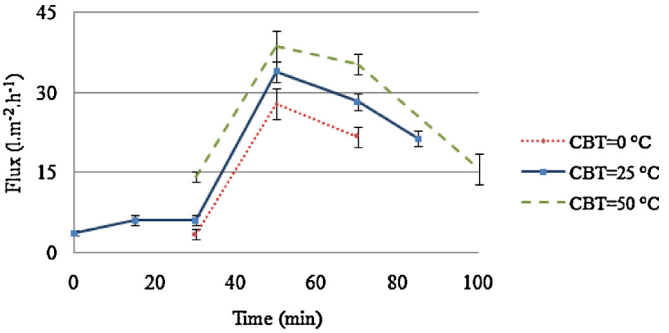

Fig. 10. Stable permeate flux of bread wastewater through the prepared membranes.

PBS. These results refer to the special membranes structure. As shown in Figs. 2 and 3, increasing PBS loading in membranes, finger-like pores in pure PES membranes suppressed gradually till are completely disappeared at rich PBS membrane. This structure inhibits passage of different pollutants through the membrane especially passage of the organic matters with long chains while it does not limit the water passage. Therefore, the rejection increase of the pollution indices is observed. According to Fig. 11, the optimum examined CBT for the treatment of bread wastewater is found to be 25 °C.

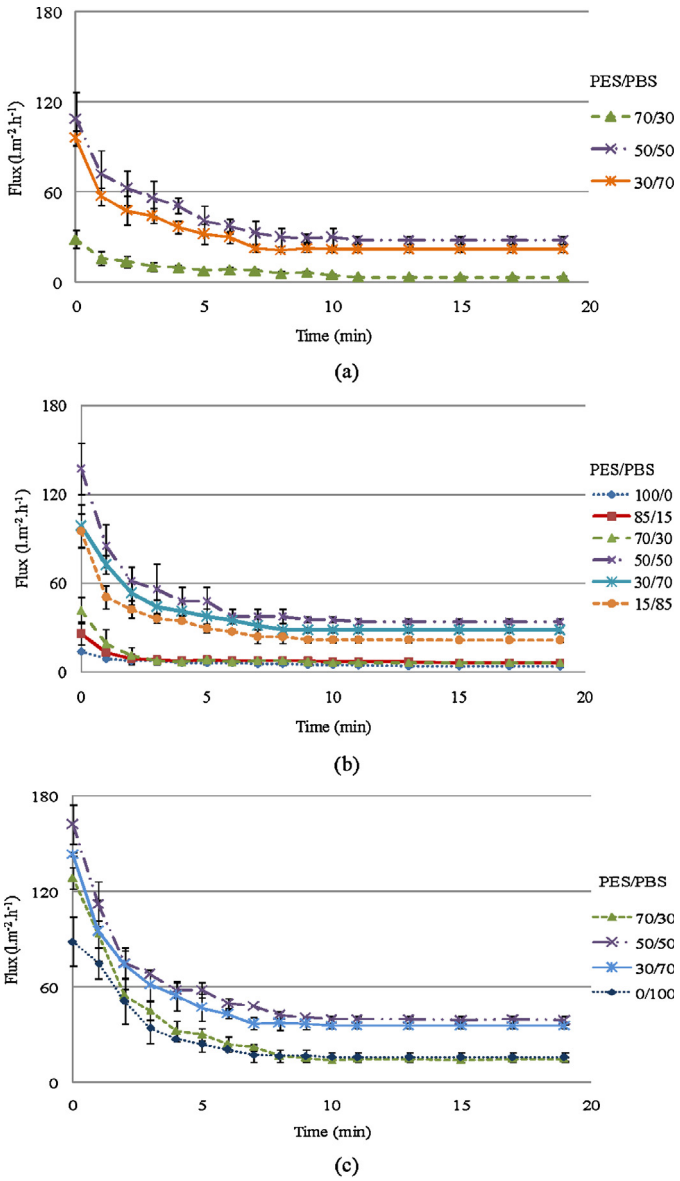

Fig. 9. Permeate flux of bread wastewater through the membranes prepared at (a) CBT = 0 °C, (b) CBT = 25 °C and (c) CBT = 50 °C.

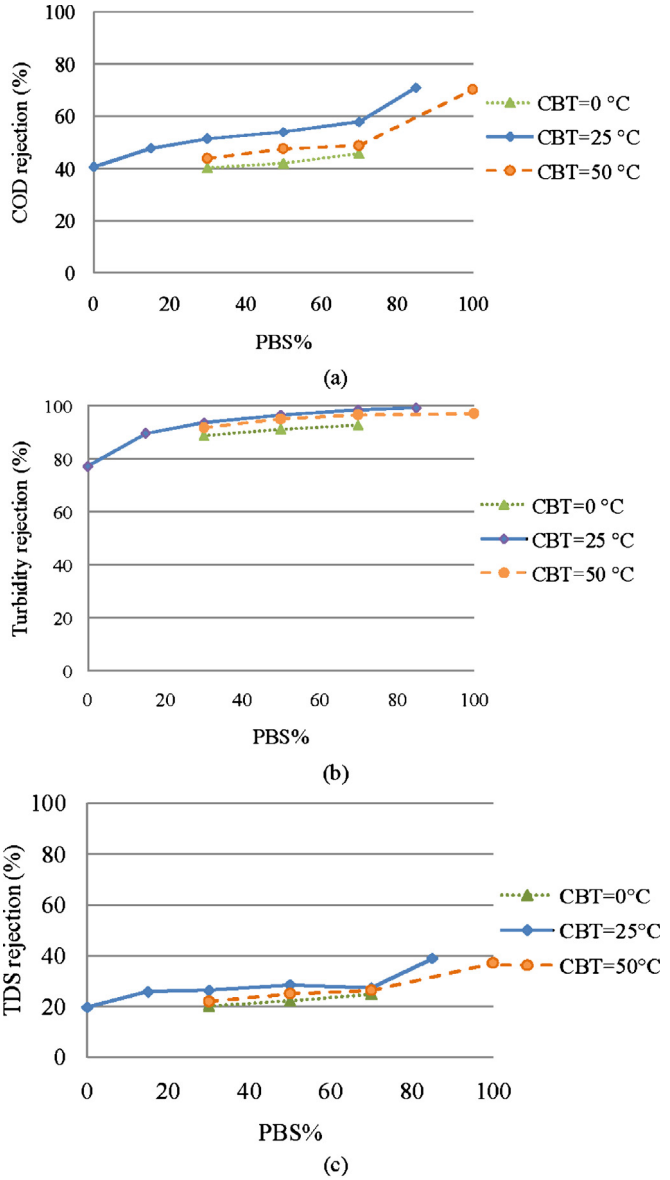

Fig. 11. Effect of PBS concentration in the casting solution and CBT on the rejection of different pollution indices by the prepared membranes.

4. Conclusion

PBS is a biodegradable polymer that is a good choice for preparation of biodegradable membranes. To overcome low tensile strength of PBS, it is suggested to be blended with PES. Therefore, a series of PES/PBS blend membranes were prepared using phase inversion induced by immersion precipitation technique. The effect of preparation conditions was evaluated on the membrane specifications including characteristic bands, morphology, thermal stability, tensile strength, biodegradability and contact angle. Furthermore, performance of the prepared membranes was evaluated in treating the bread wastewater.

Increasing PBS content in the blend membrane, the membrane morphology changed slowly from finger-like to denser structure. Variation of CBT also affected the morphology due to varying the rate of precipitation process in the coagulation bath. PES was shown to be able to improve the thermal stability and tensile strength of PBS membrane. The membrane contact angle was reduced by addition of PBS from 0% to 50%. This trend was reversed at higher PBS concentrations.

Wastewater treatment and also permeation through the prepared membranes were noticeably affected by the blend ratio and CBT according to their direct effect on the membrane structure and surface porosity. Comparing the membranes abilities in reduction of wastewater pollution indices, rich PBS membranes were found to have the highest performance.

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