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Poly(lactic acid)/Biodegradable Polymer Blend for The Preparation of Flat-Sheet Membrane

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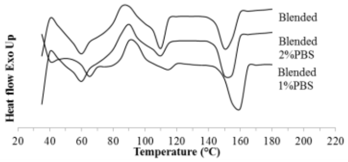
Graphical abstract



Abstract

Biodegradable polymers have been more attractive for membrane materials, especially poly(lactic acid) (PLA) because they degrade in natural environment after use. In this study, the membranes were developed from a polymer blend of PLA and other biodegradable polymers, such as poly(butylene succinate) (PBS), poly(butylene adipate-co-terphthalate) (PBAT) and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). The membranes were formed via nonsolvent induced phase separation process using n-methyl-2-pyrrolidone (NMP) as a solvent and water as a nonsolvent. The pure water flux and BSA rejection were tested to determine the filtration performance of membranes. The microstructures and tensile strength of membranes were characterized by field emission scanning electron microscope (FE-SEM) and universal testing machine (UTM), respectively. All of membranes appeared finger-like and sponge-like structures in cross-section, and porous structure on surface. PLA/PHBV blend membranes had pure water flux and BSA rejection as high as PLA/PBS and PLA/PBAT blend membranes. The pure water flux and BSA rejection of the blend ratio (PLA/PHBV/NMP) of 15:1:84 were 65 l/m^2•h and 79%, respectively.

Keywords: Poly(lactic acid); membrane; phase separation; filtration

■1.0 INTRODUCTION

Poly(lactic acid) (PLA) is the promising biodegradable polymer. In generally, bioplastics can be degraded by microbes under suitable condition such as microbial activity, pH, temperature and moisture. Due to its mechanical properties, thermoplastic processability, biocompatibility and biodegradability, PLA was used for packing film, container and medical application [1]. Furthermore, it has been developed for membrane application [2]. Porous PLA membrane can be applied in food and biomedical industries to clarify product or to remove particles from suspension as well as used in medical application [1, 3].

In the previous research, PLA-based membranes were developed to study miscibility, mechanical properties, permeablility and selectivity. Tanaka *et al*. prepared micro filtration membrane from a blend of poly(carpolactone) (PCL) and PLA. The blend ratio (PCL:PLA) of 4:1 was important to prepare the biodegradable polymer-blend membrane with the ability of the retention of yeast cells and without exfoliation of the membrane [4]. Lebourg *et al*. synthesize membranes from PCL–PLA blends by freeze extraction of a co-solution. This procedure was able to disperse homogeneously both components despite their amorphous phases being immiscible and both polymers crystallize [5]. This research focus on the preparation of flat-sheet membrane with the blends of PLA and other biodegradable polymers, such as polybutylene succinate (PBS), poly(butylene adipate-co-terphthalate) (PBAT) and Poly(3-hydroxybutyrate-co-hydroxyvalarate) (PHBV) to enhance mechanical properties. Furthermore, the prepared membranes are environment friendly.

The cross-sections of PLA/PBS blended membranes were displayed in Figure 3. The size of finger-like structure in the membrane blended 4% PBS was much larger than the other membranes. Thus the permeate flux of the membrane increased, and the selectivity of BSA decreased. The PLA membrane mixed 2% PBS could remove BSA molecules of 87.8% at the room temperature, and 1 kg/cm2. The tensile strength and elongation at break properties of membranes were improved as the added PBS as shown in Table 2.

■2.0 EXPERIMENTAL

2.1 Materials

The biodegradable polymers used in this study were PLA (NatureWork® 2003D, NatureWorks, USA), PBS (GS Pla® FZ71PD, Mitsubishi Chemical Performance Polymers, Inc., Japan), PBAT (Ecoflex® F BX 7011, BASF Co., Ltd., USA) and PHBV (ENMAT^{TM} Y 1000P, Tianan Biological Material

Co., Ltd., China). N-methyl-2-pyrrolidone (NMP) supplied from Labscan was used as the solvent. All the chemicals were of analytical grade and used without any further purification.

2.2 Membrane Preparation

The 15wt.% PLA based membrane was blended with PBS, PBAT and PHBV. The polymers were dissolved in NMP and mixed with a magnetic strirring bar at 90°C. The mixture was kept at that temperature for 24 h to degas in the solution. Then the solution was cast onto a glass plate using a casting knife with knife gab of 10 mils. After 30 s, the glass plate was immersed in to a water bath with the temperature of 30°C, resulting in the phase separation process. Then the porous flat membrane was removed from the glass plate and washed with water extensively to remove residual solvent. The compositions of membranes were summarized in Table 1

Table 1 The composition of membrane

Membrane	Compositions (%)		
	PBS	PBAT	PHBV
1%PBS blend	1	-	-
2%PBS blend	2	-	-
4%PBS blend	4	-	-
1%PBAT blend	-	1	-
2%PBAT blend	-	2	-
4%PBAT blend	-	4	-
1%PHBV blend	-	-	1
2%PHBV blend	-	-	2
4%PHBV blend	-	-	4

2.3 Characterization

The sample were characterized thermal properties with a differential scanning calorimeter (DSC, 200F3, Netzsch) using heating rate at 10ºC/min from 25ºC to 200ºC. The morphology of membrane was observed by a field emission scanning electron microscope (FE-SEM, JSM 6340F, JEOL). The surface and cross-section of the samples were coated with gold by a sputtering coater. The tensile strength and elongation at break were measured by a universal testing machine (UTM, Tensiometer10, Monsanto) with a speed rate of 10 mm/s.

The membrane performance was determined in terms of permeation flux. A cross-flow filtration cell was used for experiment and distilled water was used to measure the permeation resistance of the membranes. The filtration was tested at a transmembrane pressure of 1 bar at room temperature. The permeation flux of pure water can be calculated using the following equation 1,

$$J = \frac{Q}{A \cdot t} \qquad (1)$$

where J is the permeation flux ($L{\cdot}m^{-2}h^{-1}$), Q is the permeation volume (L), A is the filtration area (m^2), and t is the permeation time (h).

The selectivity of membranes was evaluated in terms of the percentage rejection of bovine serum albumin (BSA, MWCO = 66.5 KDa), having concentration of 1000 ppm. The same filtration cell from the permeation flux experiment was used similar to pure water permeation flux experiment at transmembrane pressure of 1 bar. After, the feed and permeate were characterized via a UV-visible spectrophotometer at wavelength of 280 nm, and calculated the % rejection as equation 2,

$$rejection\,(\%) = \left(1 - \frac{C_p}{C_f}\right) x100 \qquad (2)$$

where C_f and C_p are the concentration of the feed and permeate (mg/l), respectively.

3.0 RESULTS AND DISCUSSION

3.1 PLA/PBS Blended Membranes

Figure 1 presented thermograms of the PLA/PBS blended membranes. The crystallization temperature (T_c) of PLA/PBS membrane appeared the broad peaks having around 87.5 to 91.0°C, because the T_C of both PLA and PBS are nearly ($T_{c,PLA}$= 91.2°C, $T_{c,PBS}$ = 115°C) [6]. When the PBS content increased, the T_c had a tendency to decline. Moreover, the two endothermic peaks of the blends were indentified the melting temperature (T_m) of PBS and PLA. The additions of PBS affect the lowered T_m of PLA. Generally, in miscible blends, the melting point of the crystalline component decreased in comparison with pure polymer as a result from favorable thermodynamic interactions at crystal fronts [7]. This reason correspond to the surface structure as shown in Figure 2. PBS was dispersed completely and showed single phase.

3.2 PLA/PBAT Blend Membrane

The addition of PBAT to PLA membranes had influence on the decreasing of temperature behaviors, which were the same as the PBS additions, as shown in Figure 4. For the increase in PBAT content from 1 to 2 and 4%, the T_c and T_m decreased slightly. The two peaks of Tc, which were around 75°C and 90°C, were the chraracters of PBAT and PLA, respectively. The T_m of membranes appeared around 155°C.

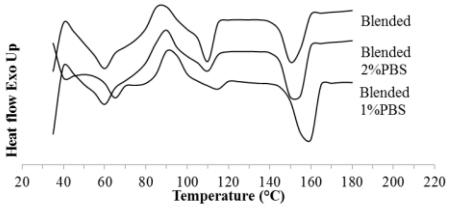


Figure 1 Thermogram of the PLA/PBS blended membranes

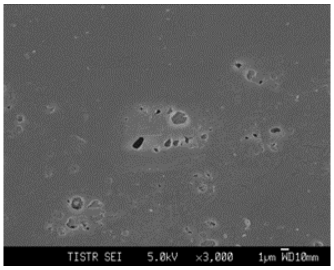


Figure 2 Surface of PLA/4% PBS blended membrane

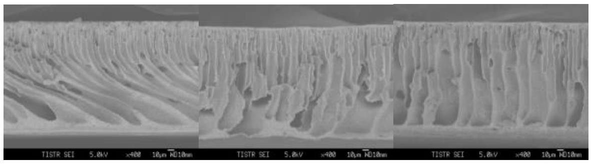

(a) (b) (c)

Figure 3 Cross-section of PBS-PLA blend membrane: (a) Blended 1%PBS; (b) Blended 2%PBS; (c) Blened 4%PBS

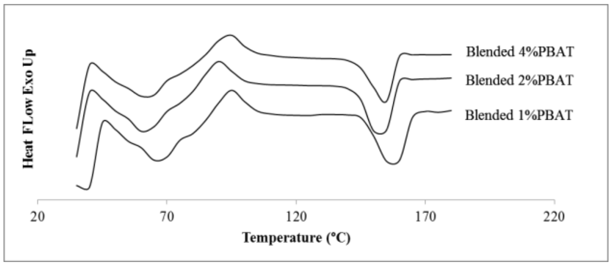


Figure 4 Thermogram of the PLA/PBAT blended membranes

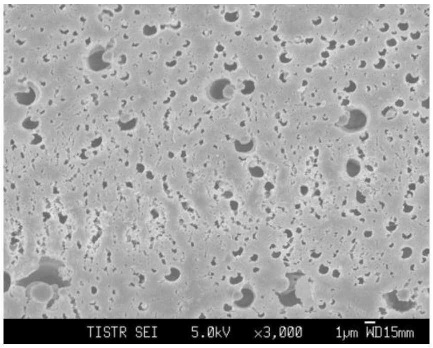


Figure 5 Surface of PLA/4%wt PBAT blended membrane

Because all the PLA/PBAT blended membrane possessed the large pore in the surface, the membrane could not reject the BSA as presented in Figure 5. Moreover, both the tensile strength and elongation were not be improved as the addition of PBAT in PLA membranes as presented in Table 2

Table 2 Properties of PLA-biodegradable blend membrane

Membrane	Flux(l/m^2·h)	BSA rejection(%)	Tensile strength (MPa)	Elongation at break (%)
PLA	19.1	0.2	3.1	21.0
1%PBS-PLA	11.0	75.5	3.4	46.3
2%PBS-PLA	18.0	87.8	3.8	35.8
4%PBS-PLA	27.6	16.1	3.8	41.8
1%PBAT-PLA	10.4	29.1	3.0	18.0
2%PBAT-PLA	18.7	5.7	3.1	10.5
4% PBAT-PLA	13.6	27.5	3.5	14.4
1% PHBV-PLA	65.2	78.7	4.9	51.8
2% PHBV-PLA	6.5	86.1	3.6	18.0
4% PHBV-PLA	25.5	16.0	2.8	36.8

3.3 PLA/PHBV Blend Membranes

For the membranes blended with PHBV, they appeared the one board Tc peak and the two Tm peaks as shown in Figure 6. T_{m1} (150-155°C) was a temperature character of PLA and T_{m2} (~170°C) was that of PHBV. The T_{m2} were prone to increase as the high of PHBV content, which were higher than PLA and PHBV pure membrane. Tm of PLA and PHBV were 168ºC and 170ºC, respectively. Generally, in miscible blends, the melting point of polymer blends increased in comparison with pure polymer [7]. Thus the blends of PLA/PHBV membrane was immiscible. The tensile strength and elongation of 1% PHBV blended membrane had higher than the PLA membrane. At 1% PHBV blended, not only the tensile strength and elongation at break but also the pure water flux and BSA rejection increased. Although the flux of membrane reduced, the selection of that increased slightly as the added 2% PHBV. The water flux and BSA rejection of the 2% blended PHBV membrane were 6.5 l/m^2.h and 86.1%, respectively.

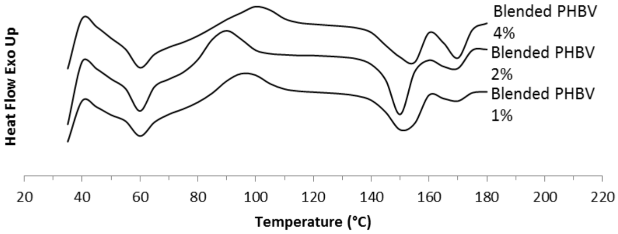


Figure 5 Thermogram of the PLA-PHBV blened membranes

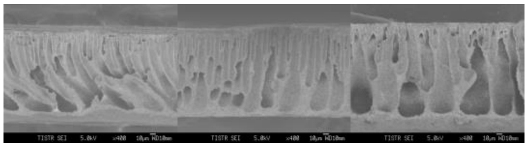

(a) (b) (c)

Figure 6 Cross-section of PLA-PHBV blended membrane: (a) 1%PHBV; (b) 2%PHBV; (c) 4%PHBV

■4.0 CONCLUSION

The membranes prepared from the blends of PLA/biodegradable polymer were successful for filtrations. The PLA based membranes consisting of PBS and PHBV had more missible than that of PBAT. Thus the tensile strength and elongation at break of membranes were enhanced. However, the addition of PBAT to PLA based membrane could not improved the mechanical properteies. PLA-PHBV blend membranes had pure water flux and BSA rejection as high as PLA-PBS and PLA-PBAT blend membranes. The pure water flux and BSA rejection of the blend ratio (PLA-PHBV-NMP) of 15:1:84 were 65 l/m^2•h and 79%, respectively.

References

[1] Gupta, B., Revagade, N., Hilborn. J. 2007. *Prog. Polym. Sci.* 32: 455–482.

[2] Tanaka, T., Lloyd, D. R. 2004. *J. Member. Sci.* 238: 65–73.

[3] Mulder, M. 1996. *Basic Principles of Membrane Technology*. Kluwer Acadimic Publishers.

[4] Tanaka, T., Tsuchiya, T, Takahashi H., Taniguchi, M., Lloyd. D. R. 2006. *Desalination.* 193: 367–374.

[5] Lebourg, M., Suay Anton, J., Gomez Ribelles. J. L. 2008. *Eur Polym J*. 44: 2207–2218.

[6] Jiang, L., Zhang. J. 2013. *Handbook of Biopolymers and Biodegradable Plastics: Properties, Processing and Applications*. Elsevier.

[7] Park, J. W., Im. S. S. 2003. *Poly*. 44: 4341–4354.