

Activated Carbon Effects on Morphology and Permeability of Poly(L-lactic acid)-Poly(ethylene glycol) Membranes[†]

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Poly(lactic acid) (PLA) is a bio-based polymer from plant resources and has been demonstrated to form porous, hydrophilic and strong structure when copolymerized with poly(ethylene glycol) (PEG). Thin film based on PLLA-PEG polyurethane copolymer has an interesting potential application as a disposable biodegradable water filtration membrane. This study aims to develop PLA-PEG polyurethane copolymer thin film membrane with a series of activated carbon (AC) contents of 2, 4, 6, 8, and 10 wt.%. Membrane matrix was first synthesized via chain extension reaction of dihydroxyl terminated PLLA and PEG prepolymers with hexamethylene diisocyanate, before the addition of AC, followed by membrane fabrication. Combining PLLA-PEG with AC resulted in changes in the morphology, thermal properties, and permeability of the membrane. Formation of urethane groups was observed in the ATR-FTIR spectrum based on the appearance of a new peak at 1619 cm⁻¹ corresponding to -NH- group. FESEM analysis showed that membrane with 6% AC had more uniform pores compared to membranes with 2% and 10% AC. Permeation water flux test demonstrated that exerted pressure gave insignificant effect towards the resistance of membrane water fluxes, with the increment of AC resulted in increasing resistance. It was also found that the membrane with 2% AC had the highest total mean in permeation water flux, followed by 6% and 10% AC.

Key words: Poly(l-lactic acid); poly(ethylene glycol); activated carbon; membrane; and polyurethane

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A membrane thickness can be thick or thin, and its structure can be homogenous or heterogeneous. While in transport it can be active or passive in which passive transport can be driven by a difference in pressure, concentration or temperature. Also, membranes can be natural or synthetic, neutral or charged [1]. Porous synthetic membranes are used for filtration in research, industry, and biotechnology. They are commonly made from polymers, which are materials constructed from repeating building blocks. Membranes made with block copolymers, which are comprised of two types of building blocks, have more uniform pores than single polymer membranes, so that they can filter particles more selectively. One of the copolymer building blocks of particular interest is polyurethane.

Polyurethane is a class of polymers with various functional groups, allowing flexibility to combine different building blocks to produce copolymers with desirable physicochemical properties. For the same reason, activated carbon powdered was selected as the filler due to the

presence of different functional groups, the facility of the surface modification, and large surface area [2]. Activated carbon is a black solid substance resembling granular or powdered charcoal [3]. It is a processed carbon material with highly developed porous structure and large internal specific surface area which become highly absorbent materials. Adsorption process is one of the promising approaches for the removal of organics in water and wastewater. Previous studies show that adsorption is efficient for the removal of a wide range of organic compounds, and different type of adsorbents has been produced to remove organic content of water and industrial effluent [4].

Poly(lactic acid) (PLA) is a biodegradable and bio-based polymer. It has the advantages of high modulus, high strength, thermoplasticity, transparency, and biocompatibility, when compared to other biopolymers such as starch [5]. However, PLA also has the drawbacks of inherent brittleness and poor toughness, which impede its wide application [6, 7, 8]. Meanwhile, PEG shows hydrophilicity and

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biocompatibility [9, 10], and it is soluble in water and organic solvents [11]. Other than that, it was found that PEG can increase the porosity and thickness of membrane [12] and also an excellent plasticizer for PLA because of its good miscibility [13]. The elongation at break of PLA increases in the presence of PEG, but the impact resistance remains poor [5]. Therefore, it is interesting to synthesis biodegradable PLLA-PEG polyurethane multiblock copolymers to be used as membrane and to incorporate activated carbon (AC) as filler and absorbent. Previously, the effect of PEG molecular weight on the performance of PLLA-PEG/AC membranes in terms of permeation water flux, palm oil mill effluent permeation and contact angle was evaluated [14]. The purpose of this article is to investigate the effect of AC concentration on the morphology and water permeation of PLLA-PEG/AC membranes.

MATERIALS AND METHODS

Materials

Poly(L-lactic acid) (PLLA), poly(ethylene glycol) (PEG) ($M_w = 10000$ g/mol), tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$), 1,6-hexamethylene diisocyanate (HMDI) and AC powder were purchased from Sigma-Aldrich (Malaysia). Dichloromethane (DCM) and tetrahydrofuran (THF) solvents were purchased from Chemiz (Malaysia). All chemicals were used as received without further purification.

Preparation of PLLA-PEG/AC Membrane

PLLA-PEG/AC copolymer membranes were prepared in three steps, where the first step is the synthesis of PLLA-PEG polyurethane copolymer, followed by addition of AC and homogenization in the second step. In the third step, the solution mixture undergone solvent casting and phase inversion techniques to produce porous thin films.

The following is the procedure to prepare PLLA-PEG/2%AC. First, 5.0 g of PLLA pellets were dissolved into 30 ml of DCM, stirred and covered with a greased flask stopper. At the same time, 0.2 g of AC powder (45-63 μm , previously sieved) was stirred in 15 ml of THF in a beaker and covered with parafilms. After 2 hours, 5.0 g of PEG was added into the flask containing PLLA solution, followed by 0.036 g of $\text{Sn}(\text{Oct})_2$ catalyst and 0.7 g of HMDI. The solution was stirred and allowed to react for 2 hours at 45°C to form PLLA-PEG polyurethane copolymer. Then, the AC-THF suspension was added into the flask containing PLLA-PEG solution and excess AC was rinsed with 15 ml of THF. The mixture was stirred for another 24 hours for homogenization.

The membrane was fabricated using solvent casting and phase inversion techniques. The PLLA-PEG/AC solution produced was poured onto a glass plate and made into a thin solution film using a casting knife with an adjusted thickness of 0.1 mm.

The solution film was allowed to evaporate at room temperature for 1 minute before being immersed in 2 litre of distilled water, where membrane film started to form. The membrane sample was dried at room temperature.

This preparation method was repeated using 0.4, 0.6, 0.8 and 1.0 g of AC for producing membranes containing 4%, 6%, 8% and 10% AC, respectively (Table 1).

Table 1. Sample designation and composition of activated carbon.

Sample designation	Composition of activated carbon (g)
PLLA-PEG/2%AC	0.2
PLLA-PEG/4%AC	0.4
PLLA-PEG/6%AC	0.6
PLLA-PEG/8%AC	0.8
PLLA-PEG/10%AC	1.0

Characterization

Pure water flux (PWF) purpose is to measure the rate of liquid fluxing of the polymer membranes where stirred cell of Model 8200 was used. Membrane PWF was measured by using the ultrafiltration cross flow water permeability testing unit by using distilled water. The experiment was conducted at a transmembrane pressure of 1, 2 and 3 bar with nitrogen gas flow and permeate was collected every 1 minute. The membrane was cut into 6 cm diameter before testing. The permeation flux was defined as Equation (1):

$$PWF = \frac{Q}{A \times \Delta t} \quad (1)$$

where, Q is the permeate volume (L), A is the membrane area (m^2), and t is the time (h). The PWF test was repeated 3 times for each membrane composition.

ATR-FTIR analysis was done using a Spectrum 400 Perkin Elmer GX Spectrometer. The prepared samples were analyzed with infrared ranged from the frequency of 4000 to 650 cm^{-1} .

The morphologies in membrane cross-sections and surfaces were inspected using scanning electronic microscope (SUPRA 55VP Zeiss 2008). The membranes were fractured in liquid nitrogen and coated with platinum under vacuum before test.

The samples were analyzed using a Mettler Toledo TGA/SDTA 851° instrument for the study of thermal stability. The heating rate used was 10°C/min, and the measurement was started from

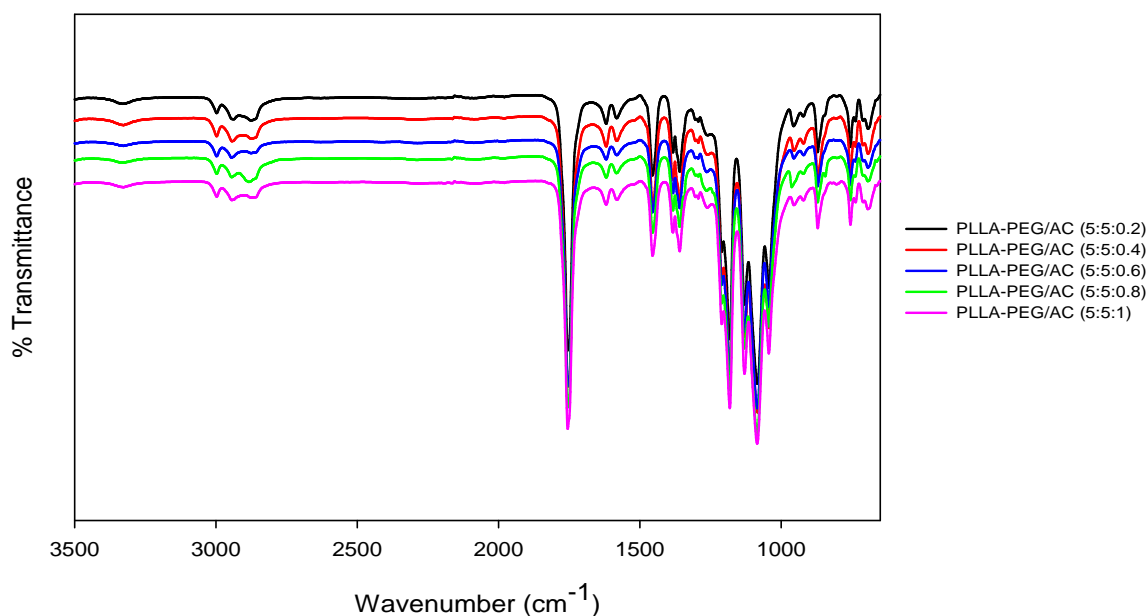


Figure 1. PLLA-PEG polyurethane copolymer structure and IR spectra of PLLA-PEG/AC membranes by different amount of AC filler.

room temperature up to 800°C. Differential scanning calorimetry (DSC) measurement was performed with a Mettler Toledo DSC 822^o instrument with heating and cooling rates of 10°C/min in the range of 30-180°C, under inert nitrogen atmosphere.

RESULTS AND DISCUSSION

Fourier Transformed Infrared Analysis

Figure 1 shows the structure of PLLA-PEG copolymer and the IR spectra of PLLA-PEG copolymer membranes containing 2, 4, 6 and 8 and 10 wt.% of AC filler which have similar wavenumbers. The peaks at 1755 cm^{-1} and 1085 cm^{-1} can be assigned to the ester C=O stretching vibration of PLLA and ether -C-O-C- stretching vibration from PEG, respectively, suggesting the presence of the two component blocks in the copolymer. Meanwhile, the peak observed at 2997 cm^{-1} and 2944 cm^{-1} are due to the C-H stretching vibration of -CH₃ and -CH- groups. Furthermore, bending of -N-H was observed at frequencies of 1619 cm^{-1} , and this proves that the urethane functional groups exist in the PLLA-PEG/AC membrane [15]. The functional group of isocyanate was reported to show a strong absorption peak at 2300 cm^{-1} [16]. This peak was not observed in the PLLA-PEG/AC spectra, therefore indicating that HMDI free molecules have been fully reacted with PLLA and PEG.

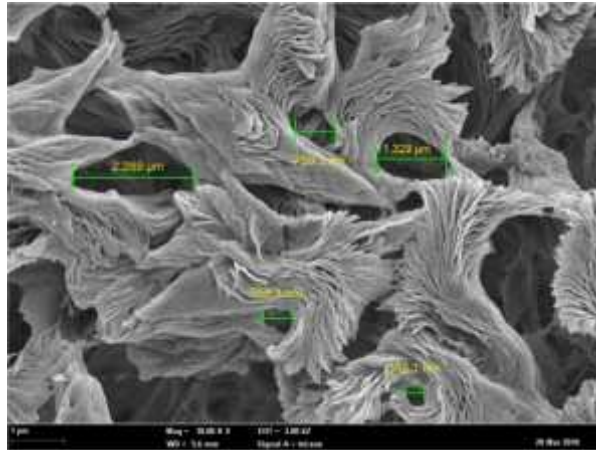
MORPHOLOGICAL ANALYSIS

The surface and cross-section of membranes were analyzed to compare the pore formation and

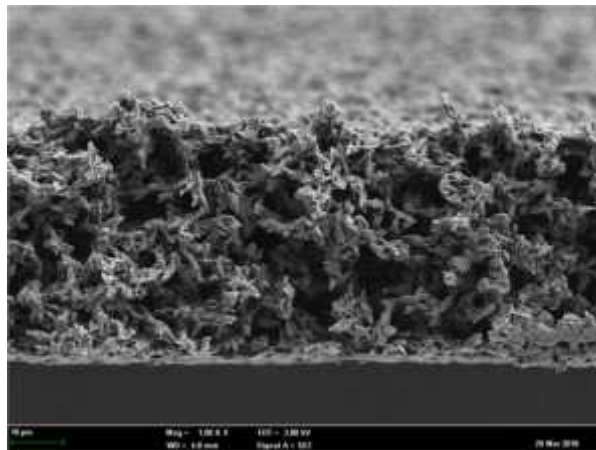
distribution before and after the addition of AC. Figure 2 illustrates the FESEM images of the surface and the cross-section of the pristine PLLA-PEG copolymer membrane and with the presence of 2, 6, and 10 wt.% of AC. The surface of pristine PLLA-PEG membrane [Figure 2(a1)] appeared as layers with mushroom-like shape stacking on top of each other. When 2 wt.% of AC was added, the membrane surface started to form a continuous porous structure and as the amount of AC was increased, the membranes pore size decreased [Figure 2(b1-d1)]. However, membrane PLLA-PEG/10%AC also had irregularly large pores. Two factors contributed to pore formation of membranes. Phase inversion technique was the first factor where during membrane fabrication, the immersion of membrane solution layer on glass plate into water led to interaction of the membrane solution layer with water, causing displacement of tetrahydrofuran and dichloromethane molecules with water. The interaction between membrane solution layer and water was improved by the presence of AC particles, making the diffusion of water easier. Subsequently, the membrane was dried, and water molecules dissipated, leaving pores on the membrane. The second factor was largely contributed by hydrophilic and highly porous AC. Efficient interaction between AC and copolymer matrix should result in filler being covered with polymer matrix, whereas inefficient interaction would result in filler particles leaching out into water, leaving vacant pores on the membrane layer. At a relatively high amount, excess AC potentially formed agglomerates with high affinity towards water, therefore producing large pores as they leached as shown in Figure 2(d1).

The cross-section images of PLLA-PEG/AC membranes revealed the characteristics of an asymmetric microporous membrane composing of porous selective layers on the top and bottom [Figure 2(a2-d2)]. A variation in pore size throughout the thickness of the membranes can be observed, with irregular shape and even distribution. It seems that

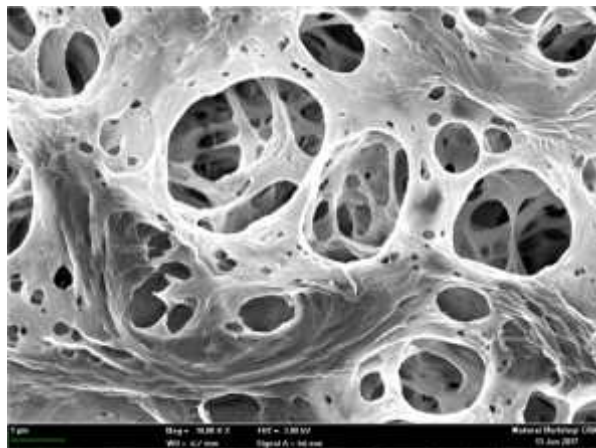
during the membrane formation, polyurethane preferentially concentrated in the surface, creating a dense layer as AC amount increasing. These characteristics may be useful for filtration because the AC particles are still present in the top layer and in the porous sub layer, which may enhance the permeate flux [17].



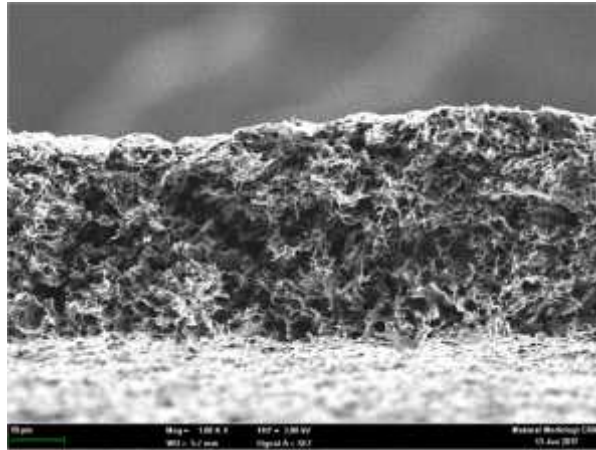
(a1)



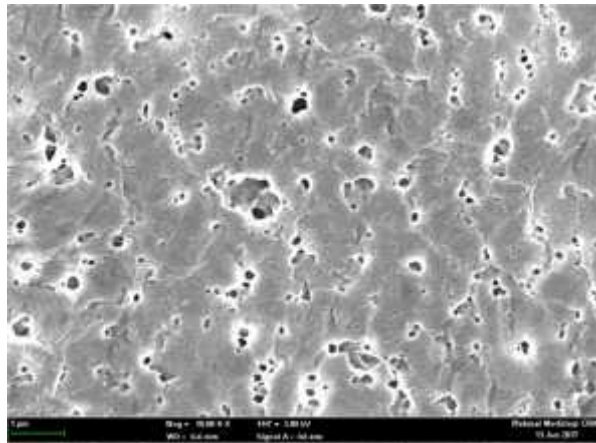
(a2)



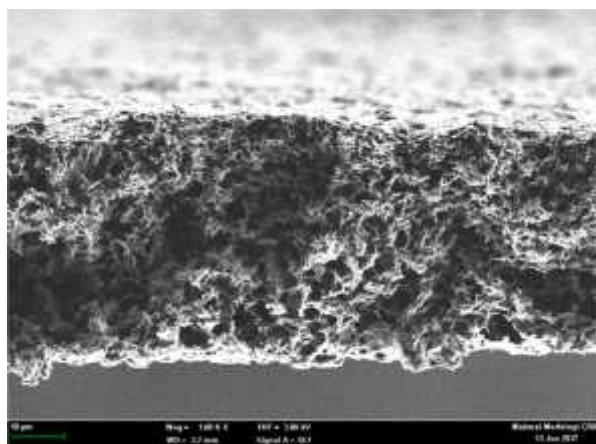
(b1)



(b2)



(c1)



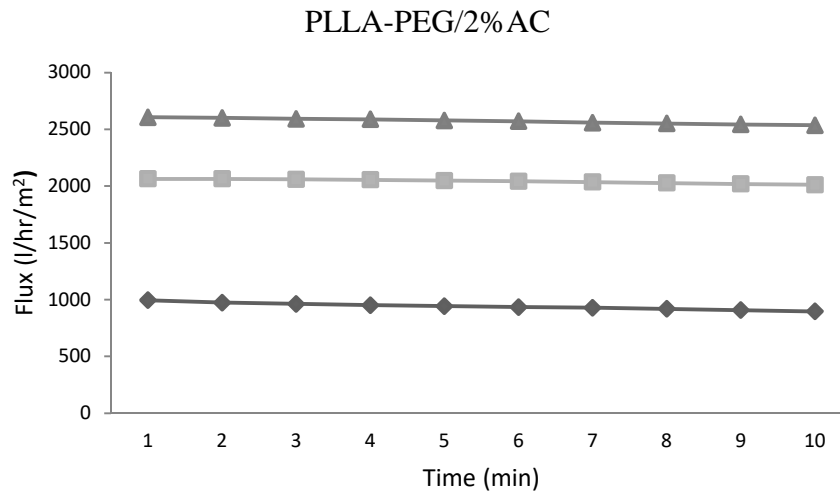
(c2)

Figure 2. FESEM photographs of (a) pristine PLLA-PEG membrane, and PLLA-PEG membranes with (b) 2 wt.%, (c) 6 wt.% and (d)10 wt.% AC filler, where 1 and 2 show the upper surface and cross-section of the membranes, respectively.

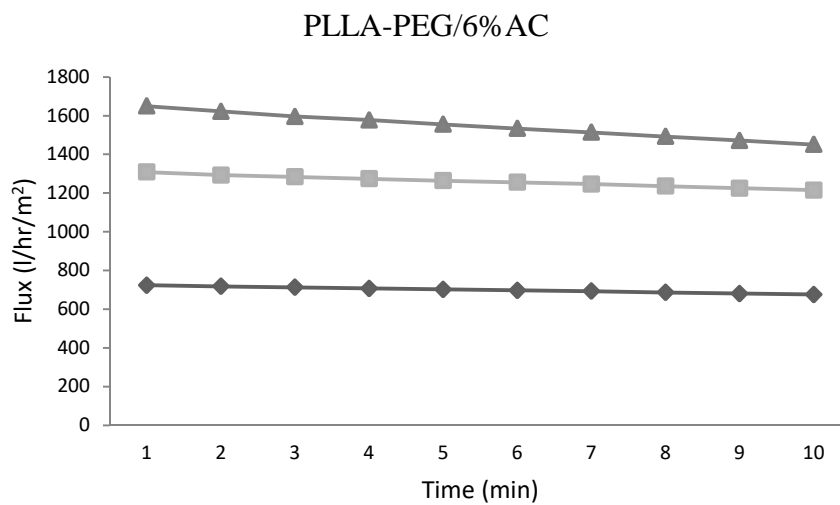
Permeation Water Flux Test

The performance of PLLA-PEG polyurethane copolymer membranes containing 2, 6, and 10 wt.% of AC filler and the capability of the membrane to resist water permeability were evaluated using water permeation flux testing unit at pressures of 1, 2 and 3 bars. Water permeation flux of the membranes as a function of time is plotted in Figure 3. Overall, the flux increases in favour of exerted pressure, and the pressure, variation does not give a significant effect on the water flux resistance for all AC compositions. The slope of the lines indicates resistance of the membranes. It can be seen that membranes containing low amount of AC exhibit less resistance towards water fluxes, as indicated by the horizontal

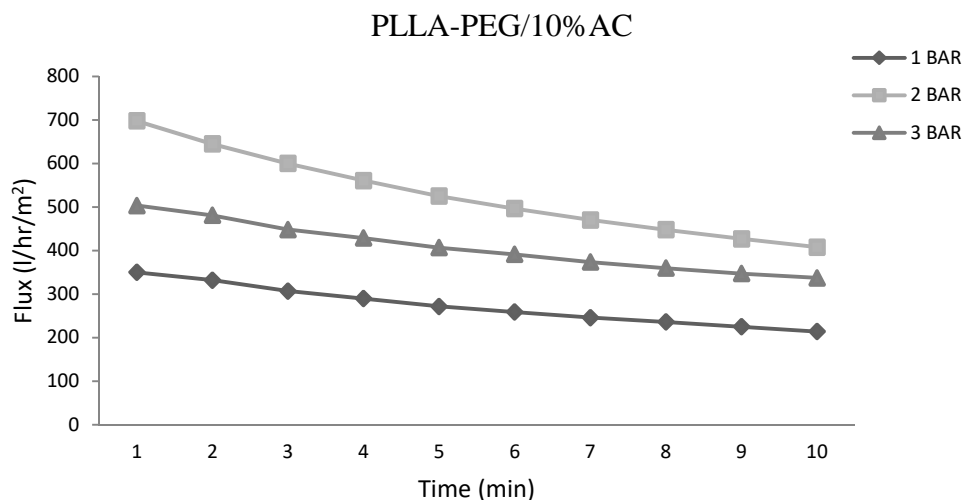
graph lines in Figure 3(a) and 3(b). PLLA-PEG/2%AC and PLLA-PEG/6%AC showed consistent permeability at 1, 2, and 3 bars. Meanwhile, the fluxes of PLLA-PEG/10%AC [Figure 3(c)] were reduced over time, with the rate of decreasing flux at 3 bars is more prominent than 1 and 2 bars. It is also found that the PLLA-PEG/2%AC has the highest total mean in permeation water flux, followed by 6% and 10%AC. According Chung *et al.* (2007), the reduction in the performance of a mixed matrix membrane can be attributed to the pore blockage of inorganic fillers by the polymer chains [18]. The filler could be obstructed from the transport process as a result of filling by the polymer chains; therefore, a decline in performance could be obtained [19].



(a)



(b)



(c)

Figure 3. Performance of water permeation flux of PLLA-PEG/AC membranes with different amount of AC filler (a) 2%, (b) 6%, and (c) 10%.

CONCLUSION

PLLA-PEG polyurethane block copolymer with different loading of activated carbon (AC), which was 2, 4, 6, 8 and 10 wt.% were fabricated into flat sheet membrane, and their structure, morphology and water permeability were investigated. Through FTIR analysis, the ester and ether functional groups of the parent polymers were observed with the addition of urethane linkage, indicating PLLA-PEG polyurethane copolymerization a success. SEM analysis showed that the PLLA-PEG/AC membranes exhibited continuous membrane matrix than pristine PLLA-PEG membrane. Increasing AC content from 2 to 6 and 10 wt.% decreased the pore size of membranes. However, at 10 wt.% of AC formation of large pores was observed due to agglomeration and leaching of AC particles. From permeation water flux test, exerted pressure gave insignificant effect towards the resistance of membrane water fluxes, with the increment of AC resulted in increasing resistance. The high permeation performance of PLLA-PEG/AC membranes, their controllable, uniform porosity, and excellent physical properties showed that this membrane system had high potential to be explored further in the application of wastewater treatment.

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REFERENCE

1. Marcel, M. (2000) *Basic Principles of Membrane Technology*, 2nd edn., Kluwer Academic, Dordrecht, the Netherlands.
2. Amaral, R. A., Habert, A. C. and Borges, C. P. (1985) Activated carbon polyurethane membrane for a model fuel desulfurization by pervaporation, *Materials Letters*, **137**, 468–470.
3. Helena, J., Andrzej, S. and Jerzy, C. (1991) *Active Carbon*, Ellis Horwood Ltd., London.
4. Muyibi, S. A., Tajari, T., Jami, M. S. and Amosa, M. K. (2014) Removal of organics from treated palm oil mill effluent (POME) using powdered activated carbon (PAC), *Advances in Environmental Biology*, **8(3)**, 590-595.
5. Gui, Z., Xu, Y., Gao, Y., Lu, C. and Cheng, S. (2012) Novel polyethylene glycol-based polyester-toughened polylactide, *Materials Letters*, **71**, 63–65.
6. Liu, H. and Zhang, J. (2011) Research progress in toughening modification of poly(lactic acid), *Journal Polymer Science Polymer Physics*, **49**, 1051–83.
7. Rasal, R. M., Janorkar, A. V. and Hirt, D. E. (2010) Poly(lactic acid) modifications, *Programme Polymer Science*, **35**, 338–56.

8. Meng, B., Tao, J., Deng, J., Wu, Z. and Yang, M. (2011) Toughening of polylactide with higher loading of nano-titania particles coated by poly(-caprolactone), *Materials Letters*, **65**, 729–732.
9. Ouchi, T., Yuyama, H. and Vogl, O. J. (1987) Syntheses of 5-fluorouracil-terminated monomethoxy poly(ethylene glycol)s, their hydrolysis behavior, and their antitumor activities, *Macromolecule Science Chemistry*, **A24(9)**, 1011-1032.
10. Desai, N. P. and Hubbell, J. A. (1992) Surface physical interpenetrating networks of poly(ethylene-terephthalate) and poly(ethylene oxide) with biomedical applications, *Macromolecules*, **25**, 226–32.
11. Leea, S. Y., Chin, I. J. and Jung, J. S. (1999) Crystallization behavior of poly(L-lactide)-poly(ethylene glycol) multiblock copolymers, *European Polymer Journal*, **35**, 2147-2153.
12. Saljoughi, E., Amirilargani, M. and Mohammadi, T. (2010) Effect of PEG additive and coagulation bath temperature on the morphology, permeability and thermal/chemical stability of asymmetric CA membranes, *Desalination*, **262**, 72–78.
13. Sheth, M., Kumar, R. A., Dave, V., Gross, R. A. and McCarthy, S. P. (1997) Biodegradable polymer blends of poly(lactic acid) and poly(ethylene glycol), *Journal Application Polymer Science*, **66**, 1495–505.
14. Sidik, A. M., Othaman, R. and Anuar, F. H. (2018) The effect of molecular weight on the surface and permeation of poly(l-lactic acid)-poly(ethylene glycol) membrane with activated carbon filler, *Sains Malaysiana*, **47(6)**, 1181-1187.
15. Wong, C. S. and Badri, K. H. (2010) Sifat terma dan kerintangan api poliuretana berasaskan minyak isirung sawit dan minyak kacang soya, *Sains Malaysiana*, **39(5)**, 775-784.
16. Hiltunen, K., Seppälä, J. V. and Härkönen, M. (1997) Lactic acid based poly(ester-urethanes): use of hydroxyl terminated prepolymer in urethane synthesis, *Journal of Polymer Science*, **63**, 1091-1100.
17. Amaral, R. A., Habert, A. C. and Borges, C. P. (2014) Activated carbon polyurethane membrane for a model fuel desulfurization by pervaporation, *Materials Letters*, **137**, 468–470.
18. Chung, T. S., Jiang L. Y., Li Y. and Kulprathipanja, S. (2007) Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, *Progress in Polymer Science*, **32**, 483-507.
19. Hülägü, D., Kramer, V. and Kraume, M. (2012) Preparation and characterization of mixed-matrix-membranes, *Technical Transactions*, **5**, 109.