Potential Application of Porous Membrane from Blends of Homopolymer for Industrial Water Treatment

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Abstract

The self-organization of matter has been extensively explored in recent years, and significant advancements have been made in the field of porous ordered films produced by the auto-assembly of different polymer materials, being block of copolymers, blends of homopolymers or amphiphilic polymers. The hierarchical ordering in micro-organized films, known also as Honeycomb (HC) structure, generates a significant increase of specifics characteristics enhancing certain properties of the materials. The preparation of self-assembled porous membrane is done by different approaches. We use hereby the bottom-up microporous structuring method specifically the breath figure (BF) approach to prepare highly-organized membrane from polymer blends. The foremost motives for using the BF are the simplicity of implementation and the adaptability to multiple systems which make it a robust and inexpensive technique for the production of structured surfaces. The honeycomb (HC) structures formed by the BF is a potential candidate for water treatment as a filtration membrane to treat stable oil-water emulsions encountered in the oil and gas industry. The use of homopolymer blends improves the selectivity, permeability and anti-fouling properties comparing to the commercial homopolymer membrane. This presentation will highlight the preparation of self-assembled blends of homopolymers membrane by BF and their performance for cleaning of industrial wastewater and the fouling/re-use potential.

Keywords: Microporous surfaces; Polymer blends; Breath figures; Water treatment

1 Introduction

Qatar National Vision 2030 strives to build an advanced society providing a high standard living for its citizens, the vision faces various concerns among them the environmental challenge. Recently the advancement in urbanization and industrialization caused alarming challenges for wastewater treatment. Indeed, Oil, gas, generated water, and solid particles are all components of the (crude oil) that comes from the oil wells. Well-defined layers of gas, crude oil, and process water are produced after transferring the mixture into primary gravity separators (Yu, Han et al., 2017). One of the utmost techniques for treating wastewater on an industrial scale is membrane filtration. Numerous processing aspects, including easy cleaning, the capacity to recycle the membrane, and pure permeate, encourage the use of a porous membrane in industry. Membrane separation is predominantly cantered on a size-sieving mechanism. The morphology of the membrane (size, porosity, thickness, and surface chemistry of pores) has a high impact on the membrane performance in filtration. In wastewater treatment, four types of membranes, specifically, microfiltration (MF), ultrafiltration (UF), nano-filtration (NF) and reverse osmosis (RO) are used in the separation process (Strathmann 2001). While the MF membrane rejects particles of microns' size and microorganisms, the UF additionally excludes bacteria and soluble macromolecules. On the other hand, the RO membrane rejects small particle-size ion salts, whereas NF's performance resides between RO and UF membranes (Sagle and Freeman 2004). The Fig. 1 shows the pores' size range of the aforementioned membrane.

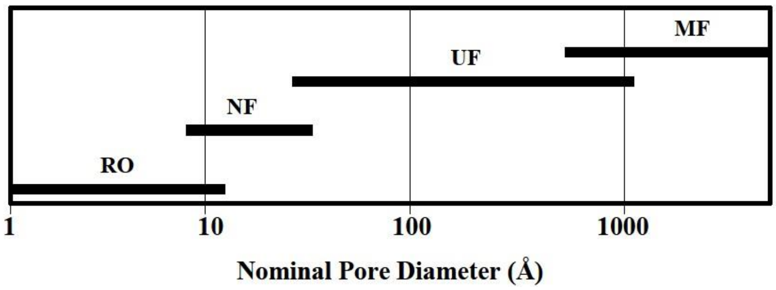

Fig. 1: Pore size scale of the industrial membrane (reproduced with permission from Sagle et al. 2004).

All developed membranes present an intrinsic trade-off between permeability and selectivity, particularly, how fast the molecules go through the membrane and the rejection of certain molecules from the rest (Park, Kamcev et al., 2017). The filtration by size exclusion approach is directly linked to the pore size and thus to the membrane selectivity (Werber, Osuji et al., 2016). The distinctive capability of amphiphilic polymer (homopolymer, blends of polymer, and block copolymer) to be self-organized in hierarchically porous domains has urged researchers to explore the usefulness of these materials in membrane filtration (Xu, Stevens et al., 2003; Yang, Ryu et al. 2006; Jackson & Hillmyer, 2010). The self-organization of matter is extensively studied in recent years, this attention is motivated by the adaptability, easiness of implementation for different applications (e.g. microelectronic, optoelectronic, photonic, sensors, catalyst, and scaffolds) (De Rosa, Park et al., 2000, Cho & Ihm, 2002, Yabu & Shimomura, 2005), and the possible applicability to large-scale.

The surface properties including, among others, the chemical composition or micro/nano-structuring play a key role in their final application (Jeon, Simon Jr et al., 2014). Considering the surface properties, for instance, superhydrophobic surfaces (Bolognesi, DiGianvincenzo et al. 2008, de León, del Campo et al., 2012), biocompatible surfaces for cell culture and adhesion (Tsuruma, Tanaka et al., 2005, Yabu, Hirai et al., 2008), active layers for magnetic, optical and conductive fields (Fukuhira, Ito et al., 2008), (Jiang, Zhang et al., 2012), (Kurono, Shimada et al., 2002), and smart systems (Connal, Franks et al., 2010), these hierarchically porous membranes have been elaborated using different approaches (Akoumeh, Elzein et al. 2020). Among these approaches, those based on surface instabilities have attracted special attention.,(Rodríguez-Hernández & Drummond, 2015) the bottom-up microporous structuring specifically, the Breath figure approach has been largely employed for the preparation of Honeycomb structures with variable pore sizes, and chemical distribution.(Escalé, Rubatat et al., 2012, Heng, Wang et al., 2013, Muñoz-Bonilla, Fernández-García et al., 2014, Dou, Jin et al., 2015, Bormashenko, 2017, Calejo, Ilmarinen et al., 2018, Yabu, 2018). Bunz et al. explained the breath figure (BF) phenomenon that occurs when water droplets condense on a cold surface (due to evaporation of the highly volatile solvent). The imprint of the water droplets left in the polymer matrix after solvent evaporation acts as the template during the formation of the microporous surfaces called honeycomb (HC) (Bunz et al. 2006, Beattie, Wong et al., 2006). Membranes prepared using star polymers, amphiphilic copolymers, block copolymers but also polymer blends are well known for their directed hierarchical self-assembly in honeycomb structures (Bertrand, Bousquet et al., 2016, Akoumeh, Elzein et al., 2020).

In this work, we discuss the elaboration of a porous stand-alone membrane by breath figure approach using a blend of biodegradable polymers: Polycaprolactone (PCL) and Polylactic acid (PLA). The choice of these two polymers is justified by multiple reasons. First of all, PCL addition to PLA shows a significant improvement in the ductility and toughness of PLA (Kawano, Sato et al., 2014). Second, the PLA might exhibit reversible pH-responsive wettability due to the presence of carboxylic groups. Thus, hydrophobic and hydrophilic characteristic in membranes provides a better fouling resistance (Banerjee, Pangule et al., 2011). Both the morphology of the prepared micro-structured membrane and the chemical distribution on the surface is thoroughly studied.

2 Materials and Methods

2.1 Materials

Poly (ε-caprolactone) (PCL) (PBI 010) and poly(lactic acid) (PLE 003) were purchased from Natureplast. All other solvents were employed as received without further purification and purchased from Sigma Aldrich.

2.2 Characterisation Technique

Scanning electron microscopy (SEM) micrographs were taken using a Philips XL30 with an acceleration voltage of 25 kV. The samples were coated with gold prior to scanning.

Confocal RAMAN imaging was done using the WITec alpha 300RA+ Raman microscope, which was equipped with Frequency Doubled Nd: YAG 532 nm laser and a CCD detector (cooled to −65 degree). A 50 X Objective from Zeiss LD Epiplan Naofluar 50X DIC; working distance: 9.1mm; Numerical Aperture: 0.55 NA was used for this measurement. For each image, a surface of 50×50 μm^2 was analysed, and an integration time of 0.5s was used. Confocal RAMAN data analysis was performed using WITec Project 4.10 software. Raman images were generated based on the integrated intensity of marker bands and were calculated without pre-processing. Cluster analysis was carried out after cosmic ray removal and background subtraction.

Contact Angle: The wettability of the surface was characterized by contact angle measurement with an OCA35 from Dataphysics instruments. All of the measurements were performed at room temperature.

2.3 Elaboration of Micro-Structured Membrane

Polymer blend with a composition of 85/15 (PLA/PCL) was prepared by dissolving homopolymer pellets in the appropriated amount of chloroform. The polymer solution, with a concentration of 100 mg/mL, was evaporated using a circular glass cell culture dish as support. The relative humidity was maintained constant for all the experiments to 90%.

3 Results and Discussion

Elaboration of micro-structured Honeycomb stand-alone membrane. The used approach allows the preparation of large micro-structured stand-alone membrane (dm^2) without the use of any extensive materials or equipment such as dip or spin coaters

*Micro structuring and morphology of the Honeycomb films. A*s evidenced in the SEM images, the pores' size is between 10 to 18 microns, and the porosity was observed over the entire membrane indicating homogeneous evaporation and a convenient water vapour condensation.

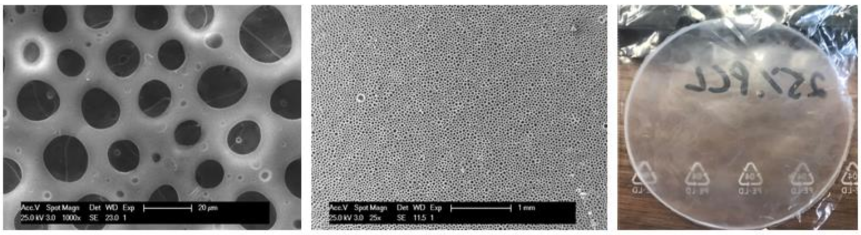

Fig. 2: SEM images of the PCL-PLA membrane scale 20µm (left) , 1mm (middle), real photograph of the membrane (right)

Analysis of the surface chemistry and evaluation of the functional group distribution: Contact angle measurement provides information about the wettability of a given surface, and consequently an idea about the chemical aspect of the analysed surface at the macroscopic scale. The Honeycomb membrane was first treated with a basic buffer solution (pH=12). The contact angle measurement shows a decrease in the contact angle from 80° to 60° after the treatment referring to the ionization of the PLA, as the base attack the hydrogens at the alpha position which is fairly acidic forming enolates (Fig. 3).

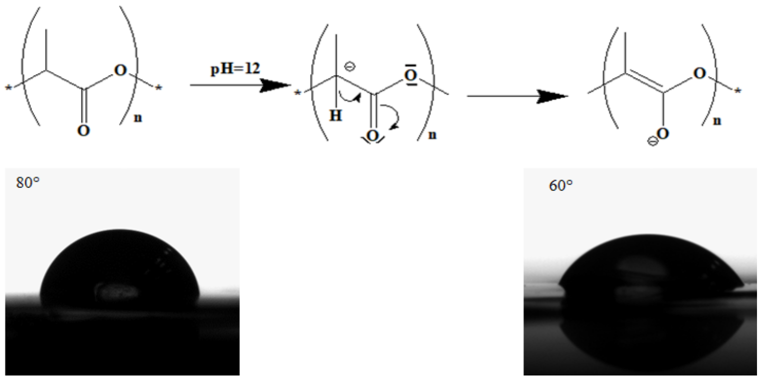

Fig. 3: Represents the shape of a water droplet on the untreated and treated HC membrane and the possible reaction of forming the enolates

To understand the phase separation, and the chemical distribution of both PCL and PLA on the surface, Raman Confocal was employed. The characteristic peaks of both PCL and PLA were defined as per previous work (Akoumeh, Elzein et al., 2020). In particular, peaks at 1723 cm^{-1} and a shoulder peak at 2869 cm^{-1} are characteristic of PCL, and peaks at 868 cm^{-1} and 2999 cm^{-1} are characteristic of PLA. The presented images in (Figure 4) were generated from the aforementioned peaks.

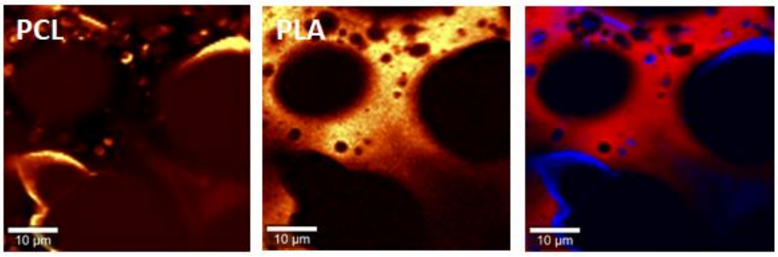

Fig. 4: Raman Imaging of PCL (left), PLA (middle), and an overlay of both component (right)

The Raman imaging proved that micrometre-scale PCL domains are randomly distributed in the wall of the pores while the rest of the porous structure is formed by a continuous PLA matrix. The role of water condensation on phase separation has been emphasized in previous studies. The formation of macrophase separation is avoided and reduced to microphase separation under humidity and water condensation

4 Conclusion

In this article, a large micro-structured stand-alone membrane formed from blends of two commercial homopolymers PLA and PCL was successfully prepared. The chosen homopolymers used to prepare honeycomb-like membranes were thoroughly characterized to investigate the topography, the chemistry, and subsequently the miscibility of the blend. The wettability measurement shows a pH-responsive surface. Further experimental works should be conducted to study the efficiency of these membranes in water filtration.

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Cite as: Akoumeh R., Elzein T., Rodriguez-Hernandez J. & Hassan M.K., "Potential Application of Porous Membrane from Blends of Homopolymer for Industrial Water Treatment", *The 2nd International Conference on Civil Infrastructure and Construction (CIC 2023)*, Doha, Qatar, 5-8 February 2023, DOI: https://doi.org/10.29117/cic.2023.0170