Study on Lignin-free Lignocellulosic Biomass and PSF-PEG Membrane Compatibility

Abiodun A. Amusa,[a] Abdul L. Ahmad,[a,*] and Jimoh K. Adewole [b]

Lignocellulosic biomass was delignified by combining physical and chemical pretreatment techniques. Then, a polysulfone-polyethylene glycol blend, which was compatible with the lignin-free biomass (0 wt% to 3.0 wt%), was used to fabricate composite membranes. The presence of hydroxyl groups after the pretreatment was evaluated *via* Fourier transform infrared spectroscopy. The rheology of the polymer solutions was assessed *via* the viscometric method. Also, the hydrophobicity of the fabricated membranes was determined using contact angle and porosity measurements. The fabricated membranes with near superhydrophobic properties (a contact angle of approximately 140°) based on this study revealed that contactor systems and biomedical applications would benefit from this modification.

Keywords: Lignin; Solubilization; Polysulfone; Polyethylene glycol; Membrane; Compatibility

*Contact information: a: School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Acme University, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia; b: Process Engineering Department, International Maritime College, Suhar Port Falaj Al Qabail, Suhar 332 Sultanate of Oman; *Corresponding author: chlatif@usm.my*

INTRODUCTION

Agro-based biomass constitutes lignocellulosic waste materials in the form of wood, grass, and forestry left-overs. From the total biomass, approximately 60% of it is plant biomass (lignocellulose). Lignocellulosic biomass (LCB) serves as an excellent feedstock resource (both renewable and nonrenewable) for modern industrially evolving societies. The valorization of LCBs is not overemphasized, depending on the source of the biomass, *e.g.*, grasses, hardwoods, or softwoods, for various applications, *e.g,* gas separation, energy sources, biofuels, and incorporation into the production of fine chemicals (Irshad *et al*. 2013). Date seed is one of the lignocellulosic materials that continues to attract attention from research scientists.

The date palm, known as *Phoenix dactylifera* L, belongs to the Arecaceae family. Dates could be relevant to upcoming generations based on their remarkable nutritional value, environmental friendliness, and economic prowess. Global date palm cultivation is estimated to include approximately 2000 different species. Every species provides date seed and the fleshy pericarp (Farooq *et al*. 2018).

One of the top three countries in the world in terms of producing date fruits is Saudi Arabia. This region accounts for approximately 15% of the total amount of annual global dates cultivated (approximately 100 million) (Zhang *et al.* 2017). Al-Jasass *et al.* (2015) reported that even in the United States, dates that are bright in color are favored by customers. However, studies by Bouhlali *et al*. (2017) reported that the types of dates and stages of maturity can affect the color of the date fruit. Sukkari date seeds are one of the varieties of the discarded by-products of date palm fruits. The seed weighs approximately

11% to 18% of the total weight of the date palm fruit. Therefore, Sukkari (which means sweet) dates, which are gold in color and therefore draw the attention of the consumer and the most popular, were chosen for this work (Azeem *et al*. 2016).

Researchers have analyzed date seeds to determine their constituents and nutritional value, which has led to date seeds being used as raw materials for various applications, *e.g*., the synthesis of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (Purama *et al*. 2018), poly(3-hydroxybutyrate) (Yousuf and Winterburn 2017), polyhydroxybutyrate, polyhydroxyalkanoates (Yousuf and Winterburn 2016), and activated carbon (Ogungbenro *et al*. 2017). Besides, date seeds are been used to produce nanocomposites (Adewole 2016), cosmetic products (Adeosun *et al*. 2016), oil (Habib *et al*. 2013), fats (Ben-Youssef *et al*. 2017), biodiesel (Azeem *et al*. 2016), for enhanced oil recovery (Adewole and Sultan 2013), and other products (Adewole and Ahmad 2016; Blaisi 2018).

A date seed, like any other LCB, is made up of cellulose, hemicellulose, and lignin as the primary components. One of the challenges is the complex structure of the lignin in the biomass, which limits its processability. The proposal to use LCB as a filler is gaining an increased amount of interest for various applications in membrane engineering (Amusa *et al*. 2020). The two divisions of membranes are polymeric and inorganic. However, unlike inorganic membranes, polymeric membranes are flexible, easily prepared, and have other desirable properties, which has influenced their wide application in gas and liquid separation processes. The properties of ultrafiltration membranes can be improved by using polymer blends to incorporate certain missing properties into a polymer matrix (Gullinkala and Escobar 2008).

Polysulfone (PSF) is an excellent polymer for membrane fabrication, with unique properties and high stability (chemical or mechanical). The biocompatibility properties of PSF are better than those of other materials (Kubala *et al*. 2002). In comparison to polyacrylonitrile and polymethylmethacrylate membranes, a study by Yamashita and Tomisawa (2009) established that α-chymotrypsinogen A and cytochrome C (with molecular weights of 25,000 and 12,400, respectively) did not show any affinity towards PSF. The hydrophilicity of the membrane has been improved by blending it with biocompatible polymers, *e.g.*, polyethylene glycol (PEG) (Ostuni *et al*. 2001). Sinha *et al*. (2013) blended PSF and dimethylacetamide (DMAc), and Chakrabarty *et al*. (2008) used N-methyl-2-pyrrolidone (NMP) as the solvent.

In this study, LCB was pretreated and incorporated into a PSF-PEG blend to fabricate a flat sheet, mixed matrix membrane. Then, its compatibility was investigated *via* Fourier Transform Infrared Spectrometry (FTIR), as well as determining its contact angle and the polymer solution flow was studied using a viscometer. Detailed delignification process evaluation and membrane characterization and performance study were not covered as part of the scope of this study as they are parts of the authors' ongoing research.

EXPERIMENTAL

Materials

The date pits (Sukkari, LCB) were sourced from Riyadh, Saudi Arabia. The hydrogen peroxide (H_2O_2, 30%), n-hexane (99%), boric acid (H_3BO_3, 99.5%), sodium hydroxide (NaOH, 99%), potassium hydroxide (KOH, 99%), sodium chloride (NaCl, 99%), ethanol (C_2H_5OH, 99%), hydrochloric acid (HCl, 37 %), and N-methyl-2-pyrrolidone (NMP, 99%) were used without any further purification, *i.e.*, as purchased

from Sigma Aldrich (St. Louis, MO). The polysulfone (PSF pellets) and polyethylene glycol (PEG) were purchased from Amoco Chemicals (Chicago, IL).

Methods

Lignin-free pretreatment techniques

The date pits were processed into fine powder by adapting the methods reported by Karinkanta *et al.* (2018) and Mayer-Laigle *et al.* (2018) with some modifications. The date pits were washed, soaked in hot water for 72 h, ground, dried under a vacuum at a temperature of 50 °C, and then re-ground to a fine powder. Approximately 20 g of finely powdered samples were then de-oiled to remove the extractives in a Soxhlet apparatus using n-hexane as the solvent, and the recovery of the solvent was achieved using a rotary evaporator. Then, the deoiled samples were dried at a temperature of 80 °C in a vacuum oven until the weight became constant, which indicated the removal of traces of residual solvents. The lignins were solubilized using the Van Soest method (Van Soest *et al.* 1991) with some modifications. First, a NaOH alkaline solution was prepared at 7 wt.%. Then, the de-oiled sample (DP) and the NaOH alkaline solution were mechanically stirred for 3 h at 80 °C (in a solid to solvent ratio of 1 to 10). Distilled water was used to wash the treated samples to a neutral pH after the treatment was performed three times. Additional lignification steps to remove the remaining lignins, accompanied by bleaching, were performed using acidified sodium chlorite (1.7 wt%). The treated samples were transferred to 10 mL of a freshly prepared (11%, v/v) hydrogen peroxide solution. At a temperature of 45 °C, the acidified sodium hydroxide solution was used to adjust the pH of the mixture to 11 *via* vigorous stirring for 3 h. The residue was then treated with 10 wt.% KOH, which contained 1% H_3BO_3, at room temperature and a 1 to 25 solid to liquid ratio. This was stirred for 10 h. After each treatment, the powdered-particles were washed with distilled water. This process was repeated twice while maintaining the same conditions, resulting in effective lignin solubilization. Finally, the sample was filtered and freeze-dried, and the dried date pits cellulose (DPC) samples were kept in a glass bottle for further analysis. Afterward, the particle size of the synthesized DPCs was examined using a particle size analyzer (CILAS 1180, CILAS, Orléans, France). The composition and functional groups of the synthesized DPC samples were investigated *via* Fourier transform infrared spectroscopy (FTIR) with an IRAffinity-1S (Shimadzu Co., Kyoto, Japan).

Fabrication of the cellulose embedded composite

The polysulfone pellets were dried in an oven at 120 °C overnight before being used for moisture removal. A mixing-casting process was used for the fabrication of membrane samples, as reported by Ismail and Lai (2004), with some modifications. For the fabrication of pristine PSF membranes, the casting solution was prepared by dissolving 20 wt.% of a PSF-PEG blend with NMP on a hot plate at 60 °C for 24 h, stirring until a clear solution was obtained. For the composite membranes (CMBs), a calculated amount of DPC (0 wt% to 3 wt%) was dispersed into NMP and stirred for 3 h; then the suspension was placed in an ultrasonic bath for 1 h to obtain a homogeneous dispersion. Then, PSF and PEG were gradually added, and the suspension was stirred overnight until the solution became homogeneous. Next, the solution was degassed for 4 h to remove any trapped bubbles. Thereafter, the pure PSF solution and the CMB suspensions were cast at room temperature with a casting knife on a flat glass plate with a gap setting of 25 μm. Solvent evaporation was expected while allowing a free-standing time of 30 s, since other free-standing times (10 s and 60 s) did not yield the desired morphology. Next, the samples

were immersed in a water-containing coagulation bath for 48 h at room temperature; the water was changed after 24 h for the complete phase separation process. The membranes were removed and dried for 72 h in the open air and labelled PC-0, PC-0.5, PC-1, PC-2, and PC-3 for the pristine PSF membrane and the CMBs with DPC loads of 0.5 wt%, 1 wt%, 2 wt%, and 3 wt%, respectively. Then, the fabricated membranes were analyzed to determine their wettability, porosity, and mean pore size.

RESULTS AND DISCUSSION

Delignification and Dope Solution Retrospect

The removal of the non-cellulosic components *via* the pretreatment of LCB is aimed at maximizing the accessibility to the hydroxyl groups. However, lignin functionalization is closely related to the delignification of LCB because the solubility of the process liquid is due to the formation of functional groups. This implies polymer dissolution *via* the addition of hydrophobic groups. Hansen and Björkman (1998) postulated that hydrogen bonds, dipole-dipole, and nonpolar interactions must be broken for effective lignin solubilization. The use of organosolv (Salapa *et al.* 2017) or solvents (dioxane and acetone) (Saha *et al*. 2019) to solubilize lignins have their drawbacks. The alkaline delignification method is better in terms of ease, safety, and scalability (Cavali *et al*. 2020).

Other varieties of date pits (DP) possessed similar chemical composition as found in this study (Habib and Ibrahim 2009; Essa and Elsebaie 2018). The obtained physicochemical properties of the collected DP and the properties of other agro-based waste products were comparable (Fernández-López *et al*. 2004; Alfredo *et al.* 2009). As shown in Fig. 1, the lignin-free sample was approximately 20 µm.

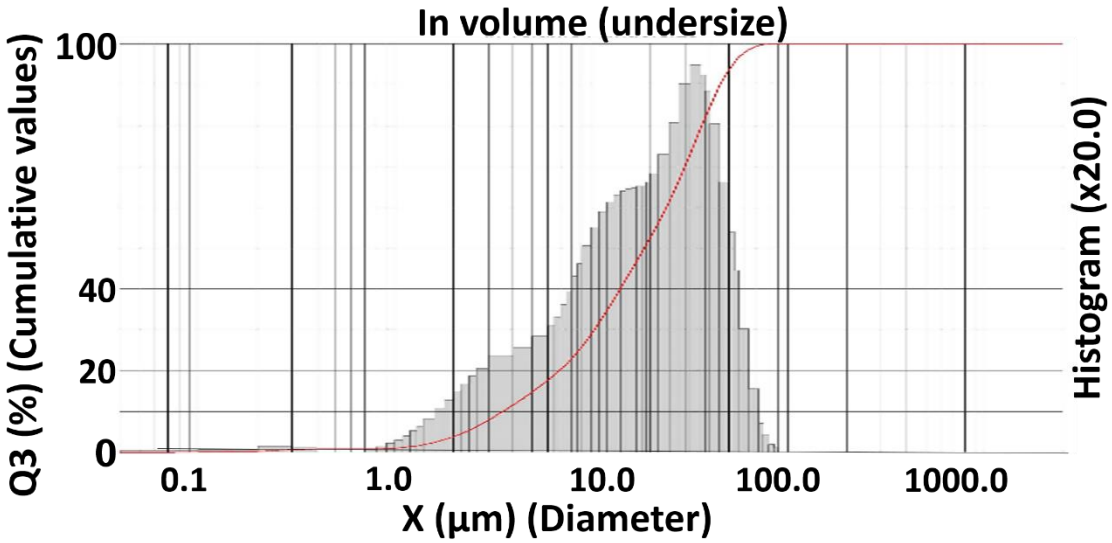

Fig. 1. Lignin-free particle size analysis

The dope solution formed by a polymer and/or additive with a solvent in this study was a homogeneous polymer solution without agglomeration. A thermodynamically

unstable polymer solution was avoided by ensuring that demixing did not occur as the synthesized DPC was dispersed in the polymer solutions. The materials were uniform, as reflected in the FTIR and other analyses to be discussed.

Fourier Transform Infrared Spectroscopy Analysis (FTIR)

The generation of a superoxide radical that is highly reactive resulted in the formation of carboxylic acid compounds *via* lignin aromatic rings and some hemicellulose oxidation. The oxidative mechanism results in the removal of an electron from the lignin phenolic units, followed by other fast reactions involving oxygen and carboxyl. Under these conditions, the cellulose is not degraded; rather, the lignin structure is subject to attack from the aggressive oxidizing agent (Sun *et al*. 2004; Peng *et al*. 2010; Sun *et al.* 2015). Therefore, hemicellulose and cellulose became predominant. The structural transformation of the LCB samples is revealed in Fig. 2a; the lignin absorbance was at 1230 cm^{-1} and the aromatic parts were associated with an absorbance peak at 1517 cm^{-1}, which all hardwood LCB spectra contain. The C=O stretching, and skeletal vibrations of the aromatic rings were represented by the peak at 1614 cm^{-1}. The $-CH_3$ and $-CH_4$ asymmetry and deformation of C-H can give rise to the peak at 1444 cm^{-1} (Scholze and Meier 2001). The band at 1745 cm^{-1} was associated with the hemicellulose C=O stretching vibration which formed broadband at 1590 cm^{-1} to 1745 cm^{-1} after pretreatment, which was likely due to the overlap of the ester stretching of C=O at 1650 cm^{-1} (Liang *et al*. 2006). These bands disappeared on the DPC absorbance spectra. The lignin carbonyl groups, ester linkages, and acetyl groups were represented with the peak at 1240 cm^{-1} and the decrease indicated lignin dissolution. The methyl and phenol OH aliphatic C-H stretching gave rise to peaks at 1370 cm^{-1} and 2349 to 2923 cm^{-1}. The hemiacetal and carbonyl groups correspond to the enhanced peak at 1630 cm^{-1}. Cellulose contributed to the alcoholic hydroxyl group of the C-O stretching vibration peak at 1000 cm^{-1}. The presence of OH groups was indicated by the O-H stretching broadband appearance at 3000 cm^{-1} to 3500 cm^{-1} for the pretreated samples. The lignocellulosic biomass absorption bands reported agreed with the data from the following studies: Gandini and Belgacem (2008) and Briones *et al.* (2011).

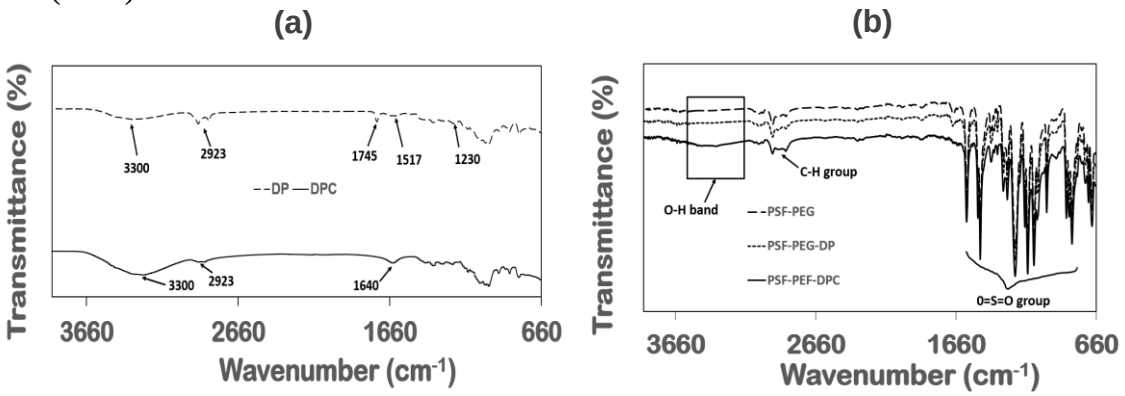

Fig. 2. The FTIR spectra of (a) the date pits (DP) and lignin-free samples (DPC) and (b) the PSF-PEG, PSF-PEG-DP, and PSF-PEG-DPC membranes

As shown in Fig. 2b, the incorporation of DPC into PEF-PEG did not affect the PSF absorption spectra from being retained. A polysulfone membrane is characterized by an aromatic framework (C=C) and an O=S=O group for the spectra in the range of 1400 cm^{-1} to 1600 cm^{-1} and 1000 cm^{-1} to 1300 cm^{-1}, respectively. The aromatic stretching of the

C-H group corresponded to the peak at 2930 cm^{-1} (Farrokhara and Dorosti 2020). The incorporation of DP into PSF-PEG did not yield different results in terms of the spectra. However, the appearance of a broad peak at 3100 to 3500 cm^{-1} for the CMB membrane, which was missing on the PSF-PEG and PSF-PEG-DP membrane spectra (the lignin recalcitrance effects in the DP), was attributed to the O-H band stretching of the DPC, which indicated the accessibility of the OH groups in the mixed matrix membrane. This result was also in agreement with the PSF incorporated with commercial cellulose as reported by Bai *et al.* (2015).

Surface Energy and Water Contact Angle Analyses

Different measurement types, *e.g.*, sessile drop (or static) contact angle, tilting plate method, an add and remove method, time-dependent dynamic studies, and Wilhelmy plate method were reported by Drelich (2019). The static contact angle method was used in this study using a Model 590 H automated goniometer/tensiometer (Ramé-Hart Instrument Co., Succasunna, NJ) using DROPimage Advanced software (version Model: 250-F1). The incorporation of the synthesized DPC into the PSF-PEG membrane was investigated to measure the changes in surface wettability. Figure 3 represents the image for the contact angle measurement for the samples. Sample 3a shows a flattening water droplet, which signifies hydrophilicity, and which conformed with the obtained measurement (72.0°), contrary to the modified samples (3b to 3e).

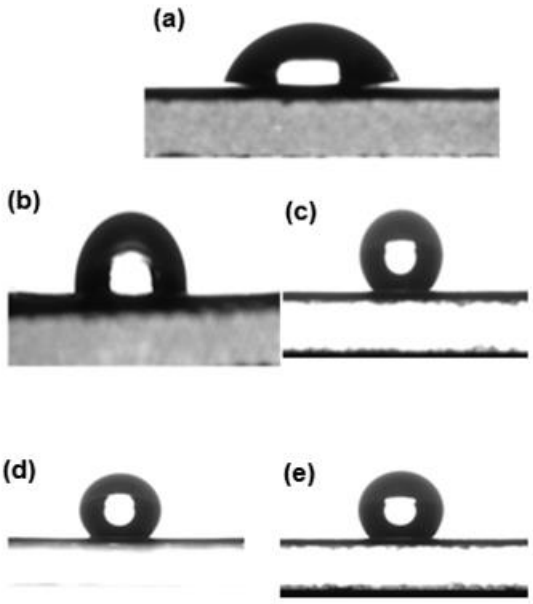

Fig. 3. Pictograms of the water contact angles for (a) PC-0, (b) PC-0.5, (c) PC-1, (d) PC-2, and (e) PC-3, for the pristine membrane and the CMB's with the DPC loads of 0.5 wt%, 1 wt%, 2 wt%, and 3 wt%, respectively.

The analysis of the water contact angle, porosity, and mean pore size for the PSF-PEG and the CMB membranes are shown in Table 1. This study showed that the contact angle values drastically increased from 72.0°, which was in accordance with other reports (Benkhaya *et al.* 2020; Camacho *et al.* 2020), with values ranging from 94.5° and 153.3° for the PSF-PEG and CMB membranes, respectively (hydrophobicity is any value greater

than 90°). This was attributed to the fundamental theory related to the wetting action via changes in the surface roughness of a material. In general, the higher contact angle is consistent with increased fine-scale roughness of the membrane material upon the incorporation of the DPC (Hubbe *et al.* 2015). The incorporation of DPC to the PSF-PEG polymer matrix increased the heterogeneity of the surface of the composite membrane. The contact angle increased by a certain roughness factor which is associated with the roughness area ratio of the surface heterogeneity (roughness) of the composite membrane. The surface roughness factor is independent of the surface profile. However, it is difficult to quantitatively evaluate the roughness area ratio, which would be needed to fully confirm this concept (Wenzel 1949).

The DPC loading relationship with the membrane porosity and mean pore size were estimated using bubble point measurements (Tylkowski and Tsibranska 2015) and are presented in Table 1. The relative spreading of water on the membrane surface based on the unbalanced interaction of molecules, *i.e.*, the wettability, was further examined. It was observed that the membrane porosity increased after the DPCs were added while the mean pore size decreased. This could be attributed to the viscous nature of the dope solutions, which resulted in pore growth restrictions (Said *et al*. 2017). This necessitated an investigation into the flow of the dope solution, as shown in the next section.

Table 1. Effect of the Content of Lignin-Free Particles in Composite Membranes on the Contact Angle, Surface Energy, Porosity, and Mean Pore Size

Sample	DPC loading (wt%)	Contact angle (º)	Porosity (%)	Mean pore size (nm)
PC-0	0	72.0 ± 0.4	50.6 ± 0.7	11.4 ± 0.02
PC-0.5	0.5	94.5 ± 0.9	59.0 ± 0.3	9.8 ± 0.02
PC-1	1	157.2 ± 0.6	61.7 ± 0.3	9.3 ± 0.05
PC-2	2	155.1 ± 0.2	58.2 ± 0.5	9.6 ± 0.03
PC-3	3	153.3 ± 0.5	54.0 ± 0.5	9.2 ± 0.03

Rheological Investigations

The behavior of the polymers during processing are widely connected to their viscosity, which is related to their shear rate, shear stress, and torque. In this study, an RVDV-IIIU programmable rheometer (Brookfield, Middleboro, MA), with spindle number 27, was used. After turning on the motor and maintaining the temperature (at 21.5 °C), the speed of rotation was set between 10 and 250 rpm, and the values were recorded. The average of three experimental data measurements for viscosity, torque, shear stress, and shear rate were used for the PSF-PEG and CMB polymer solutions.

Figure 4a depicts the steady-state viscosity as a function of shear rate for the polymer solutions. The illustrated trend is a non-Newtonian behavior, since the plots are non-linear and do not pass through the origin, with shear-thickening as the shear rate increases. The same pattern is obtained for a log-log plot of the viscosity against the shear rate. In contrast to the polymer solutions being pseudoplastic, the viscosity increases as the shear rate increases (Hubbe *et al.* 2017). As shown in Fig. 4, the addition of DPC to the PSF-PEG solution shifts the viscosity curve to higher values. This can be attributed to the viscoelastic nature of the incorporated DPC with coil conformation, which is flexible in solution. It can also be attributed to the formation of hydrogen bonds between the NMP and PSF molecules, as well as between the PEG and the accessible hydroxyl groups from

the DPC, as confirmed by the FTIR spectra. Also, anisotropic chain alignment due to the reorganization of polymer solutions can cause shear thickening behavior, as well as an increasing shear value between the particles as the lubrication regimes change (Fernandez *et al*. 2013).

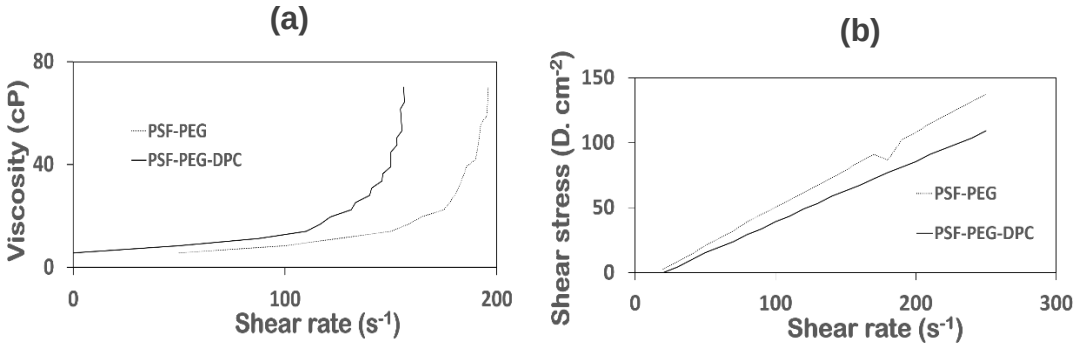

Fig. 4. Viscoelastic properties of the (a) polymer solutions and (b) flow curves of polymer solutions at 21.5 °C

Figure 4b confirms the non-Newtonian properties of these polymer solutions in agreement with Fig. 4a. The PSF-PEG plot shows certain deformation at an approximate shear rate of 180 s^{-1}, which can be attributed to a form of deviation from its linear viscoplastic nature to the closeness of exhibiting some non-linearity properties related to chain entanglements. This linear pattern is attributed to the micro-scallop average velocity of the shear thickening fluid, which increases due to the interactions among the polymer chains and becomes a definite, linear relationship, *i.e.*, does not pass through the origin for shear stress deformation, with the incorporation of DPC, which is in line with the Power Law rheology model (Martínez-Pedrero and Tierno 2018). This finding will be helpful during the process of piping systems predicting flow behavior.

CONCLUSIONS

1. Polysulfone-poly(ethylene glycol) (PSF-PEG) with incorporation of different wt.% of date pits cellulose (DPC) were fabricated as flat sheet CMB membranes and investigated for compatibilities. The obtained results confirmed that the OH groups of the DPC were present in the fabricated CMB membranes (via FTIR). The hydrophobic nature of the membranes was enhanced, as shown by contact angle measurements.
2. The membrane materials exhibiting shear-thickening properties and achieved the highest porosity with a 1 wt% DPC load. The stability of the composite membranes can be guaranteed based on the reaction mechanism of the alkaline pretreatments of the date pits (DP) and the obtained near superhydrophobic values from the contact angle measurements.
3. Overall, the pretreated lignin-free LCB was successfully incorporated into the PSF-PEG polymer matrix to modify its pore and resistance to wetting, which could be used for various applications in contactor systems and biomedical devices (Amusa *et al.* 2018).

ACKNOWLEDGMENTS

The authors acknowledge the Ministry of Higher Education (MOHE), under the TRGS grant (Grant no.: 203/PJKIMIA/67612001, project code: TRGS/1/2018/USM/01/5/1) and USM-RUI grant (Grant no. 1001/PJKIMIA/8014063, project code: U01631) for this research work.

REFERENCES CITED

Adeosun, A. M., Oni, S. O., Ighodaro, O. M., Durosinlorun, O. H., and Oyedele, O. M. (2016). "Phytochemical, minerals and free radical scavenging profiles of *Phoenix dactilyfera* L. seed extract," *Journal of Taibah University Medical Sciences* 11(1), 1-6. DOI: 10.1016/j.jtumed.2015.11.006

Adewole, J. K. (2016). "Transport properties of gases through integrally skinned asymmetric composite membranes prepared from date pit powder and polysulfone," *Journal of Applied Polymer Science* 133(28), 1-8. DOI: 10.1002/app.43606

Adewole, J. K., and Ahmad, A. L. (2016). "Process modeling and optimization studies of high pressure membrane separation of CO_2 from natural gas," *Korean Journal of Chemical Engineering* 33(10), 2998-3010. DOI: 10.1007/s11814-016-0165-8

Adewole, J. K., and Sultan, A. S. (2013). "Synthesis and performance evaluation of date pit based surfactant-polymer formulation for enhanced chemical flooding," in: *SPE Saudi Arabia Section Technical Symposium and Exhibition*, 19-22 May, Al-Khobar, Saudi Arabia, pp. 1-15.

Alfredo, V.-O., Gabriel, R.-R., Luis, C.-G., and David, B.-A. (2009). "Physicochemical properties of a fibrous fraction from chia (*Salvia hispanica* L.)," *LWT - Food Science and Technology* 42(1), 168-173. DOI: 10.1016/j.lwt.2008.05.012

Al-Jasass, F. M., Siddiq, M., and Sogi, D. S. (2015). "Antioxidants activity and color evaluation of date fruit of selected cultivars commercially available in the United States," *Advances in Chemistry* 2015, 1-5. DOI: 10.1155/2015/567203

Amusa, A. A., Ahmad, A. L., and Adewole, K. J. (2018). "A review on recent developments and progress in natural gas processing and separating using nanoparticles incorporated membranes," *Soc. Pet. Eng.* 1-36. DOI:10.2118/192426-ms

Amusa, A. A., Ahmad, A. L., and Adewole, K. J. (2020). "Mechanism and compatibility of pretreated lignocellulosic biomass and polymeric mixed matrix membranes: A review," *Membranes* 10(12), 1-29. DOI: 10.3390/membranes10120370

Azeem, M. W., Hanif, M. A., Al-Sabahi, J. N., Khan, A. A., Naz, S., and Ijaz, A. (2016). "Production of biodiesel from low priced, renewable and abundant date seed oil," *Renewable Energy* 86, 124-132. DOI: 10.1016/j.renene.2015.08.006

Bai, H., Zhou, Y., and Zhang, L. (2015). "Morphology and mechanical properties of a new nanocrystalline cellulose/polysulfone composite membrane," *Advances in Polymer Technology* 34(1), 1-8. DOI: 10.1002/adv.21471

Ben-Youssef, S., Fakhfakh, J., Breil, C., Abert-Vian, M., Chemat, F., and Allouche, N. (2017). "Green extraction procedures of lipids from Tunisian date palm seeds," *Industrial Crops and Products* 108, 520-525. DOI: 10.1016/j.indcrop.2017.07.010

Blaisi, N. I. (2018). "Environmental assessment of utilizing date palm ash as partial replacement of cement in mortar," *Journal of Hazardous Materials* 357, 175-179. DOI: 10.1016/J.JHAZMAT.2018.06.013

Bouhlali, E. d. T., Alem, C., Ennassir, J., Benlyas, M., Mbark, A. N., and Zegzouti, Y. F. (2017). "Phytochemical compositions and antioxidant capacity of three date (*Phoenix dactylifera* L.) seeds varieties grown in the South East Morocco," *Journal of the Saudi Society of Agricultural Sciences* 16(4), 350-357. DOI: 10.1016/J.JSSAS.2015.11.002

Briones, R., Serrano, L., Younes, R. B., Mondragon, I., and Labidi, J. (2011). "Polyol production by chemical modification of date seeds," *Industrial Crops and Products* 34(1), 1035-1040. DOI: 10.1016/j.indcrop.2011.03.012

Cavali, M., Soccol, C. R., Tavares, D., Torres, L. A. Z., Tanobe, V. O. de A. T., Filho, Z. A., and Woiciechowski, A. L. (2020). "Effect of sequential acid-alkaline treatment on physical and chemical characteristics of lignin and cellulose from pine (*Pinus* spp.) residual sawdust," *Bioresource Technology* 316, 123884. DOI: 10.1016/j.biortech.2020.123884

Chakrabarty, B., Ghoshal, A. K., and Purkait, M. K. (2008). "Preparation, characterization and performance studies of polysulfone membranes using PVP as an additive," *Journal of Membrane Science* 315(1-2), 36-47. DOI: 10.1016/j.memsci.2008.02.027

Drelich, J. W. (2019). "Contact angles: From past mistakes to new developments through liquid-solid adhesion measurements," *Advances in Colloid and Interface Science* 267, 1-14. DOI: 10.1016/j.cis.2019.02.002

Essa, R., and Elsebaie, E. M. (2018). "Effect of using date pits powder as a fat replacer and anti-oxidative agent on beef burger quality," *Journal of Food and Dairy Sciences* 9(2), 91-96. DOI: 10.21608/jfds.2018.35225

Farooq, M., Ramli, A., Naeem, A., Mahmood, T., Ahmad, S., Humayun, M., and Islam, M. G. U. (2018). "Biodiesel production from date seed oil (*Phoenix dactylifera* L.) via egg shell derived heterogeneous catalyst," *Chemical Engineering Research and Design* 132, 644-651.DOI: 10.1016/j.cherd.2018.02.002

Farrokhara, M., and Dorosti, F. (2020). "New high permeable polysulfone/ionic liquid membrane for gas separation," *Chinese Journal of Chemical Engineering* (in press). DOI: 10.1016/j.cjche.2020.04.002

Fernandez, N., Mani, R., Rinaldi, D., Kadau, D., Mosquet, M., Lombois-Burger, H., Cayer-Baaioz, J., Herrmann, H. J., Spencer, N. D., and Isa, L. (2013). "Microscopic mechanism for shear thickening of non-brownian suspensions," *Physical Review Letters* 111(10), 108301. DOI: 10.1103/PhysRevLett.111.108301

Fernández-López, J., Fernández-Ginés, J. M., Aleson-Carbonell, L., Sendra, E., Sayas-Barberá, E., and Pérez-Alvarez, J. A. (2004). "Application of functional citrus by-products to meat products," *Trends in Food Science and Technology* 15(3-4), 176-185. DOI: 10.1016/j.tifs.2003.08.007

Gandini, A., and Belgacem, M. N. (2008). "Lignins as components of macromolecular materials," in: *Monomers, Polymers and Composites from Renewable Resources*, M. N. Belgacem and A. Gandini (ed.), Elsevier Science, Amsderdam, Netherlands. DOI: 10.1016/B978-0-08-045316-3.00011-9

Gullinkala, T., and Escobar, I. (2008). "Study of the hydrophilic-enhanced ultrafiltration membrane," *Environmental Progress* 27(2), 210-217. DOI: 10.1002/ep.10276

Habib, H. M., and Ibrahim, W. H. (2009). "Nutritional quality evaluation of eighteen date pit varieties," *International Journal of Food Sciences and Nutrition* 60(sup1), 99-111. DOI: 10.1080/09637480802314639

Habib, H. M., Kamal, H., Ibrahim, W. H., and Dhaheri, A. S. A. (2013). "Carotenoids, fat soluble vitamins and fatty acid profiles of 18 varieties of date seed oil," *Industrial*

Crops and Products 42, 567-572. DOI: 10.1016/j.indcrop.2012.06.039

Hansen, C. M., and Björkman, A. (1998). "The ultrastructure of wood from a solubility parameter point of view," *Holzforschung* 52(4), 335-344. DOI: 10.1515/hfsg.1998.52.4.335

Hubbe, M. A., Gardner, P. J., and Shen, W. (2015). "Contact Angles and Wettability of Cellulosic Surfaces: A review of Proposed Mechanisms and Test Strategies" *BioResources* 10(4), 8657-8749. DOI: 10.15376/biores.10.4.Hubbe_Gardner_Shen

Hubbe, M. A., Tayeb, P., Joyce, M., Tyagi, P., Kehoe, M., Dimic-Misic, K., and Pal, L. (2017). "Rheology of nanocellulosic-rich aqueous suspensions: A review" *BioResources* 12(4), 9556-9661. DOI: 10.15376/biores.12.4.hubbe

Irshad, M. N., Anwar, Z., But, H. I., Afroz, A., Ikram, N., and Rashid, U. (2013). "The industrial applicability of purified cellulase complex indigenously produced by Trichoderma viride through solid-state bio-processing of agro-industrial and municipal paper wastes," *BioResources* 8(1), 145-157. DOI: 10.15376/biores.8.1.145-157

Ismail, A. F., and Lai, P. Y. (2004). "Development of defect-free asymmetric polysulfone membranes for gas separation using response surface methodology," *Separation and Purification Technology* 40(2), 191-207. DOI: 10.1016/j.seppur.2004.02.011

Karinkanta, P., Ämmälä, A., Illikainen, M., and Niinimäki, J. (2018). "Fine grinding of wood – Overview from wood breakage to applications," *Biomass and Bioenergy* 113, 31-44. DOI: 10.1016/j.biombioe.2018.03.007

Kubala, L., Číž, M., Soška, V., Černý, J., and Lojek, A. (2002). "Influence of polysulfone and hemophan hemodialysis membranes on phagocytes," *General Physiology and Biophysics* 21(4), 367-380.

Liang, L., Mao, Z., Li, Y., Wan, C., Wang, T., Zhang, L., and Zhang, L. (2006). "Liquefaction of crop residues for polyol production," *BioResources* 1(2), 1-9. DOI: 10.15376/biores.1.2.248-256

Martínez-Pedrero, F., and Tierno, P. (2018). "Advances in colloidal manipulation and transport via hydrodynamic interactions," *Journal of Colloid and Interface Science* 519(6), 296-311. DOI: 10.1016/j.jcis.2018.02.062

Mayer-Laigle, C., Rajaonarivony, R. K., Blanc, N., and Rouau, X. (2018). "Comminution of dry lignocellulosic biomass: Part II. technologies, improvement of milling performances, and security issues," *Bioengineering* 5(3), 1-17. DOI: 10.3390/bioengineering5030050

Ogungbenro, A. E., Quang, D. V., Al-Ali, K., and Abu-Zahra, M. R. M. (2017). "Activated carbon from date seeds for CO_2 capture applications," *Energy Procedia* 114, 2313-2321. DOI: 10.1016/j.egypro.2017.03.1370

Ostuni, E., Chapman, R. G., Holmlin, R. E., Takayama, S., and Whitesides, G. M. (2001). "A survey of structure-property relationships of surfaces that resist the adsorption of protein," *Langmuir* 17(18), 5605-5620. DOI: 10.1021/la010384m

Peng, F., Ren, J.-L., Xu, F., Bian, J., Peng, P., and Sun, R.-C. (2010). "Fractional study of alkali-soluble hemicelluloses obtained by graded ethanol precipitation from sugar cane bagasse," *Journal of Agricultural and Food Chemistry* 58(3), 1768-1776. DOI: 10.1021/jf9033255

Purama, R. K., Al-Sabahi, J. N., and Sudesh, K. (2018). "Evaluation of date seed oil and date molasses as novel carbon sources for the production of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) by *Cupriavidus necator* H16 Re 2058/pCB113," *Industrial Crops and Products* 119, 83-92. DOI: 10.1016/J.INDCROP.2018.04.013

Saha, M., Saynik, P. B., Borah, A., Malani, R. S., Arya, P., Shivangi, and Moholkar, V. S. (2019). "Dioxane-based extraction process for production of high quality lignin," *Bioresource Technology Reports* 5(2), 206-211. DOI: 10.1016/j.biteb.2019.01.018

Said, N., Hasbullah, H., Ismail, A. F., Othman, M. H. D., Goh, P. S., Abidin, M. N. Z., Kadir, S. H. S. A., Kamal, F., Abdullah, M. S., and Ng, B. C. (2017). "Enhanced hydrophilic polysulfone hollow fiber membranes with addition of iron oxide nanoparticles," *Polymer International* 66(11), 1424-1429. DOI: 10.1002/pi.5401

Salapa, I., Katsimpouras, C., Topakas, E., and Sidiras, D. (2017). "Organosolv pretreatment of wheat straw for efficient ethanol production using various solvents," *Biomass and Bioenergy* 100(5), 10-16. DOI: 10.1016/j.biombioe.2017.03.011

Scholze, B., and Meier, D. (2001). "Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY-GC/MS, FTIR, and functional groups," *Journal of Analytical and Applied Pyrolysis* 60(1), 41-54. DOI: 10.1016/S0165-2370(00)00110-8

Sinha, M. K., and Purkait, M. K. (2013). "Increase in hydrophilicity of polysulfone membrane using polyethylene glycol methyl ether," *Journal of Membrane Science* 437(6), 7-16. DOI: 10.1016/j.memsci.2013.03.003

Sun, B., Hou, Q., Liu, Z., and Ni, Y. (2015). "Sodium periodate oxidation of cellulose nanocrystal and its application as a paper wet strength additive," *Cellulose* 22(2), 1135-1146. DOI: 10.1007/s10570-015-0575-5

Sun, J. X., Sun, X. F., Sun, R. C., and Su, Y. Q. (2004). "Fractional extraction and structural characterization of sugarcane bagasse hemicelluloses," *Carbohydrate Polymers* 56(2), 195-204. DOI: 10.1016/j.carbpol.2004.02.002

Tylkowski, B., and Tsibranska, I. (2015). "Overview of main techniques used for membrane characterization," *Journal of Chemical Technology and Metallurgy* 50(1), 3-12.

Van Soest, P. J., Robertson, J. B., and Lewis, B. A. (1991). "Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition," *Journal of Dairy Science* 74(10), 3583-3597. DOI: 10.3168/jds.S0022-0302(91)78551-2

Wenzel, R. N. (1949). "Surface Roughness and Contact Angle" *The Journal of Physical and Colloid Chemistry* 53(9), 1466-1467. DOI: 10.1021/j150474a015

Yamashita, A. C., and Tomisawa, N. (2009). "Importance of membrane materials for blood purification devices in critical care," *Transfusion and Apheresis Science* 40(1), 23-31. DOI: 10.1016/j.transci.2008.11.005

Yousuf, R. G., and Winterburn, J. B. (2016). "Date seed characterisation, substrate extraction and process modelling for the production of polyhydroxybutyrate by *Cupriavidus necator*," *Bioresource Technology* 222, 242-251. DOI: 10.1016/j.biortech.2016.09.107

Yousuf, R. G., and Winterburn, J. B. (2017). "Waste date seed oil extract as an alternative feedstock for poly(3-hydroxybutyrate) synthesis," *Biochemical Engineering Journal* 127, 68-76. DOI: 10.1016/J.BEJ.2017.08.007

Zhang, C.-R., Aldosari, S. A., Vidyasagar, P. S. P. V., Shukla, P., and Nair, M. G. (2017). "Health-benefits of date fruits produced in Saudi Arabia based on *in vitro* antioxidant, anti-inflammatory and human tumor cell proliferation inhibitory assays," *J. Saudi Society of Agricultural Sciences* 16(3), 287-293. DOI: 10.1016/J.JSSAS.2015.09.004

Article submitted: September 1, 2020; Peer review completed: November 15, 2020; Revised version received: December 8, 2020; Accepted: December 11, 2020; Published: December 17, 2020.
DOI: 10.15376/biores.16.1.1063-1075