

Investigating the Structure and Water Permeation of Membranes Modified with Natural and Synthetic Additives Using Tensile, Porosity, and Glass Transition Temperature Studies

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ABSTRACT: This article reports the results of a study on the effect of using different additives (lignin, polyethylene glycol [PEG], and polyvinyl pyrrolidone [PVP]) to fabricate ultrafiltration polysulfone (PSf) membranes. The main focus of this study was on the difference in permeation properties brought about by the absence or presence of a fabric when fabricating the membranes. Differential scanning calorimetry was used to characterize the thermal properties and was also used to predict the other membrane properties. An Instron machine was used to evaluate the mechanical properties. The bulk porosity of lignin and PVP-modified membranes was observed to be higher than that of the membranes modified with PEG. There was a strong negative correlation between the bulk porosity and the glass transition temperature irrespective of the additive used. Membranes cast on a fabric showed higher flux compared with membranes cast on glass. There was a strong positive correlation between the bulk porosity and the observed permeability regardless of whether the membrane was cast on a nonwoven fabric or on a glass plate. Pore-size distribution results showed that lignin and PVP-modified membranes had a narrow pore-size distribution ranging between 10 and 25 nm when compared with PEG-modified membranes with a pore-size distribution ranging between 2.5 and 20 nm. These results indicate that thermal, bulk porosity, and mechanical properties can be used to probe the membrane structure. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40616.

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INTRODUCTION

Materials with excellent mechanical, physical, and chemical properties have been used in membrane preparation. These include polysulfone, polyether sulfone, and polyvinylidene fluoride, among others.^{1,2} However, their separation properties are compromised when used as is, and therefore inorganic and organic additives are often used to improve permeability. A number of reports in the literature have indicated that many compounds are suitable additives. Common examples of such additives are polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG), water, alcohols, and maleic acid.^{3–5} The additives, whether used as pore-forming agents or suppressors, are known to improve the performance of the resultant membrane as there is an increase in the membrane's porosity.⁶

Pore interconnectivity is improved when a nonsolvent additive is used because the dope solution stability is reduced and that increases the solvent diffusion into the coagulation bath during

the phase-inversion process.⁷ When the concentration of the non-solvent additive is increased, the coagulant tolerance is reduced and this brings the polymer dope solution nearer to the precipitation point.⁸ Pore-size formation is influenced by the nature of the additive and its molecular weight. This phenomenon was postulated and proved by Wang et al.⁹ In their findings, it was reported that the use of low-molecular-weight PVP produced membranes with small pores, whereas high-molecular-weight PVP gave membranes with fairly large pores. However, membranes with compromised mechanical properties are produced when using high-molecular-weight additives because the additives are not leached out completely and also block or hinder the pore interconnectivity.^{9–11} It is assumed that the additives act as templates on which pores will be formed.⁷

Although membranes are normally used at room temperature, there is a need to explore extreme possibilities. For example, the mechanical properties of membranes are compromised at

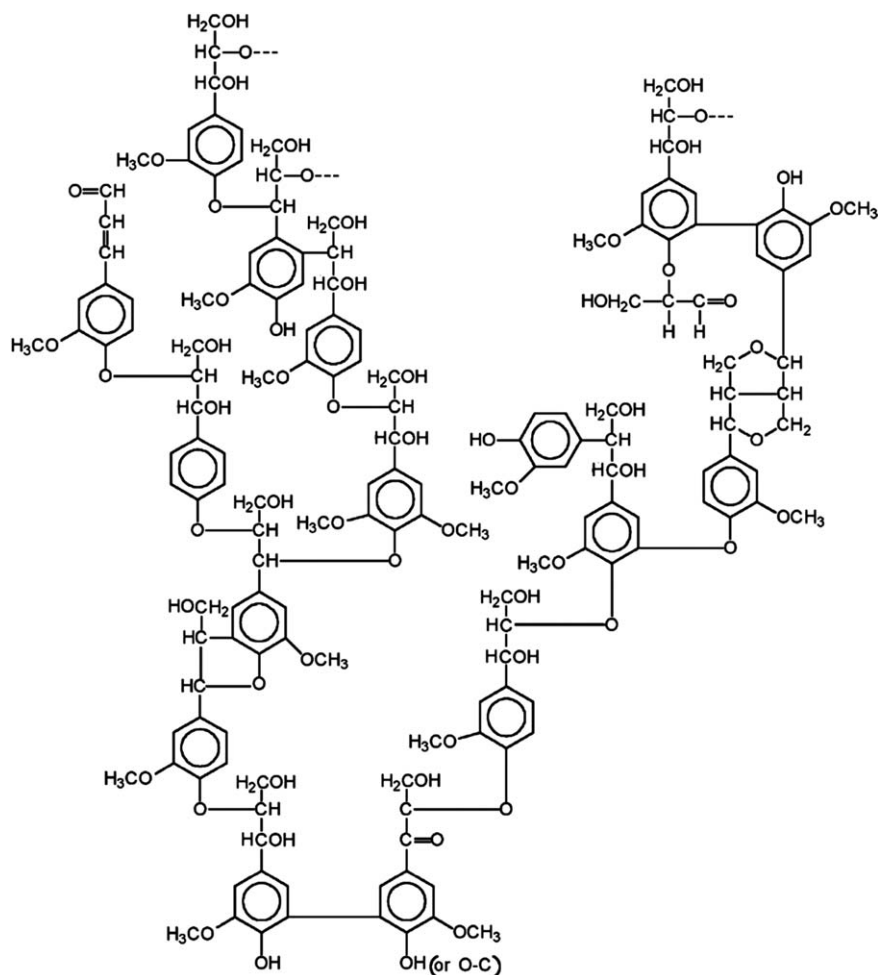


Figure 1. A hypothetical structure of lignin from wheat straw. (Reprinted from Ref. 23, with permission from Elsevier)

elevated temperatures due to the fact that the additives (normally PVP and PEG) remain in the membrane during phase separation even though they are hydrophilic.¹² Recently, Adams et al. reported that the tensile strength of polysulfone membranes decreased when the content of β -cyclodextrin polyurethane additive was increased.¹³ In another study by Ma et al., a decrease in the mechanical strength was observed when the concentration of PEG additive was increased.¹⁴ In both studies, the presence of macrovoids was cited as the cause of the decrease in strength. In another study, Ma et al. reported that an increase in clay dosage weakened the mechanical properties of polysulfone membranes.¹⁵ In a contrasting study conducted by Zafar et al., an increase in PEG content was found to increase the mechanical strength and modulus of cellulose acetate membranes; instead of leaching out, PEG interacted with the polymer resulting in increased toughness.¹⁶ On another note, biopolymers such as lignin and cellulose have been used to improve the modulus of polymers in polymer composites.^{17,18} Lignin derivatives have been used as additives in membrane fabrication. For example, Zhang et al. used lignosulfonate in polysulfone membranes to impart electrolyte transference and Nevarez et al. used propionated lignin to fabricate cellulose triacetate membranes.^{19,20}

Extensive membrane characterization includes establishing the thermal properties in addition to permeation properties. The glass transition temperature (T_g) has been used in membrane technology to elucidate the morphological properties of membranes.²¹ A shift of the T_g to lower temperatures indicates the presence of free volume fraction and hence a looser structure.^{21,22}

Based on the literature presented in this study, additives such as PEG and PVP tend to compromise the tensile strength and modulus of membranes but an increase in permeability has been reported as well. It has also been reported that membranes that have high free volume fractions have lower mechanical strength because they have higher porosity. This means that differential scanning calorimetry (DSC) can be used to predict the morphology of polysulfone membranes and ultimately the permeation properties. In this study, native lignin (28 kDa), PEG 10 kDa, and PVP 29 kDa were used to determine the membrane properties and these were correlated with the glass transition temperature. The selected additives have to be comparable in size so that the effect of molecular weight is eliminated; however, PEG 35 kDa was unstable during membrane preparation and was therefore replaced with PEG 10 kDa. The fact that lignin is readily available means that it can be used to reduce the overall cost of membranes. Currently, there is a debate about

the exact structure of lignin but the structure given in Figure 1 is universally accepted.²³

EXPERIMENTAL

Materials

The polymer solutions were prepared from polysulfone beads (22 kDa), lignin alkali (28 kDa), polyvinylpyrrolidone (PVP; 29 and 360 kDa), PEG (10 and 35 kDa), and *N,N*-dimethyl formamide (DMF), obtained from Sigma Aldrich, and *N*-methyl pyrrolidone (NMP), bought from Merck. The PEG 10 kDa and PEG 35 kDa and PVP 360 kDa were used to determine the pore size and pore-size distribution of the membranes.

Membrane Fabrication

The membranes were prepared using the Loeb–Sourirajan wet-phase separation method with minor alterations.^{24,25} Polymer solutions were prepared by first dissolving the additives in a 3 : 1 (NMP : DMF) solvent ratio under magnetic stirring while heating in a water bath at 50°C for a period of 30 min. The 3 : 1 ratio was adapted from Yip et al. where they found that it was an optimal mixture of the solvents to obtain a membrane with the desired properties.²⁶ Sufficient quantity of polysulfone was dissolved in a cooled solution of solvent (83 wt %) and additive (0, 0.125, and 0.5 wt %) for a period of 8 h and the solution was allowed to settle overnight to remove air bubbles. The polymer dope solutions were then hand-cast on an 85- μm nonwoven fabric (obtained from Hirose Co., Japan) and on a glass plate using a casting knife with the blade adjusted to a casting height of 150 μm , and thereafter the glass plate was immediately immersed in a deionized (DI) water coagulation bath at room temperature. This was done to monitor the permeability variations of membranes cast on a glass plate and on a fabric. The formed membranes were then rinsed thrice with DI water for 30 min each time and then stored in a refrigerator before performance testing and characterization.

Characterization

Morphology. The morphology of the membranes was determined using a scanning electron microscope (SEM; quanta FEI-SIRION SEM). To obtain SEM images of membrane cross sections, membrane samples were first freeze-fractured in liquid nitrogen and then gold coated to impart electrical conductivity.

Membrane Porosity. The bulk porosity of unsupported membrane (membranes cast on a glass plate) was estimated using eq. (1). This was done by immersing the membranes in deionized water at 23°C for a period of 6 h, and thereafter they were dried in an oven at 80°C overnight. Replicates were performed from four similar membranes cast on different days using a similar method.

$$\varepsilon = \frac{(m_{\text{wet}} - m_{\text{dry}})/\rho_w}{V} \times 100\%, \quad (1)$$

where m_{wet} is the wet mass of the membrane, m_{dry} is the dry mass of the membrane, ρ_w is the density of the wetting solvent (water), and V is the wet volume of the membrane.

Thermal Studies. DSC measurements were performed on a DSC Q2000 Differential Scanning Calorimeter (DSC supplied by TA Instruments—Waters LLC, New Castle, DE). These

analyses were carried out at temperatures ranging between 30 and 300°C at a heating and cooling rate of 10°C/min. The experiments were performed under nitrogen atmosphere at a flow rate of 20 mL/min. The glass transition temperature (T_g) values of the polymers were taken from the second heating scan.

Mechanical Tests. An Instron® model number 5966 was used to test the tensile strength of the membranes. Samples of about 25 mm \times 0.11 mm \times 10 mm with a gauge width of 3.2 mm were used for the analysis in accordance with ASTM D 638 Standard Test Method. The samples were analyzed at a cross-head speed of 5 mm/min and seven replicates were analyzed with the average values reported.

Pure Water Permeability. The membrane's pure water permeability, L_p , was obtained using a high-pressure dead-end filtration cell with an effective surface area of 12.57 cm². The membranes cast on a glass plate and on a nonwoven fabric were first compacted at 400 KPa until the permeate flow rate had stabilized, with less than 6% difference in a 30-min interval. Pure water permeability was computed as the gradient in a plot of flux and pressure. As the membranes cast on glass plate had low flux values, only the membranes cast on a fabric were tested for PEG and PVP rejections. This was accomplished by replacing the DI water in the cell with 100 mL of 500 mg/L of solute with constant stirring at 400 rpm/min. The first 3 mL was discarded to eliminate the possibility of permeate dilution by the water that had remained in the cell. A 5% yield was then collected to minimize solute adsorption on the membrane surface and diluted. The permeate solution and stock solutions were analyzed using a total organic carbon (TOC) analyzer (Teledyne Tekmar, TOC fusion). The rejection parameter was calculated using eq. (2)¹²:

$$R_o = \left(1 - \frac{C_p}{C_f}\right) \times 100, \quad (2)$$

where R_o is the percent solute rejection, and C_p and C_f are the permeate and feed concentrations, respectively.

Membranes cast on a glass plate showed very low water flux and as such they were not used to investigate the pore-size distribution.

Pore Size and Pore-Size Distribution. The pore sizes and pore-size distribution of the support membranes were determined by solute-rejection experiments. Pore-size distribution was obtained by rejecting PEG and PVP solutes of known molecular sizes under a hydraulic pressure of 200 KPa. The solutes were PEG 10 kDa, PEG 35 kDa, and PVP 360 kDa. The solute sizes, d_s , were obtained using eqs. (3) and (4).²⁷

For PEG:

$$r = 16.73 \times 10^{-3} \times M^{0.557} \quad (3)$$

For PVP:

$$r = 8.40 \times 10^{-3} \times M^{0.593}, \quad (4)$$

where r is the solute radius in nm and M is the molecular weight in g/mol.

The solute rejection (R_o) was then plotted against the solute diameter (d_s) on a log-normal probability sheet and a straight line was obtained. From this straight line, the effective mean

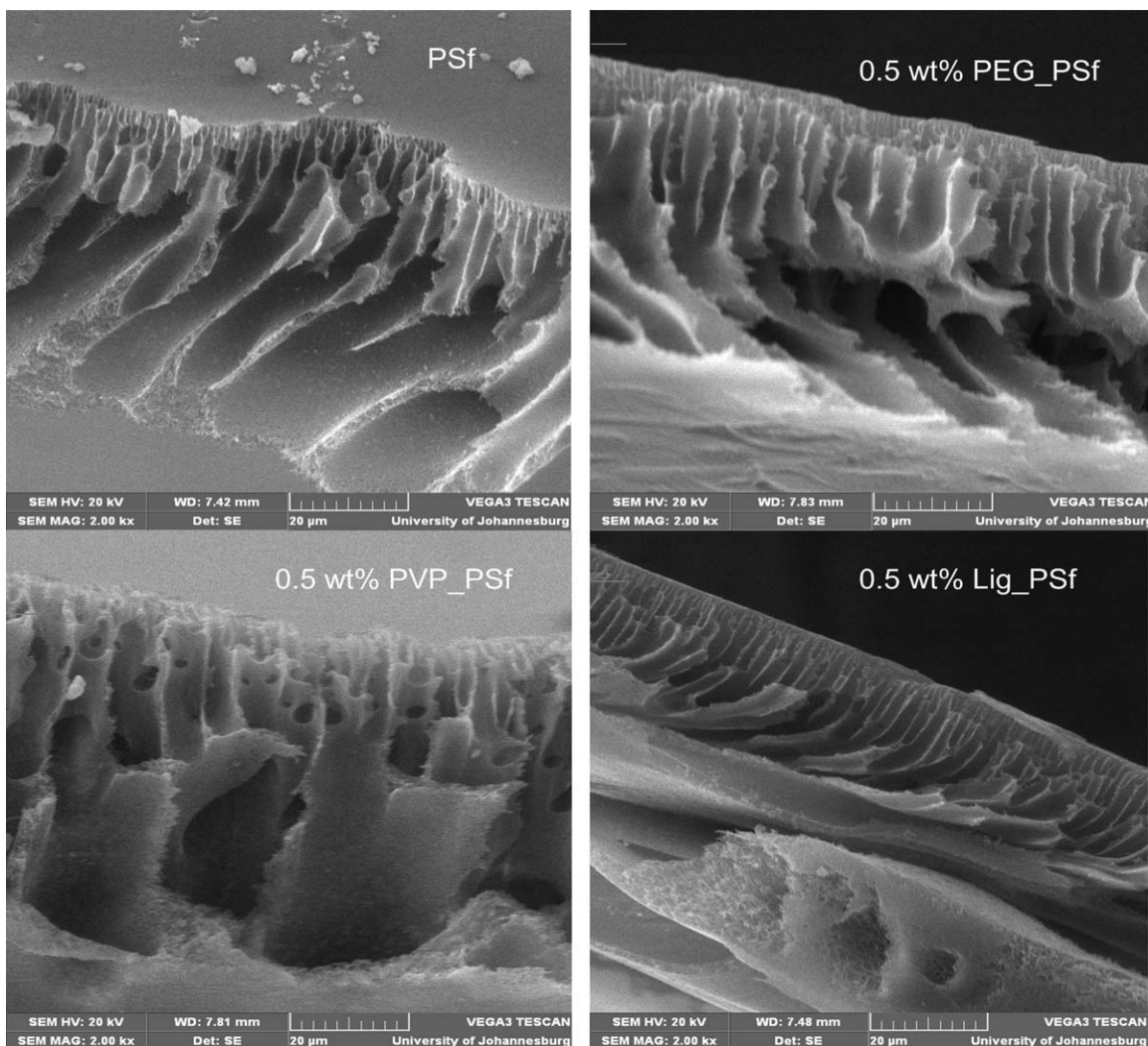


Figure 2. Cross-sectional SEM images of polysulfone (PSf) and PSf modified with 0.5 wt % PEG, PVP, and lignin additives.

pore size (μ_p) was estimated at $R_o = 50\%$ and the geometric standard deviation, σ_p , was obtained as the ratio of R_o at 84.13% over that at 50%. Therefore, using μ_p and σ_p , the pore-size distribution can be obtained from the probability density function in eq. (5).²⁸

$$\frac{dR(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left[-\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right], \quad (5)$$

where d_p is the pore radius of the membrane.

RESULTS AND DISCUSSION

Membrane Morphology

Cross-sectional images of neat polysulfone and additive modified polysulfone membranes are shown in Figure 2. There is an observed increase in the thickness of the bottom skin layer and it also becomes spongy after the incorporation of 5 wt % of each additives. This is because during phase separation, there is a delayed demixing on the glass surface as this side is not in direct contact with the coagulant. Barzin and Sadatnia have

shown that delayed demixing results in a spongy structure.²⁹ The presence of the hydrophilic additives improved the water tolerance of the casting solution and hence the solvent outflux rate decreased significantly on the glass-contacting (bottom) surface.^{30,31} However, membranes cast on the nonwoven fabric do not show this characteristic (Figure 3). The membranes are asymmetric but there is no bottom skin layer observed on the fabric side. This is because the open fabric allows unhindered movement of the coagulant through the fabric, which makes the phase separation to take place at an equal rate. Although the membranes cast on a fabric are asymmetric like the ones cast on a glass plate, the figure-like voids of 0.5 wt % Lig_PSF are about twice as wider (20 μm) as the PVP- and PEG-modified (10 μm) membranes.

Membrane Porosity

The porosity measurements, as seen in Table I, were done to further elucidate the difference in the membrane structure brought about by the incorporation of different additives. The bulk porosity is generally defined by the presence of voids

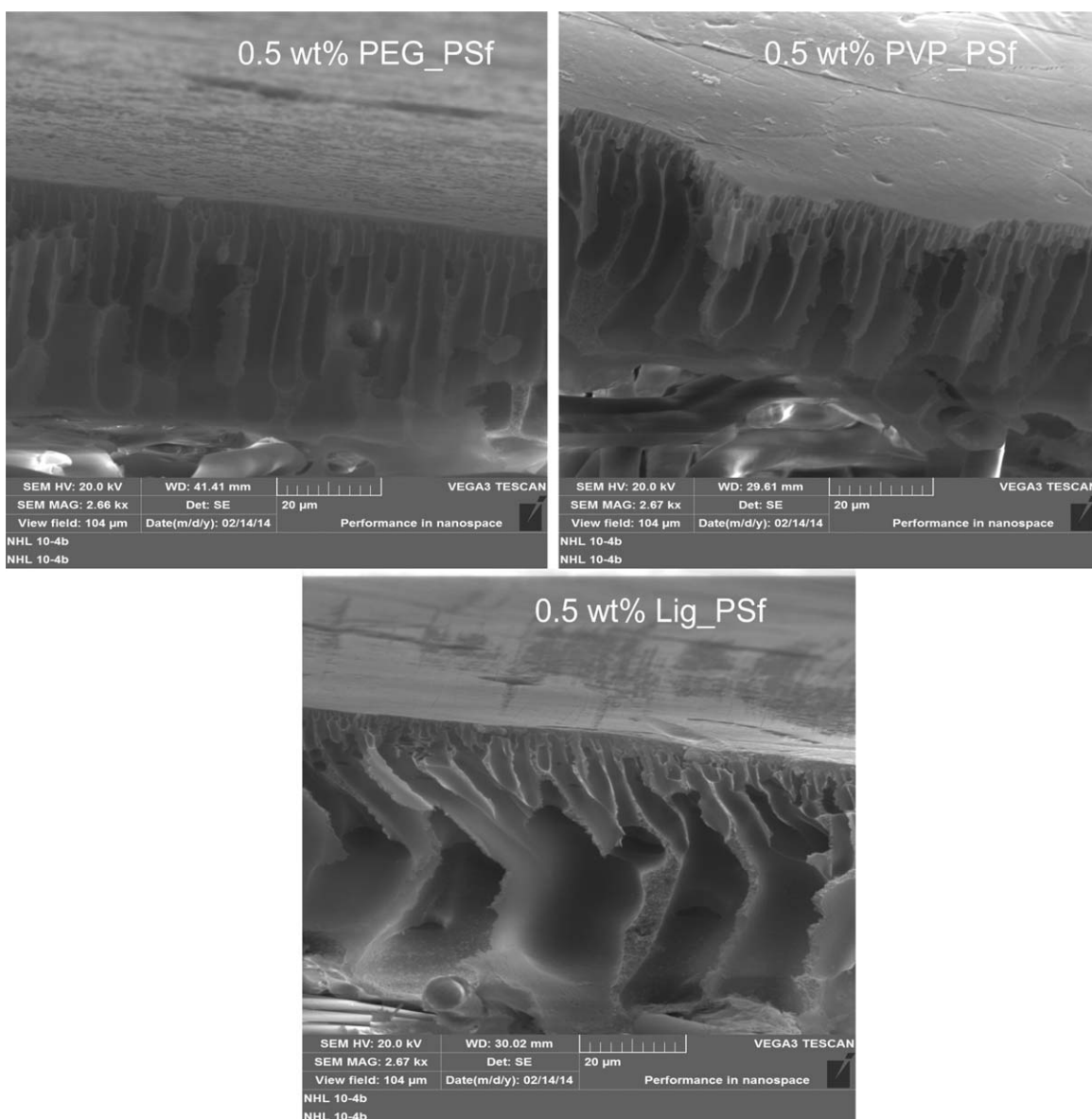


Figure 3. Cross-sectional SEM images of membranes cast on a nonwoven fabric modified with 0.5 wt % of lignin, PVP, and PEG.

within the membrane. A membrane with higher bulk porosity will have a relatively open structure. Table I results show that a more than two-fold increase in the porosity was observed after the lignin content was increased to 0.5%. This change, however, cannot be directly inferred from the SEM images because the membranes appear to have the same structure when considering the microvoids before and after the additive incorporation. The addition of the additives to polysulfone therefore does not change the thermodynamic stability of the dope solution. It has been reported that the addition of PVP into polysulfone brings the dope solution nearer to precipitation by reducing the demixing gap and in some instances the thin skin thickens due to instantaneous liquid–liquid demixing.³² The top skin layer thickness remains constant (as seen in Figure 2) for all membranes because the content of the additives used was low (up to 0.5%). Noteworthy is the porosity of the membranes modified

with PEG when compared with lignin and PVP. When 0.5% of each additive was used, the porosity of the membranes followed the order $\text{PEG_PSf} < \text{Lig_PSf} < \text{PVP_PSf}$. Membranes with lower molecular weight have been reported to have lower porosity when compared with their counterparts. This observation is in agreement with our results because PEG had a lower molecular weight (10 kDa) compared with lignin (28 kDa) and PVP (29 kDa).¹⁴ A plausible explanation could be that additives with high molecular weight have low mobility. During demixing, most additive residues adhere to the polymer as it solidifies. As the additives are soluble in water, leaching is inevitable and thus pores are formed. Besides the low mobility, each additive affects the thermodynamic and kinetic stability differently and this will result in membranes with different properties.³³ A reduction in the miscibility of the coagulant and the dope solution, which favors thermodynamic enhancement, results when adding

Table I. Effect of Lignin, PEG, and PVP Additives on the Bulk Porosity, Thermal, and Mechanical Properties of Polysulfone Ultrafiltration Membranes

Membrane	Bulk porosity (%)	Glass transition (°C)	Tensile stress at break (MPa)	Modulus (MPa)	Elongation at break (%)
PSf	20.08 (6.79)	187	6.04 (0.37)	194.9 (16.9)	20.0 (1.5)
0.125%_Lig_PSF	46.23 (5.12)	180	4.05 (0.33)	79.5 (11.4)	17.3 (4.1)
0.5%_Lig_PSF	53.99 (10.65)	-	3.49 (0.25)	47.6 (11.8)	12.4 (2.6)
Correlation coefficients					
Permeability	0.90	-0.94	-0.90	-0.90	-0.99
Glass transition	-0.99	1	0.99	0.99	0.99
0.125%_PEG_PSF	24.80 (0.35)	179	3.93 (0.90)	53.7 (7.0)	21.9 (3.8)
0.5%_PEG_PSF	30.07 (0.85)	166	4.22 (0.40)	47.0 (6.5)	29.8 (3.0)
Correlation coefficient					
Permeability	0.85	-0.56	-0.34	-0.49	0.97
Glass transition	-0.99	1	0.71	0.81	-0.98
0.125%_PVP_PSF	35.30 (8.10)	187	4.22 (0.50)	46.4 (8.9)	32.4 (1.9)
0.5%_PVP_PSF	63.26 (1.04)	185	4.24 (0.70)	46.3 (6.0)	43.0 (15.9)
Correlation coefficients					
Permeability	0.98	-0.99	-0.62	-0.62	0.91
Glass transition	-0.94	1	0.49	0.50	-0.84

The standard deviation is shown in parentheses.

additives. The kinetic hindrance, on the other hand, has a minor effect because the total amount of the additives used was too low to cause any change in the viscosity of the polymer solution. Although the bulk porosity was calculated on membranes cast on a glass plate, the macrovoids of membranes cast on fabrics show the cause of the increase in the porosity from about 20 to 54% after incorporating 0.5% of lignin. Figure 3 shows a double increase in the width of the macrovoids.

Thermal Properties

Membrane structural properties can be studied using DSC. The glass transition temperature, T_g , in particular has been used to interpret the membrane structure of amorphous polymers. It has been reported that a membrane with a lower glass transition temperature normally has more fractional free volume within the matrix and has a loose structure.^{34,35} The glass transition temperature of the virgin polysulfone membrane, 187°C, decreased to 179 and 180°C, respectively, after the addition of PEG and lignin additives as presented in Table I.²⁵ Labouffie et al. also reported a decrease in the glass transition temperature after the incorporation of PEG of different molecular weights. The plasticizing effect of PEG was cited as the reason for the reduction of the temperature.³⁶ There is also a strong negative correlation coefficient, -0.94, between the bulk porosity and the glass transition temperature. This means that an increase in the bulk porosity results in a decrease in the T_g and hence a loose structure. When heated, the membrane structure easily collapses. Membranes modified with PEG had the lowest bulk porosity and had the lowest T_g . This was unexpected because a lower T_g indicates more free volume. This could be because of the plasticizing effect of PEG. The addition of PVP into the casting solution did not result in a major decrease in the glass transition when compared with PEG-modified membranes.

Based on the notion that more free volume causes a shift of T_g to lower values, it was expected that the T_g be even lower. The cross-sectional SEM images (Figure 3) do not show an increase in the size of the macrovoids. This could be because of the formation of numerous small voids after the incorporation of PVP.

Mechanical Properties

When fabricating membranes, the incorporation of additives can have varying effects on the resultant membrane microstructure, transport properties, and the strength of the membranes also changes. Different additives and polymers have different mechanical and thermal properties.^{15,16} To evaluate the effect of additives on the mechanical properties, three additives with comparable molecular weights were used although PEG had a much lower molecular weight. A polymer solution made by adding PEG 35 kDa precipitated before casting and for that reason, PEG 10 kDa, PVP 29, and lignin with a molecular weight of 28 kDa were used. The results obtained are shown in Table I. In general, the modulus decreased significantly as the additive content was increased. This could be attributed to the formation of pores within the membrane matrix.²⁹ When comparing the decrease in modulus among membranes, Lig_PSF membranes had a higher modulus (from 194 to 79 MPa) compared with PEG_PSF and PVP_PSF, which, respectively, had a modulus of 53 and 46 MPa after adding 0.125% of each additive.²⁵ The reason is that lignin has numerous hydroxyl groups that can be used as receptors for interacting with polysulfone. Although it is known to interact poorly with commercial polymers, improvements in toughness have been reported.³⁷

Any material that increases the porosity of membranes has been reported to also decrease the tensile strength of such membranes.¹²⁻¹⁵ All additives used in this study were found to increase the porosity, and therefore a decrease in the tensile

strength was expected. A strong positive correlation with the glass transition temperature was observed for Lig_PSF membranes. Membranes modified with PEG and PVP showed a marginal increase in tensile strength when the content of the additive was increased to 0.5%. This is because fewer additive residues remained in the membrane matrix during phase inversion as only a negligible amount of additive was used.¹² Although the elongation at break is not significant in membrane application, contrasting results were obtained when comparing the bio-additive and the synthetic additives. PEG_PSF and PVP_PSF membranes showed an increase in the elongation while Lig_PSF membranes showed a steady decrease. The reported increase in the bulk porosity introduced breaking points along the membrane, which caused the membrane to rupture with minimal strain. In addition to the plasticizing effect of PEG and PVP that causes the membranes to be more flexible, these additives form thick spongy skin layers that can also increase flexibility and chain mobility.

Pore Size and Pore-Size Distribution

When determining the pore-size distribution, the observed solute rejection (R) as a function of the solute diameter was plotted on a log-normal probability paper. The straight line obtained was used to calculate the geometric mean and geometric standard deviation by means of which the pore-size distribution can be obtained using eq. (5). Figure 4 shows the pore-size distributions of PEG-, PVP-, and lignin-modified membranes. The Lig_PSF and PVP_PSF membranes were observed to have an average pore size of about 16 and 17 nm, respectively. These results are expected as both additives had similar molecular weights. In contrast, the PEG_PSF membrane showed an average pore size of 11 nm, lower than those of the other membranes, as it had a lower molecular weight (10 kDa). This means that the additives act as templates for pore formation. Low-molecular-weight additives result in smaller pore sizes while relatively high-molecular-weight additives result in bigger pores and hence higher permeability. Liang et al. also reported an increase in water permeability due to the increase in pore sizes and hydrophilicity.³⁸ Noteworthy, membranes modified with PVP and lignin had a narrow pore-size distribution ranging between 10 and 25 nm

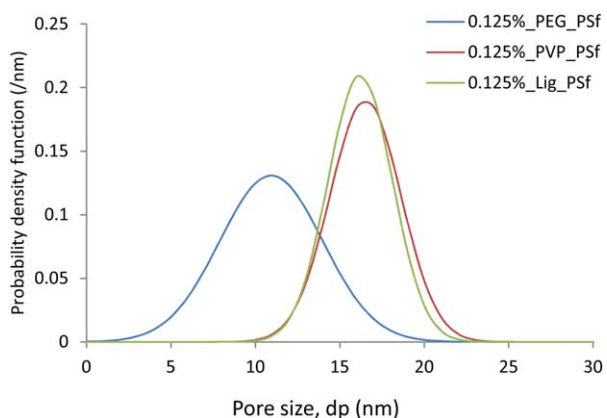


Figure 4. Pore-size distribution of polysulfone membranes cast on a nonwoven fabric using PVP, PEG, and lignin as additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Observed Permeation Properties of Membranes Cast on a Glass Plate and on a Nonwoven Fabric with an Increase in the Additive Content

Membrane	Permeability (LMH/KPa) ^a	Permeability (LMH/KPa) ^b
PSf	155.1 (9.3)	17.40 (4.91)
0.125%_Lig_PSF	203.2 (11.2)	34.35 (8.04)
0.5%_Lig_PSF	282.5 (13.1)	64.56 (4.86)
0.125%_PEG_PSF	149.3 (10.9)	23.96 (1.74)
0.5%_PEG_PSF	221.5 (14.8)	42.50 (8.13)
0.125%_PVP_PSF	167.2 (11.8)	31.03 (6.42)
0.5%_PVP_PSF	237.8 (13.2)	58.28 (3.40)

Standard deviation is shown in parentheses.

^a Membranes cast on a fabric.

^b Membranes cast on a glass plate.

when compared with membranes modified with PEG, which showed a size range of between 2.5 and 20 nm. This is also caused by the molecular weight of the additives.

Membrane Performance

Table II shows the permeation properties of the membranes. An increase in each additive used resulted in an increase in the pure water permeability. All additives showed a similar trend although lignin showed a larger increase. For example, when 0.125% of lignin, PEG, and PVP additives were incorporated, the corresponding flux increased from 17.4 to 34.35, 23.96, and 31.04 LMH/KPa, respectively. These directly correspond to an increase in the bulk porosity where the porosity, respectively, increased from 20.08 to 46.23, 24.8, and 35.3% when 0.125% of each additive was used. Membranes cast on a fabric showed high permeability values (more than threefold increase) when compared with membranes cast on a glass plate. This is due to the fact that membranes cast on a glass plate have two skin layers (top side and bottom side) that further increase the resistance to mass transfer. A relatively dense bottom skin layer on the membranes is formed on the smooth glass side and prevents an equal inflow and outflow of solvent and nonsolvent during phase separation in the entire membrane. When casting membranes on a fabric, some of the polymer seeps into the nonwoven fabric, which limits the formation of the bottom skin layer, thereby increasing the pore interconnectivities within the membrane, and hence resulting in high flux.

CONCLUSION

Lignin, PEG, and PVP have been used as additives to prepare ultrafiltration membranes. From the results obtained, lignin has been identified as the preferred additive because membranes with higher permeability values were produced. There was a notable increase in porosity after the incorporation of lignin. Although lignin incorporation into polysulfone results in higher porosity, the membranes were observed to have a higher modulus when compared with PEG_PSF and PVP_PSF membranes. Correlation coefficients obtained between porosity, permeability, and glass transition temperatures indicate that the membrane microstructure can be investigated using these techniques and confirmed using SEM. The permeability results of membranes

obtained from membranes cast on a glass plate show that phase inversion takes place at a lower rate at the bottom side (glass side) than in the bulk of the membrane. The result is a dense bottom skin layer that further hinders mass transport hence lower flux. However, more experiments are needed to further optimize the nonwoven fabric to obtain optimal membrane performance.

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