The Effect of Variations in the Ratio of Matrix/Solvent on the Physical and Mechanical Properties of Chitosan Biopolymer Membranes

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Abstract. The membranes with various ratio of matrix/solvent such as 1%, 2%, 3%, and 4% were prepared using casting method. Chitosan powder was used as a matrix and acetic acid 1% (v/v) solution as solvent. The physical properties of membranes have been characterized by different techniques including FTIR, XRD, swelling index (SI), BJH method, and filtration, while the mechanical properties have been characterized by tensile strength measurements. The results showed that increasing the amount of matrix resulted in an increased in thickness, pores size, the elongation-at-break, elastic moduli, tensile strength and the pure water flux of membranes significantly, whereas the pores density, swelling index and crystallinity index decreased. This study can be simplified to be even faster and straightforward in designing polymer membrane structures for filtration purposes.

1. Introduction

Chitosan is a natural polysaccharide biopolymer derived by deacetylation of chitin. Chitin is a major component of the shells of crustacean such as crab, shrimp and crawfish [1-3]. Chitin is insoluble in water and common organic solvents but it dissolve only in solvents such as *N,N*dimethylacetamide, hexafluoroacetone or hexafluoro-2-propanol; whereas chitosan is soluble in aqueous acidic solutions (pH < 6.0), therefore it is largely used in different applications as gels, films and fibers [4-6].

Chitosan has attracted great interest due to its biocompatibility, high charge density, non-toxicity and adhesion. It has antibacterial effect, heavy metal adsorption, antioxidation, film and membranes formability [5, 6]. The film properties of chitosan depend on its morphology, which is effected by molecular weight, degree of N-acetylation, solvent evaporation, and free amine regenerating mechanism [7]. Chitosan film has a potential to be employed for packaging, particularly as an edible packaging. Chitosan based membranes have been used in reverse osmosis, gas separation, dialysis, and pervaporation [8]. It is used as a composite, polyelectrolyte complex or a blend with another polymer [7, 8]. Chitosan as a membrane alone has high mechanical strength, permeable to urea, and able to reject high molecular weight compounds [7, 9].

Many studies have been carried out in order to understand the mechanism of the basic processes of forming chitosan polymer membranes. The use of organic acid solution such as glycolic acid, malic acid and ascorbic acid solutions for chitosan dissolution produces chitosan membranes with improved mechanical properties and enhanced hydrophilicity [10]. Le *et al* reported that the Young's Modulus of the hydroxyapatite (HA) chitosan composites is lower than pure chitosan [11]. The Young's Modulus of the composites decreases with HA content, while the failure strength and strain increase with the HA content. From ionic interaction between the chitosan and concentration of sulfuric acid, protonation and crosslinking takes place for a typical concentration of 0.1-0.5 M of 25 μm thick membranes. Beyond 0.5 M concentration of sulfuric acid, ion diffusion is favored and degree of crosslinking increases [1].

Based on those backgrounds, it becomes clear that the studies carried out so far are more related to the mechanism of forming composites chitosan membranes and their physical characteristics. Therefore, it will be interesting to investigate the effect of variations in the ratio of matrix/solvent on the physical and mechanical properties of chitosan polymeric membranes. This study reports the effect of variations in the ratio of chitosan (as a matrix) to acetic acids (as a solvent) on physical and mechanical properties of chitosan membranes include FTIR, XRD, pore size, pores density, swelling index, tensile strength, and pure water flux (PWF).

2. Materials and Methods
2.1. Materials
Chitosan with a degree of deacetylation (DD) of 87.9%, solubility in acetic acid of 99.4% and an average molecular weight of 900,000 was used as membrane materials. The chemicals used in this study were analytical grade and demineralized water was used in preparing the solutions.

2.2. Chitosan membranes preparation
Various chitosan membranes such as 1%, 2%, 3%, and 4% have been prepared by casting method. Chitosan is used as matrix and acetic acid 1% (v/v) solution as solvent. 1% (w/v) membrane solution was prepared by dissolving 2.5 g of chitosan powder in 250 ml of acetic acid 1%. The mixture was stirred for 8 hours at room temperature to obtain membrane solution. The membrane solution was poured onto a glass plate sized of 18.5 cm x 24.0 cm then dry at room temperature for 6 days. The dried membrane was immersed into 1 M NaOH for 12 minutes, washing repeatedly with distilled water and finally drying again at room temperature. The membrane obtained was chitosan membrane 1%. Other membranes have made by the same method, namely by varying the amount of chitosan in the same volume of acetic acid 1%. Finally, it obtained dry chitosan membranes, which are ready to characterize or used.

2.3. Characterization methods
The FTIR spectra of all membranes were obtained using an IR Prestige-21 FTIR spectrophotometer, Shimadzu. Spectra were taken with a resolution of 4 cm^{-1} and averaged over 10 scans. The spectra were recorded in the range of 400 to 4000 cm^{-1}.

The X-ray diffraction spectra of dry membranes have been recorded at room temperature using X-ray Difractometer (XRD). The X-ray source used was Cu-Kα radiation wavelength of 1.54 Å, with irradiation conditions were 30 kV and 40 mA and the diffraction angle, 2θ between 5° to 60°. From the spectra obtained, we can calculate the crystallinity index (CI) of the membranes using the XRD peak height method developed by Segal and coworkers, formula (1) [12]:

$$CI = \frac{(I_{110} - I_{am})}{I_{110}}$$
(1)

Where I_{110} is the highest crystalline peak (110) and I_{am} is the amorphous peak which is at about 12° in Figure 4.

The pore size and pores density of membranes were analyzed by BJH (*Barrett, Joynerand Halenda*) method using Nova 1200e instrument. Around 1.0 g of membrane was cut into small pieces and put in

sample chamber. Degassing process was done at temperature of 60 ℃ for 7 hours. The analyses of pore size and pores density were done using ASiQ software.

For filtration purposes, membrane are usually used in an aqueous environment, so the water uptake capability which called as swelling index (SI) is an important property of membranes. The membranes were cut in circulars form with diameter 3.5 cm, weighed, and they were kept in beaker with 20 ml of distilled water at 28°C for 5 minutes. Then the membranes were taken out after 5 minutes carefully, removed the excess water from the surface of the membranes with filter paper and weighed [4]. The swelling index of the membrane was calculated using the following formula:

$$SI\,(\%) \;=\; \frac{\left(m_{wet} - m_{dry}\right)}{m_{dry}}\, x\; 100\% \tag{2}$$

where m_{wet} and m_{dry} are the mass of the wet and dry membranes, respectively.

The tensile strength (TS) and elongation-at-break (ε) of membranes were measured using Screw Test Stand Machine ALX S following the guidelines of the ASTM Standard Method D638-90. The measurements have done in dry condition, at room temperature. The membranes were cut into "dogbone-shaped" specimens with the length of narrow section was 12.7-14.2 mm and width of 2-9 mm. Tensile strength was expressed in MPa and ε in percent. The measurements were replicated five times for each membrane and the average values are reported. The elastic moduli (E) of membranes were determined from the stress-strain graphs.

The measurement of pure water flux (PWF) was performed using *dead-end* filtration method with pressure 50-60 kPa. The effective surface area of membranes (A) used is $1.048 x 10^{-3}$ m^2 approximately. The membranes soaked in distilled water for around 10-15 minutes before being used as filter. The PWF was calculated using formula (3) [13].

$$PWF\,(J) = \frac{V}{At} \tag{3}$$

where V is volume of the permeate (l), A is effective surface area of the membrane (m^2) and t is time (h).

3. Results and Discussion

The thicknesses of chitosan membranes obtained were 0.041, 0.134, 0.204, and 0.236 mm, respectively, as shown in Figure 1. They were increased as increased the amount of chitosan from 1%, 2%, 3%, and 4%.

Figure 2 shows FTIR spectra of chitosan membranes 1%, 2%, 3%, and 4%. The spectra obtained were similar to the spectra that have been reported by other researchers [14-15]. All spectra showed similar pattern and in the figure only spectrum of membranes 3% is labeled, other spectra are written in Table 1.

Based on Figure 2 can be described the main bands observed in chitosan polymer membranes. The broad band at around 3692 cm^{-1} is due to overlapping of the O-H and N-H stretching vibrations of functional groups engaged in hydrogen bonds [15]. The band at around 1568 cm^{-1} is assigned to the stretching vibration of amino group of chitosan. The bands which assigned to the stretching vibration of C–O–C linkages in the saccharide structure (glucosamine rings) appear at 1181, 1044 and 899 cm^{-1} [15]. Very weak bands at around 1431 and 1609 cm^{-1} corresponding to the C–H bond in the methyl and stretching vibrations of the carbonyl group (amide I), respectively, that reveal the high degree of deacetylation of the chitosan used [16].
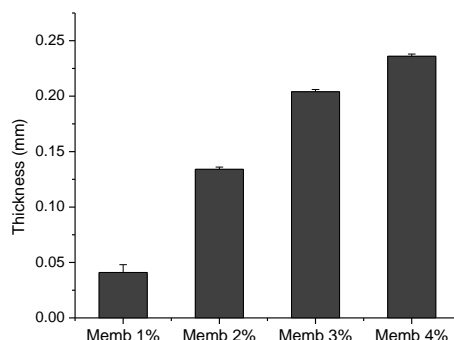
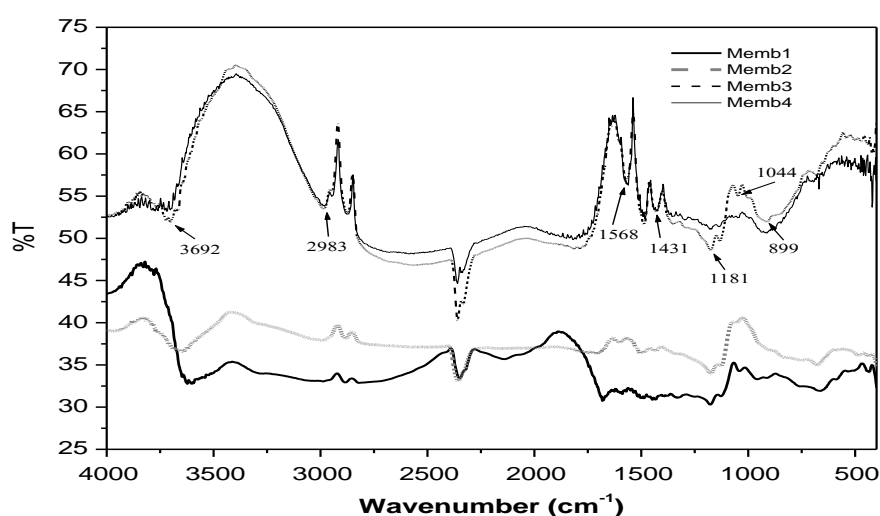**Figure 1.** Thickness of chitosan membranes: 1%, 2%, 3%, and 4%.

Figure 2. FTIR spectra of chitosan membranes: 1%, 2%, 3%, and 4%.

The data in Table 1 indicate that there are no new bands were observed, which means no new molecules are formed on the membranes by increased the amount of chitosan. Some bands have been slightly shifted to the higher wavenumbers or lower, but they are still within their group ranges.

Figure 3a shows a typical stress-strain curve of various membranes, which are similar to the characteristics of the tensile modulus plastic films [17]. The tensile strength (TS), elongation-at-break (ε) and modulus of elasticity (E) was determined from stress-strain curves (Figure 3a) and the results are shown in Figure 3b. Tensile strength is the maximum tension that can be supported by the membranes until it break. Elongation-at-break is a measure of flexibility of the membranes that can be considered as characteristic defects of the membranes before breaking [18].

Figure 3b shows membrane 1% has very small value of E and TS compared with the other membranes (2%, 3%, and 4%). The increased of the amount of matrix also resulted in an increased in elongation-at-break (ε) of the membrane gradually from 191% to 341% for membrane 1 % to 3% and decreased slightly to 329% for membrane 4%. This suggests that the increased the amount of matrix more than 3% decreased the elongation of the membrane. It reduced the ability of stretching as shown by Fig. 3a, where the graph looked steeper [18].

Table 1. The main bands observed in chitosan membranes.

Functional Groups	Wavenumbers Observed (cm^{-1})			
	Membrane 1%	Membrane 2%	Membrane 3%	Membrane 4%
NH_2 and –OH stretch	3619	3660	3692	3700
Symmetric CH_2 stretching	2973	2989	2983	2983
C=O (carbonyl group (amide I))	1609	1609	1609	1609
NH_2 in amino group (amide II)	1588	1588	1568	1568
C-H stretch	1431	1431	1431	1431
C–O–C stretch (saccharide structure)	1181, 1044 and 907	1181, 1044 and 907	1181, 1044 and 899	1181, 1044 and 907

Ref. 15-16.
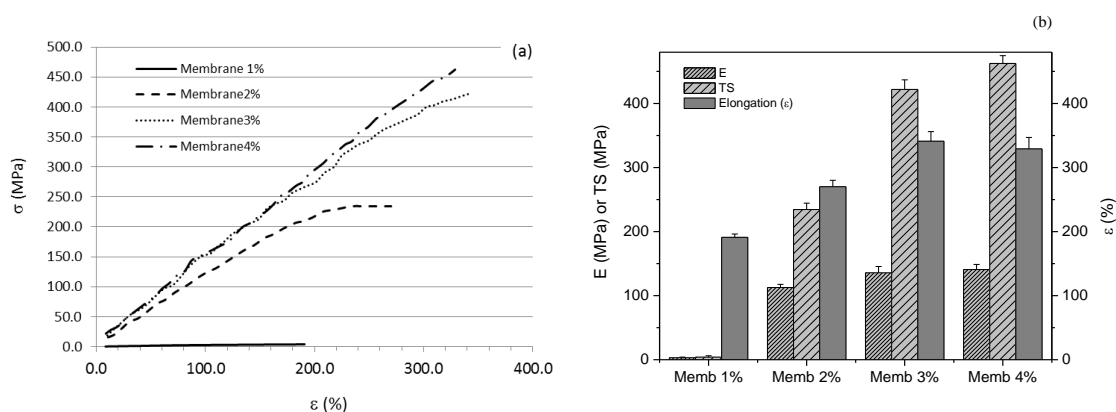
Figure 3. Mechanical properties of chitosan membranes in dry condition: (a) stress-strain curves (representative result is shown), (b) Tensile strength (TS), elongation-at-break (ε) and elastic moduli (E).

The X-ray diffraction spectra of all membranes are displayed in Figure 4. It showed two peaks located at 2θ at about 10° and 20°. This result is in agreement with that have been reported by other researchers [18]. It is known that chitosan always contains bound water (5%) even if it has been extensively dried [18]. The incorporation of bound water molecules into the crystal lattice, commonly termed hydrated crystals, generally gives rise to a more dominated amorphous part which can be normally detected by a broad crystalline peak in the corresponding X-ray pattern. Therefore, the crystalline peak I centred at around 10° is attributed to the hydrated crystalline structure of chitosan and the crystalline peak II centred at around 20° is crystalline 110 of chitosan [18].

By using formula 1 have been calculated the crystallinity index (CI) of the membranes as shows in Figure 5. The highest crystallinity index is obtained for membrane 1% of about 87%, while the other membranes (2%, 3%, and 4%) have almost same values of about 68%. This result is strengthened by the modulus of elasticity (E, Fig. 3b) of membranes where membrane 1% has very small of about 3 MPa and the other membranes have very high, about 130 MPa. This can described that the crystallinity index of membrane 1% is high so its flexibility which expressed by E be very small. Also, it is in accordance with the value of ε which is increased gradually with increasing the amount of matrix from 1% to 4%. These results suggest that the increased the amount of matrix in the membrane resulted in the less ordered structure of the membranes e.g. decreased in crystallinity, thereby increased it tensile strength (TS) [18].
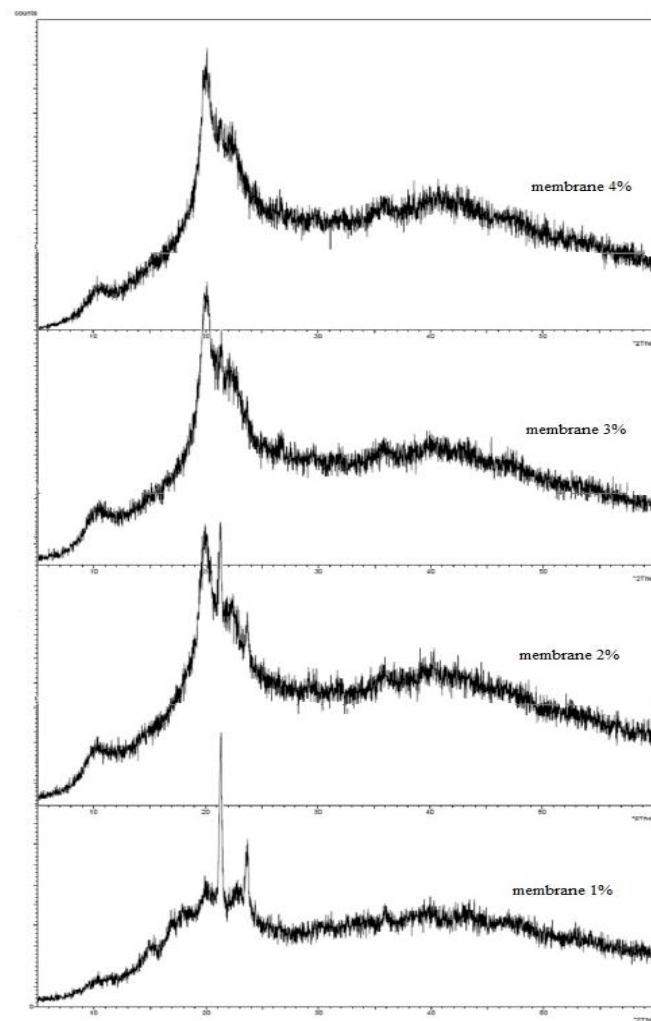
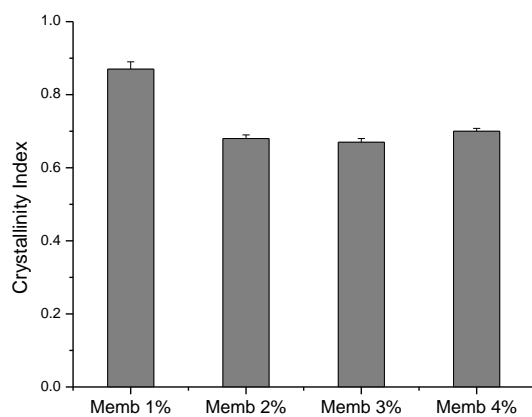**Figure 4**. X-ray diffraction spectra of chitosan membranes 1%, 2%, 3%, and 4%.

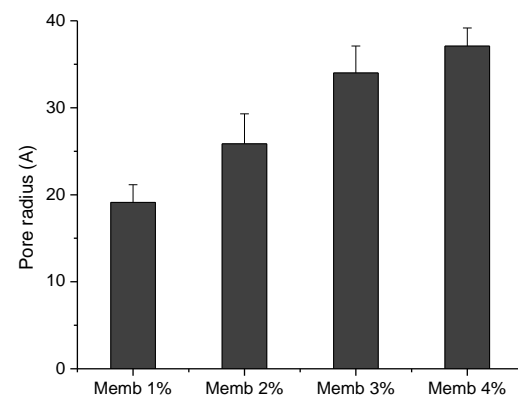**Figure 5.** The crystallinity index (CI) of chitosan membranes: 1%, 2%, 3%, and 4%.

Figure 6. The pore radius of chitosan membranes: 1%, 2%, 3%, and 4%

The pore size and pore density of various membranes obtained using BJH method are shown in Figure 6 and 7. Figure 6 shows that the pore size (means radius of the pores) increased from 19.12 Å to 37.09 Å with increasing the amount of matrix from 1% to 4%, while the pores density decreased from 2.12×10^9 to 0.98×10^9 pores/g as shown in Figure 7. Based on the IUPAC convention for nomenclature porosity, 1972 [19], all membranes are belong to mesoporous group with the pore radius ranges from 19.12 Å to 37.09 Å, which can be used in microfiltration process.
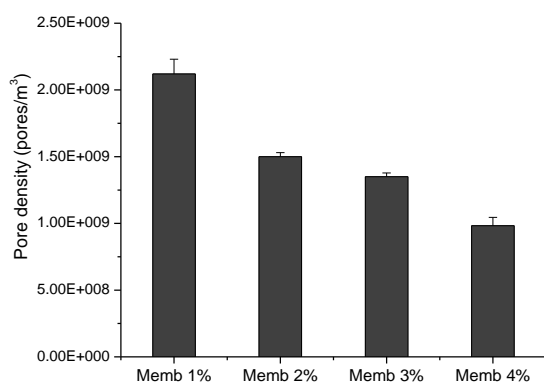

Figure 7. The pores density of chitosan membranes: 1%, 2%, 3%, and 4%.
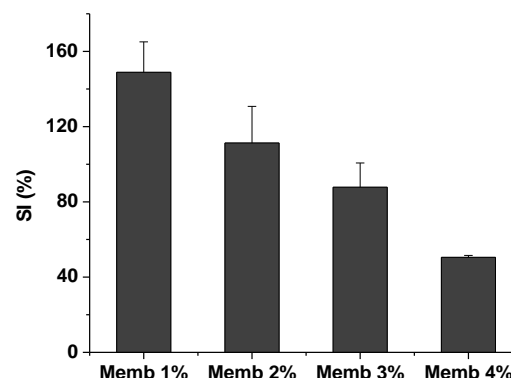

Figure 8. The swelling index (SI) of chitosan membranes: 1%, 2%, 3%, and 4%.

Figure 8 shows the swelling index (SI) of chitosan membranes 1%, 2%, 3%, and 4%. This shows the decreased of the swelling index as increasing the amount of the matrix. These results are in accordance with the pores density of the membranes (Fig. 7) which is increased as increasing the amount of matrix from 1% to 4%. The higher the pores density of the membrane will increase their water uptake capability.

Figure 9 shows the pure water flux (PWF) of all membranes. The PWF values showed significant increased with increasing the concentration of matrix from 1% to 4%. These results are consistent with the pore size of membrane samples which increased as increasing the amount of matrix. From those results (pore size, pores density and filtration), we can conclude that PWF mainly depend on the pores size of membranes. It is an important characteristic in filtration case.
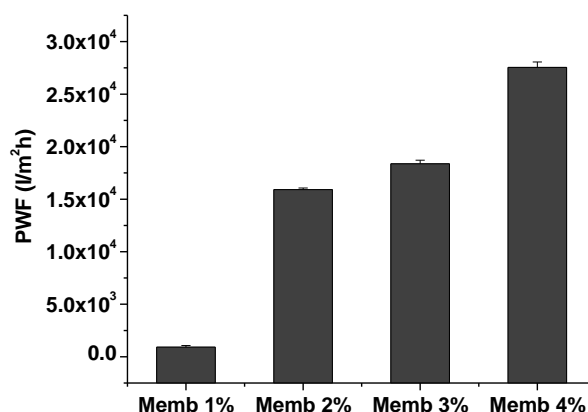

Figure 9. The pure water flux (*PWF*) of chitosan membranes: 1%, 2%, 3%, and 4%.

4. Conclusion

We have demonstrated that the variation in the ratio of matrix/solvent can affect the physical and mechanical properties of chitosan polymeric membranes. This type of study can give structural information which is correlated with performance related information, when analysing membranes

designed for filtration purposes. This work allows predicting possible ratio of matrix/solvent in designing polymer membranes, without the necessity of performing time consuming (especially in the case of filtration membranes). In this study, we have shown that increasing the amount of matrix resulted in an increased in thicknesses, pores size, the elongation-at-break, elastic moduli, tensile strength and the pure water flux of membranes, significantly, whereas the pores density, swelling index and crystallinity index decreased.

Acknowledgements

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