INFLUENCE OF CHITOSAN MOLECULAR WEIGHT AND DEGREE OF DEACETYLATION ON MEMBRANE PHYSICOCHEMICAL AND SEPARATION PROPERTIES IN ETHANOL DEHYDRATION BY THE VAPOUR PERMEATION PROCESS

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Abstract

Membranes were prepared using three chitosans with different molecular weights and degrees of deacetylation. The influence of chitosan features on membrane physicochemical properties, i.e. degree of swelling, contact angle and tensile strength, as well as membrane separation properties in ethanol dehydration by the vapour permeation process are discussed. The conducted experiments showed that an increase in the chitosan molecular weight led to an increase in the membrane surface contact angle concomitant with a decrease in the material selectivity coefficient. On the other hand, an increase in the chitosan degree of deacetylation caused a reduction in ethanol and improved the water permeate flux. There was greater selectivity in the test process for membranes prepared from chitosan with the lowest molecular weight.

Keywords: *chitosan, molecular weight, degree of deacetylation, vapour permeation, separation properties*

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1. Introduction

Over the past three decades, industrial membranes have become an indispensable element of the chemical processing industry. Membrane-based technologies are widely used for purifying, concentrating and fractioning liquid mixtures. Vapour permeation is one of membrane separation techniques; it enables separating azeotropic, close-boiling, isomeric and heat sensitive liquid mixtures.

Chitosan, due to its hydrophilicity and film-forming ability, has been regarded as one of most effective water-permselective membrane materials for pervaporative dehydration of an ethanol–water mixture [1–4]. Chitosan is only soluble in an acidic solution, so it is possible to prepare membranes with the casting-evaporation method. On the other hand, neutralization of a prepared polymer film allows a user to obtain a continuous chitosan material without additional chemical treatment. Given that chitosan is not soluble in an inert environment, it is possible to obtain membranes from the polymer itself and check the influence of different parameters on material separation properties. Chitosan properties depend on both the molecular weight and degree of deacetylation, which influence the physicochemical and separation properties of a chitosan membrane [5, 6]. Apart from the material itself, the properties of chitosan membranes are influenced by their preparation, starting from the solution, i.e. the concentration of the chitosan solution [7], acid type and concentration [8] or temperature and time of soaking membrane in sodium hydroxide solution [7, 9].

This study investigated the effect of the chitosan molecular weight and degree of deacetylation on membrane physicochemical and separation properties in ethanol dehydration by the vapour permeation process.

2. Materials and Methods

2.1. Materials

Chitosan (Acros Organics; 600,000–800,000 Daltons [Da]); chitosan (Acros Organics; 100,000–300,000); chitosan (BioLog Heppe; 90/30/A1); sodium hydroxide (pure, POCh, Poland); acetic acid (glacial, POCh, Poland); ethanol (technical grade); and ethanol (99.5%, pure for analysis, Chempur) were used in the experiments. All materials were used without previous purification.

The degree of deacetylation and molecular weight of utilized chitosans were determined by proton nuclear magnetic resonance (^{1}H NMR) [10] and a viscometric method [11], respectively. The parameters of the chitosans are presented in Table 1.

Table 1. Parameters of chitosans used in this experiment.

Chitosan	Degree of deacetylation [%]	Molecular weight, M_v [Da]
CS600	96.58	174,600
CS30	92.01	204,800
CS100	98.11	229,100

2.2. Membrane Preparation

Chitosan (1.5 g) was dissolved in 100 mL of 1% (v/v) acetic acid solution, then 10 mL of homogenous solution was cast onto a 10 cm diameter glass Petri dish and dried at 40ºC. A 2% (w/v) sodium hydroxide solution was then added to the Petri dish with the polymer film. Next, material was washed with distilled water until a neutral pH was obtained. Prepared membranes were placed into technical grade ethanol; after shrinkage, they were dried at room temperature.

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2.3. Material Characterization

2.3.1. Degree of Swelling

The pieces of membrane prepared from different chitosans were weighed before and after their immersion for 24 h in distilled water, 50% v/v ethanol and 99.5% ethanol. The degree of swelling in every solvent was calculated based on weight difference between the wet and dry membrane using Eq. (1):

$$DS = \frac{m_s - m_d}{m_d} \cdot 100\,[\%], \tag{1}$$

where m_s is the weight of the swollen membrane [g] and m_d is the weight of the dried membrane samples [g].

2.3.2. Tensile Strength

To determine the breaking strength of a given membrane, three strips – about 6 cm long and 1 cm wide – were prepared. The strips were subjected to the tensile force test to determine the value at which the continuity of the polymer film was broken. Measurements were made on an MTS Insight equipped with a 100 N head at a stretching speed of 10 mm/min.

2.3.3. Contact Angle

To compare wettability of chitosan membranes, the contact angle between the sample surface and water was measured in air using the sessile drop method. Measurements were carried out at room temperature with an OCA DataPhysics goniometer. Deionized water was dropped onto at least 5–7 different sites on upper and lower surface of each membrane sample. An average value was obtained for the measured contact angle.

2.4. Membrane Separation Properties

2.4.1. Vapour Permeation Process

To study the permeation of water and ethanol, vapours were applied to prepared membranes using a special permeation vessel (Fig. 1). Ten millilitres of the investigated mixture was placed in a cylindrical vessel. The top of the vessel was covered with the membrane; the upper surface (which contacted the air during drying) faced inside the vessel. Then, a measuring vessel was fixed with a ring and placed into a desiccator to avoid the influence of vapour absorption from the environmental air on the process.

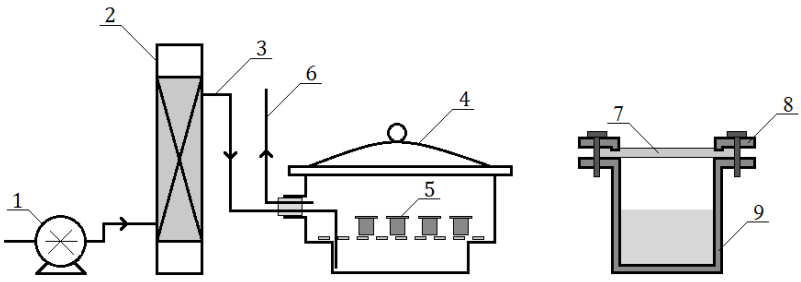

Figure 1. Scheme of the vapour permeation setup: air pump (1), desiccant cartridge with calcium sulfate ($CaSO_4$) (2), air inlet (3), desiccator (4), measuring vessels (5), air outlet (6), investigated membrane (7), fixing ring (8) and cylindrical measuring cell (9).

Moreover, the desiccator was purged with dry air to prevent the accumulation of vapors permeating through the membrane. The air flow was 25 mL/min and did not impact the ongoing process.

The flux of permeate was determined based on the estimated weight loss of the measuring vessel, which was measured in fixed time periods at room temperature using an analytical balance. The determined fluxes were an average of three measurements.

Membranes were tested for a 50% v/v ethanol solution as well as for pure substances: water or ethanol (99.5%). Experiments were performed at room temperature with an effective membrane area of 6.16 cm^2. The thickness of the membranes were measured as an average value of five points by using a waterproof ELMETRON MG-401 precise coating thickness gauge. The membranes obtained had a thickness of 19–28 μm.

The composition of the liquid in the vessel after the ethanol mixture separation process was determined by gas chromatography performed on an Agilent Technologies GC 6850 equipped with an Elite–WAX column and a flame ionization detector.

2.4.2. Evaluation of the Permeation Process Parameters

In order to characterize the system, we need to know the membrane flux, selectivity coefficient and membrane permeability, which is dependent of their solubility and diffusivity.

The flux (*J*) was calculated from Eq. (2):

$$J = \frac{m}{A \cdot t}\left[\frac{kg}{m^2 \cdot h}\right], \tag{2}$$

where *m* is the mass of the permeate [kg], *A* is the effective membrane area [m^2] and *t* is the evaluation time [h].

The diffusion coefficient for each compound of a mixture was calculated with Eq. (3):

$$D_A = \frac{J_A \cdot l}{\Delta c}\left[\frac{cm^2}{s}\right], \tag{3}$$

where J_A is the flux obtained for mixture component A, *l* is the membrane thickness [cm] and **Δc** is the difference in the component A concentration at both sides of the membrane [kg/m^3]. For pure water or ethanol, the diffusion coefficient was determined by a time lag method [12].

The permeability coefficient, which indicates how fast the penetrant can pass through the membrane, was designated in the same way as in a previous work [12] using Eq. (4):

$$P_A = \frac{J_{SA} \cdot l}{\Delta p}\left[\frac{cm^3_{STP} \cdot cm}{cm^2 \cdot s \cdot cmHg}\right], \tag{4}$$

where J_{SA} is the diffusive mass flux in a stationary state [$cm^3_{STP}/cm^2 \cdot s$], *l* is the membrane thickness [cm] and **Δ***p* is the difference in gas pressure at both sides of the membrane [cmHg].

The solubility coefficient is equal to the ratio of permeability of separated components, calculated according to Eq. (5):

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$$S_A = \frac{P_A}{D_A}\left[\frac{cm^3_{STP}}{cm^3 \cdot cmHg}\right]. \quad (5)$$

Permeability and solubility coefficients were calculated in the same way for the mixture and pure solvents.

The selectivity coefficient was used as an indicator for separation performance of polymer membranes and was determined using Eq. (6):

$$\alpha = \frac{P_A}{P_B}\ , \quad (6)$$

where P_A and P_B are the permeability of water and ethanol, respectively.

3. Results and Discussion

3.1. Degree of Swelling

The degree of swelling of the obtained chitosan membranes in different solvents, i.e. water, ethanol (99.5%) and 50% v/v ethanol mixture, is shown in Fig. 2. The highest degree of swelling in water was for the membrane prepared with medium molecular weight chitosan (CS30). Moreover, the membrane made with chitosan CS600, which had the lowest molecular weight, swelled less in water than the membrane from chitosan with the highest molecular weight (CS100).

The molecular weight of chitosan significantly affected the degree of swelling of the obtained membranes (Fig. 2A). The increased chitosan molecular weight caused greater entanglement between polymer chains and contributed to the formation of more hydrogen bonds and van der Waals interactions [13]. Moreover, the increase in chain length makes polymer expansion in the solution difficult and facilitates the creation of a porous membrane structure [14]. Even though the material has a high affinity to water, ethanol penetration in porous material was easier, and the CS100 membrane swelled the most of the prepared membranes. On the other hand, the CS600 membrane

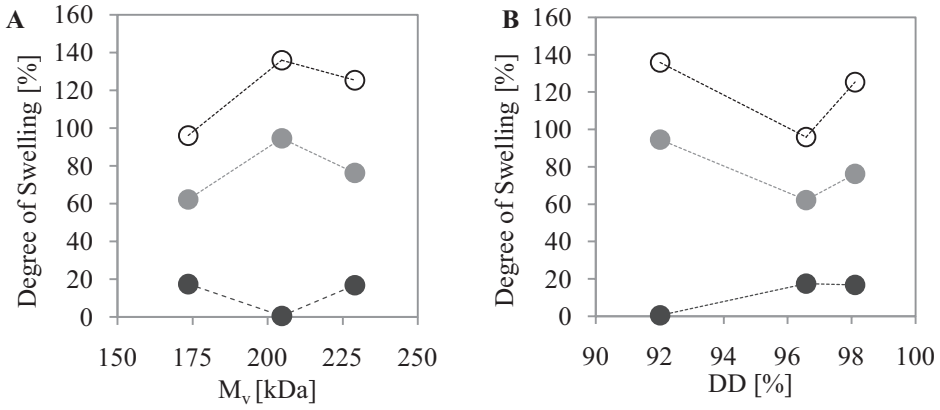

Figure 2. Influence of chitosan (A) average viscosity molecular weight (M_v) and (B) degree of deacetylation (DD) on the membrane degree of swelling in: water (white), 50% v/v ethanol (light grey) and 99.5% ethanol (dark grey).

degree of swelling in ethanol was similar to the CS100 membrane, despite the markedly lower molecular weight.

The presented relationships between degree of swelling and molecular weight were not linear, a factor that is related to the low degree of deacetylation of chitosan CS30 (M_v = 204,800 Da, DD = 92.01%). To confirm this finding, we examined the correlation between the degree of swelling and chitosan degree of deacetylation (Fig. 2B).

The presence of acetyl groups in the chitosan chain breaks the crystalline zone and water molecules can more easily diffuse into the polymer matrix, leading to a higher swelling ratio [15, 16]. Increasing the degree of chitosan deacetylation reduces the amount of acetyl groups in polymer chains, makes them more flexible and facilitates the formation of hydrogen bonds between chains [17]. When more groups are arranged in inter- and intramolecular interactions, then fewer functional groups ($–NH_2$ and –OH) interact with water molecules. Hence, for the CS600 and CS100 membranes, swelling in water is less than for the CS30 membrane [17]. Limited availability of hydrophilic functional groups likely change membrane characters; therefore, penetration of ethanol molecules into the membrane was facilitated and material swelled more in ethanol solution. On the other hand, there was a non-linear relationship between the chitosan degree of deacetylation and membrane swelling. The degree of deacetylation determines the solubility of chitosan in an acidic solution and its ability to re-create the supramolecular polymer structure during swelling [18]. In other words, the degree of swelling of the dry polymer film in water should be higher for chitosan CS100, which has a higher degree of deacetylation, but at the same time its high molecular weight decreases membrane swelling in water. By contrast, for chitosan CS600 (DD = 96.58%), the degree of swelling in water is low despite the high number of hydrogen bonds and dense membrane structure formed by shorter polymer chains. The obtained results demonstrated that molecular weight and degree of deacetylation affect sorption properties of chitosan membranes.

Marked swelling of chitosan membranes in water shows their high affinity for water molecules, a property that is desirable for the membrane dehydration process. All prepared membranes had a high degree of swelling in 50% ethanol, which is undesirable because excessive material swelling influences material density and affects membrane separation properties. However, in the ethanol–water vapour permeation process, the membrane was not in direct contact with the separated mixture; therefore, their swelling properties under the influence of vapour compounds could be different. On the other hand, the prepared chitosan membranes had great differences in swelling properties in water and 99.5% ethanol. These findings suggest that their separation properties for more concentrated ethanol solutions could be good.

3.2. Contact Angle

Membrane swelling values were obtained by immersing material in each solution, so the properties of each side of the membrane were not determined. More information about membrane surface properties was obtained by contact angle measurements (Fig. 3A). All tested chitosans have hydrophilic properties, as evidenced by the obtained contact angles that were < 90º. In addition, there was a difference between the upper – contact with the air – and lower – contact with the glass – surfaces for all prepared membranes.

The influence of chitosan molecular weight and degree of deacetylation on the contact angle for both membrane sides is shown in Fig. 3B. The degree of deacetylation did not significantly affect the membrane contact angle [14], and it was similar for both material sides. Thus, the observed differences in surface contact angles were due to the molecular weight or other membrane preparation parameters.

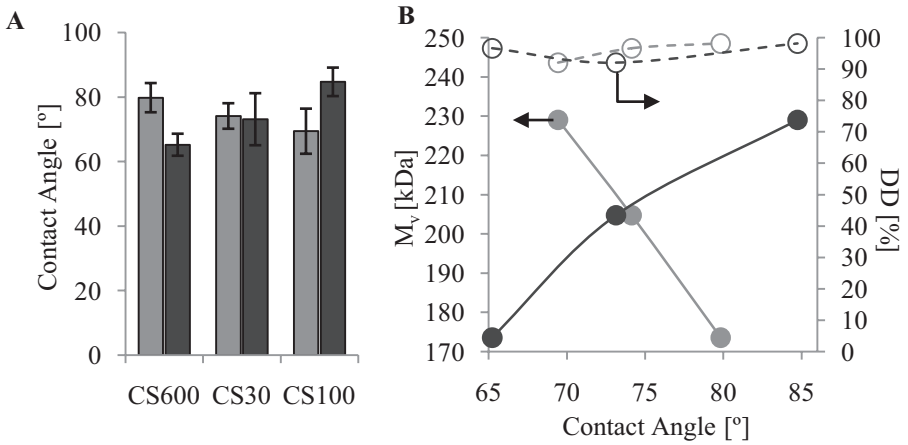

Figure 3. (A) Contact angle obtained for the upper and lower surfaces of chitosan membranes and (B) their dependence on molecular weight (M_v) and degree of deacetylation (DD). Light grey and dark grey bars or dots correspond to the upper and lower sides of the membrane, respectively.

A low chitosan concentration in solution as well as the short polymer chain of chitosan CS600 leads to altered molecular conformation and the creation of hydrogen bonds with the glass substrate [19, 20]. Moreover, a high degree of deacetylation as well as protonation of amino groups influences polymer hydrophilicity and its exclusion from the air–solution interface [21]. During the drying process, water and acetic acid from the solution was evaporated; the pH of the casting solution increased (> 6–6.5) and protonation of amino groups was reduced. Less amino group protonation increases the hydrophobic character of chitosan chains and they began to form aggregates, which do not form micelle-like structures due to the stiffness of chitosan molecules [22]. Aggregates collected on the air–chitosan solution interface act like surfactants, i.e. decrease surface tension [23]. According to the Marangoni phenomenon, when the surface tension gradient is created, aggregates flow from the thinner to the thicker part and produce the hydrophobic polymer layer at the interface [9]. Thus, the upper surface of the chitosan CS600 membrane surface had a higher contact angle than the lower layer, which contacted the glass. In addition, straight polymer chains facilitated the formation of a denser membrane structure and improved their mechanical properties.

When chitosan chains are longer, their entanglement is greater and more inter- and intramolecular hydrogen bonds in the polysaccharide are formed. However, more solvent-exposed hydroxyl groups of chitosan chains tend to form hydrogen bonds with water molecules rather than with amino or other hydroxyl groups within the polysaccharide itself [24]. The difficulty in rotating the polymer chains means that despite solution evaporation, the hydroxyl groups are more exposed on the membrane surface. Therefore, the CS30 membrane had a smaller contact angle and better surface wettability compared with the CS100 membrane. On the other hand, entanglement of chitosan chains makes the membrane structure more porous, which increases the lower surface contact angle.

The wettability of the membrane surface is important in the vapour permeation process due to the solution-diffusion mechanism, where the separation process is based on the selective dissolution of particles in the material. In the dehydration process, high

affinity of the membrane for water is required to make separation more effective. When there is contact between the separated mixture and a membrane surface with a smaller contact angle, there can be higher water content in permeate flux [19]. However, differences between the upper and lower surfaces of the obtained membranes were not significant and they did not influence the water content in the permeate flux.

3.3. Tensile Strength

A membrane for practical or industrial applications must have good mechanical strength. This property is important for technological reasons – i.e. membrane manufacturing and processing before placing in the module – as well as during processes where there is a pressure difference on both sides of the membrane. The dependence of tensile strength and elongation of dry chitosan membranes on chitosan molecular weight and degree of deacetylation are presented in Fig. 4.

Chitosan CS600, with the lowest molecular weight, had the highest tensile strength, while the highest elongation was observed for chitosan with the highest molecular weight (CS100). The value of the tensile strength increased in the series CS30 < CS100 < CS600, which did not coincide with the increase in molecular weight value (CS600 < CS30 < CS100). A membrane prepared from lower-molecular-weight chitosan created a dense polymer film that had greater mechanical resistance due to more hydrogen bonds between polymer chains. For longer polymer chains (CS100), chain entanglement was greater than for chitosan CS30; thus, their tensile strength value was superior. A higher degree of deacetylation positively influenced the tensile strength of the chitosan membranes, but only for polymers whose M_v was < 240 kDa, because for M_v > 580 kDa, the degree of deacetylation does not significantly affect the membrane's tensile strength [25].

Elongation for the chitosan films increased as CS30 < CS600 < CS100, which coincides with the increase in the chitosan degree of deacetylation (Fig. 3B). The elongation value also depends on the chitosan membrane solution [8, 26] and the crystallinity of the polymer film, which is related to the chitosan degree of deacetylation [27–29]. However, for chitosans with a degree of deacetylation > 90%, protonation of amino groups does not influence polymer crystallinity because membrane

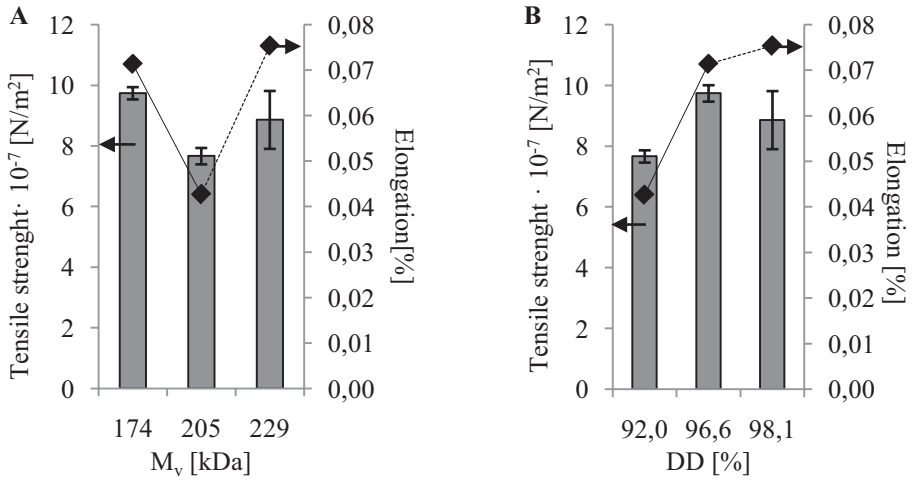

Figure 4. Effect of chitosan (A) molecular weight (M_v) and (B) degree of deacetylation (DD) on tensile strength and elongation of the prepared polymer films.

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neutralization employed during the preparation process nullifies the crystalline formation [17]. Moreover, when the concentration of chitosan solution is below 6 wt%, interactions between polymer chains are reduced and membranes are amorphous [29]. Therefore, polymer chains that are not involved in the creation of crystal domains are more elastic and elongation increases as the chitosan degree of deacetylation increases [30]. The obtained results suggest that the degree of deacetylation significantly affects the mechanical properties of the membrane material, whereas the chitosan CS600 membrane had better mechanical properties than the other obtained polymer films.

Even though the chitosan membranes were stored dry, during the separation process they contacted a separated mixture and their mechanical properties changed. The effect of membrane swelling on the mechanical properties of chitosan film has been studied by other researchers [5, 17, 25, 31]. They have concluded that wet chitosan membrane material has inferior strength but is more flexible compared with dry material, which is both durable and brittle. These opposing behaviours of chitosan membranes could determine their application in membrane separation techniques, especially in those processes where high forces act on the membrane during separation process.

3.4. Vapour Permeation Process

The vapour permeation of ethanol–water mixture was performed to investigate the influence of chitosan features on the prepared membrane. First, the membrane vapour permeation process was carried out with pure water and ethanol solvents, which aimed to determine the transport parameters of the individual components of the mixture without interacting with each other. In turn, to determine the separation properties of prepared chitosan membranes, the process was carried out with a 50% v/v ethanol mixture. The water and ethanol flux values as well as selectivity coefficients obtained for different chitosan membranes are summarized in Table 2.

Table 2. Water and ethanol fluxes obtained for pure solvents and 50% ethanol mixture with calculated ideal and practical separation coefficient.

	Pure solvents			50% ethanol mixture		
	$J \cdot 10^3$ [kg/m^2·h]		α_{ideal}	$J \cdot 10^3$ [kg/m^2·h]		$\alpha_{practical}$
Membrane	Water	Ethanol		Water	Ethanol	
CS600	151.07	45.46	11.63	29.73	14.92	11.96
CS30	129.93	131.43	0.85	27.38	18.75	9.34
CS100	153.64	56.05	1.57	30.77	13.50	2.14

The fluxes of water and ethanol obtained for pure solvents were higher than those obtained when the process utilized a 50% v/v ethanol solution. It is well known that volume changes after ethanol and water are mixed, and the minimum volume at a concentration of 50% v/v was observed [32]. The contraction phenomenon is attributed to hydrogen bond formation between water and ethanol molecules, which additionally limited the evaporation rate and reduced the value of obtained water and ethanol fluxes. In turn, water flux values obtained for the ethanol mixture were similar to values obtained for the pure solvents, higher than for ethanol, an outcome that is associated with the hydrophilic nature of chitosan membranes. The exception was the membrane prepared from chitosan CS30, where for pure solvents there were similar water and ethanol fluxes.

The initial assessment of the separation properties of the obtained chitosan membranes was made based on an ideal selectivity coefficient, which is the permeability ratio of pure substances. It was also a reference point to the practical selectivity coefficient – obtained as permeability ratio of substances in the mixture. The CS600 membrane showed the best separation properties, for which the ideal and practical coefficient of selectivity were the highest, whereas the CS100 membrane showed worse properties, and both separation coefficients were almost 6 times lower than for the CS600 membrane. For the CS30 membrane, the ideal selectivity coefficient was < 1, data that indicate a lack of material selectivity for water molecules. On the other hand, for a mixture this value increased more than 10 times; in other words, during the vapour permeation process, there were strong interactions between the molecules and membrane material [33].

Similar values of the ideal and practical selectivity coefficient for the CS600 and CS100 membranes would mean that the water and ethanol particles do not interact with the membrane material or that the material structure is more responsible for its separation capacity. The differences between water and ethanol fluxes obtained for the prepared chitosan membranes in vapour permeation of pure solvents as well as the ethanol mixture were small; however, there were clear differences in the selectivity coefficients from the different transport properties. Membrane transport parameters calculated for pure solvents and the separated mixture are presented in Table 3.

Table 3. Transport coefficients calculated for water and ethanol from pure solvent and 50% v/v ethanol solution for membranes prepared from different chitosans.

		$P \cdot 10^7$ [$cm^3_{STP} \cdot cm/cm^2 \cdot s \cdot cmHg$]		$D \cdot 10^{11}$ [cm^2/s]		S [$cm^3_{STP}/cm^3 \cdot cmHg$]	
Membrane	Solution	Water	Ethanol	Water	Ethanol	Water	Ethanol
CS600	Pure solvents	29.29	2.52	3,892	670	75.27	38.61
	50% ethanol	12.68	1.06	17.83	9.27	7,107	1,184
CS30	Pure solvents	11.57	13.62	17,822	17,187	6.49	7.92
	50% ethanol	11.37	1.22	11.99	11.37	9,848	1,402
CS100	Pure solvents	15.32	9.73	13,368	5,008	11.46	19.43
	50% ethanol	5.26	2.46	17.03	7.47	3,087	3,286

The observed decrease in the values of water and ethanol permeability coefficients for the mixture compared with pure solvents coincides with the tendency obtained for permeate streams and the decrease in permeability results from the interaction between water and alcohol. The observed differences in the diffusivity and sorption of water and ethanol translate into the separation capacity of the obtained membranes due to the properties of the materials.

The difference in the hydrophilic and hydrophobic properties between the upper and lower surfaces of the membrane contributed to the observed results. The low value of ideal selectivity coefficient obtained for the CS30 membrane was associated with the similar hydrophilicity of both membrane sides. Due to the homogeneity of the material, the diffusion and solubility coefficients for pure water and ethanol solvents were similar, and the membrane presented a lack selectivity. On the other hand, when 50% v/v ethanol solution was used in the vapour permeation process, there was a more pronounced

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difference between the water and ethanol solubility coefficient and thus an elevated membrane separation coefficient. Furthermore, the slight difference between the water and ethanol diffusion coefficients means that the sorption stage plays a key role in the separation process on membrane from chitosan CS30.

Membranes obtained from chitosan CS100 and CS600 had variable hydrophilic and hydrophobic surface properties, a factor that could have influenced on obtained values of the ideal selectivity coefficient.

For the CS100 membrane, where the more hydrophilic side had contact with vapours, the water solubility coefficient was almost two times lower than that of ethanol. Moreover, the less hydrophilic side of the membrane could make ethanol diffusion in the membrane easier, but the determined ethanol diffusion coefficient was almost half the value for water. During the ethanol mixture vapour permeation, similar to CS30 membrane, the transport properties changed. Contrary to suppositions, the membrane did not show differences in sorption, and there were similar values of solubility coefficients for water and ethanol. The material selectivity coefficient only depended on differences between mixture component diffusion coefficients. Hence, the main stage of the separation process for the CS100 chitosan membrane was the diffusion step.

Contrary to the CS100 membrane, the less hydrophilic side of the CS600 membrane was directed inside the vessel and had contact with solvent vapours. Solubility and diffusion coefficients obtained for the CS600 membrane were higher for water than ethanol; this result was the same for pure solvents and the ethanol mixture, although during the mixture vapour permeation process, the balance between water and ethanol solubility and diffusion coefficients was reversed. The values of the ideal and practical selectivity coefficient obtained for the CS600 membrane were similar despite the changes in the transport parameter shares. These data suggest that both sorption and diffusion did not affect separation properties of CS600 membrane.

Different transport and separation results obtained for the prepared membranes depended on membrane properties, which were correlated with chitosan molecular weight and degree of deacetylation. The influence of chitosan features on water and ethanol flux as well as selectivity coefficient are presented in Figs. 5 and 6, respectively.

The chitosan molecular weight slightly affected values of water or ethanol permeate fluxes, while the chitosan degree of deacetylation influenced both. Moreover, an increase

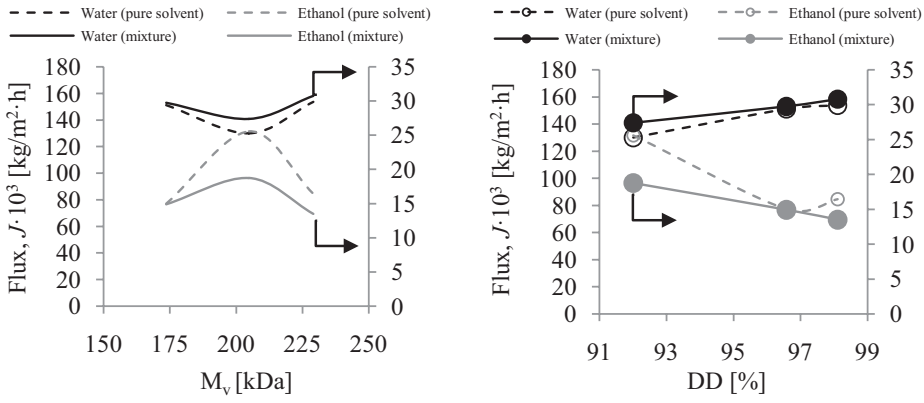

Figure 5. The effect of chitosan (A) molecular weight (M_v) and (B) degree of deacetylation (DD) on water and ethanol permeate fluxes.

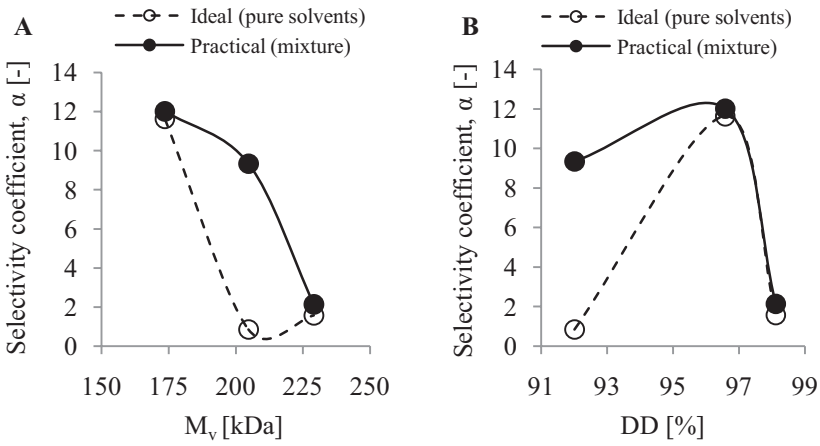

Figure 6. The effect of chitosan (A) molecular weight (M_v) and (B) degree of deacetylation (DD) on membrane selectivity coefficient.

in the chitosan degree of deacetylation caused a greater difference between water and ethanol fluxes, which had a positive effect on the separation process. However, for membranes prepared from chitosan with a degree of deacetylation < 96%, there was no difference between the fluxes obtained for pure solvents. A similar effect was observed for separation properties for membranes prepared with chitosan with a degree of deacetylation < 96%; the membrane material presented a better practical than ideal selectivity coefficient. On the other hand, for chitosan with a degree of deacetylation > 96%, the selectivity coefficient remained unchanged, although membrane transport coefficients were altered. This outcome also means that it was easier to predict the separation properties of membranes made by chitosan with a high degree of deacetylation. In addition, the selectivity coefficient showed a strong dependence on chitosan molecular weight and decreased with increasing polymer chain length.

4. Conclusion

In this paper, membranes prepared from chitosan with different molecular weights and degrees of deacetylation were obtained. The influenced of these chitosan features on the prepared membranes' physicochemical and separation properties in the vapour permeation process was studied. Despite the small difference in molecular weight and the degree of deacetylation, the obtained membranes had quite different physicochemical and separation properties. Molecular weight and degree of deacetylation affected sorption properties of the chitosan materials. Membrane surface properties mainly depended on chitosan molecular weight and were more hydrophilic when polymer chains were longer. The tensile strength was the highest for chitosan with low molecular weight (CS600) due to the dense structure of the obtained membrane. The CS100 chitosan membrane, with the highest degree of deacetylation as well as molecular weight, had the greatest elongation value. The obtained membranes presented various transport properties that were related to the structure of the obtained membranes. The membranes that showed different properties on each side (CS600 and CS100) had similar ideal and practical selectivity coefficients; however, their transport parameters changed depending on whether pure solvents or an ethanol mixture was tested in the vapour permeation process.

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By contrast, for the CS30 membrane, where both sides had a similar contact angle, the ideal and practical selectivity coefficients as well as transport parameters depended on the utilized solution. Moreover, an increase in the chitosan degree of deacetylation reduced ethanol and improved water permeate flux. The selectivity coefficient decreased with an increase in the chitosan molecular weight.

5. Acknowledgements

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