INFLUENCE OF INITIAL STATE OF CHITOSAN MEMBRANES ON THEIR SEPARATION PROPERTIES IN PERVAPORATIVE DEHYDRATION

Małgorzata Gnus

The Łukasiewicz Research Network – Institute for Engineering of Polymer Materials and Dyes, M. Sklodowska-Curie 55 Street, 87-100 Toruń, Poland
ORCID: 0000-0002-1066-4412

corresponding author: malgorzata.gnus@impib.lukasiewicz.gov.pl

Abstract

In this study, membranes from chitosan with different molecular weights (175-230 kDa) and degree of deacetylation (92%-98%) were prepared and dehydration of a ethanol-water azeotropic mixture by pervaporation on membranes in the swollen and dry initial state was investigated. The influence of chitosan characteristics and the effect of the initial membrane state on separation properties are discussed. The structure of the obtained membranes changed during the drying process and affected the membrane transport parameters and time to membrane stabilisation. The impact of chitosan characteristics on the transport parameters depended on the initial membrane state. The chitosan molecular weight influenced ethanol transport, whereas the chitosan degree of deacetylation affected water transport. In addition, chitosan with the lowest molecular weight improved the separation properties of the membranes.

Keywords: *Chitosan, membrane initial state, pervaporation, ethanol dehydration, transport parameters*

1. Introduction

Pervaporation is a separation technique that allows dehydration of organic solvents without the use of toxic and environmentally unfriendly azeotropic substances. The separation process is based on a solution-diffusion mechanism divided into the selective dissolution of one of the components of the separating mixture in a non-porous material and its transport to the other side of the membrane. The effectiveness of the dehydration process directly depends on the properties of the used material and the process conditions. Currently, polymer membranes based on polyvinyl alcohol are used in industrial-scale pervaporation. However, polysaccharide polymers like chitosan or alginate are gaining more and more attention as potential membrane materials.

Chitosan is a natural polymer obtained in the process of chitin deacetylation. Products with different molecular weights and degrees of deacetylation (DD) are obtained depending on the source of chitin and the deacetylation parameters. Chitosan has a very high affinity for water, although it is not soluble in pure water. This makes it possible to use it as a membrane material without interfering with the polymer structure. Unfortunately, due to its affinity for water, chitosan exhibits a high degree of swelling in solutions with a high water concentration. When it swells, the separation properties of membranes made from chitosan deteriorate. On the other hand, distillation produces a solution containing at least 80% ethanol [1], which effectively limits the degree of swelling of the material in pervaporation and allows testing pristine chitosan membranes and determining the impact of molecular weight and DD on polymer physicochemical properties [2-6].

During pervaporation, the membrane material is washed by the circulating feed and swells, which affects its structure and transport parameters. Theoretically, the material should, regardless of its initial state (i.e., dry or swollen), show the same separation properties when transport equilibrium is established. There is no information about the condition of the chitosan membrane placed in the membrane module and the influence of the membrane's initial state on its separation properties in the ethanol dehydration process. Chitosan membranes become rigid and corrugated after drying, making their placement in the membrane module difficult. On the other hand, chitosan material stored in distilled water is flexible and could be easily placed in the membrane chamber, but their degradation is faster than for membranes stored in a dry state [7, 8]. Differences in the mechanical properties presented by wet and dry chitosan films [2, 4, 5, 9, 10] suggest that storing the initial membrane in a separate liquid could influence its separation properties.

In this study, membranes were made from chitosan with different molecular weights and DD. The ability of swollen and dry membranes to remove ethanol by pervaporation was investigated. The influences of chitosan molecular weight and DD as well as the initial membrane state on the separation process are discussed.

2. Materials and Methods

2.1. Materials

The following chemicals were used: chitosan CS600 (Acros Organics, M_η = 175,000 Da, DD = 96.58%), chitosan CS30 (BioLog, M_η = 205,000 Da, DD = 92.01%), chitosan CS100 (Acros Organics, M_η = 229,000 Da, DD = 98.11%), sodium hydroxide (pure, POCh, Poland), acetic acid (glacial, POCh, Poland), ethanol (technical grade), and ethanol (96%, pure for analysis, POCh). All materials were used without purification.

2.2. Membrane Preparation

Membranes were prepared according to the method described in previous work [11]. First, 1.5 wt.% chitosan in 1 vol.% acetic acid solution was cast onto a glass Petri dish and

dried at 40°C. Then, 2 wt.% sodium hydroxide solution was added to the polymer film and incubated for 1 h. Next, the material was washed with distilled water until it reached a neutral pH.

The prepared membranes were divided into two groups. In the first group, the membranes were stored in distilled water. In the second group, the membranes were placed in technical-grade ethanol for 1 min and after shrinkage, the material was placed on a disc (7 cm in diameter disc), which limited its further shrinkage during drying. The membrane with the disc was covered to slow down the drying process. Drying was carried out at room temperature.

The thickness of each membrane was measured by waterproof precise ELMETRON MG-401 coating thickness gauge at 20 different sites. The average of these readings was calculated.

2.3. Material Characterisation

Physicochemical parameters of membranes – tensile strength, contact angle, and the degree of swelling – have been described extensively in previous work [11]. In the present work, the focus was on the degree of swelling in the ethanol-water azeotropic mixture which was subjected to dehydration.

The membranes prepared from different chitosan were weighed before and after their immersion in 96% ethanol for 24 h. The degree of swelling was calculated based on the weight difference between wet and dry membranes with Equation (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].

2.4. Ethanol Dehydration

2.4.1. Pervaporation

Membranes used for pervaporation were stored in two different forms, namely swollen in deionised water and dry. Membranes kept in deionised water were immersed in ethanol for 1 min, and after they shrank, they were placed in a stainless steel membrane chamber. On the other hand, dry materials were placed directly into the membrane cell. A separate mixture (96% ethanol) was introduced into the feed tank and transported by a circulation pump to the membrane module, where the solution washed one side of the membrane and the separation process took place. The component that was retained by the membrane (retentate) was returned via a line to the feed tank while substances transported across the membrane (permeate) were collected in cooling traps. The pressure was reduced on the permeate side by utilising a vacuum pump; the pressure was controlled by a vacuum gauge. Experiments were performed at room temperature on a membrane chamber with an effective membrane area of 6.91 cm^2.

The composition of the feed, as well as permeate samples, was measured by gas chromatography. Measurements were performed on an Agilent Technologies GC 6850 instrument equipped with an EliteWAX column and a flame ionisation detector.

2.4.2. Separation and Transport Parameter Evaluation

The pervaporation separation performance was evaluated based on the flux, separation factor, selectivity coefficient, pervaporation separation index and permeability, and diffusion and solubility coefficients.

The flux (*J*) was calculated with Equation (2):

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

(2)

where: *m* is the mass of the permeate [kg], *A* is the effective membrane area [m²], and *t* is the evaluation time [h].

The separation factor (*α*) was calculated with Equation (3):

$$\beta = \frac{x_A / x_B}{y_A / y_B}$$

(3)

where x_i and y_i (*i* = A, B) are the concentrations of component *i* in the permeate and feed [wt.%], respectively, and subscripts *A* and *B* refer to water and ethanol, respectively.

The selectivity coefficient was calculated with Equation (4):

$$\alpha = \frac{P_A}{P_B}$$

(4)

where P_A and P_B are permeability of water and ethanol, respectively. The methodology used to calculate permeability, diffusion, and the solubility coefficient have been described previously [12].

The pervaporation separation index (PSI) was calculated with Equation (5):

$$PSI = J(\beta - 1) \left[\frac{kg}{m^2 \cdot h} \right]$$

(5)

3. Results and Discussion

3.1. Degree of Swelling in Ethanol-Water Azeotropic Mixture

The influence of the chitosan DD and average viscosity molecular weight on the swelling of obtained membranes in the ethanol azeotropic mixture is shown in Figure 1A and B, respectively. The degree of swelling increased almost linearly with the increase in the DD, which is similar to results obtained for pure ethanol [11]. This is due to the chitosan structure in solution and its intermolecular and intramolecular interactions [13, 14], which facilitates ethanol penetration across the membrane. Furthermore, there was greater swelling in the ethanol azeotropic mixture than for pure ethanol, which is related to the presence of water in the examined solution, which in itself causes significant swelling of the chitosan membranes [11].
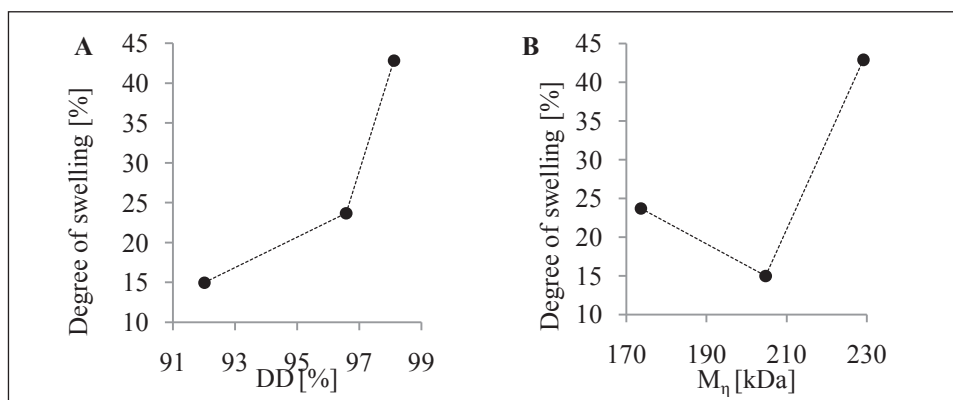
Figure 1. Influence of the chitosan degree of deacetylation (A) and average viscosity molecular weight (B) on chitosan membrane degree of swelling in 96% ethanol solution.

The relationship between the degree of swelling and chitosan molecular weight was not linear (Figure 1B), but it is similar to results obtained for membranes immersed in pure ethanol [11]. Among the tested membranes, CS100 had the highest degree of swelling for both the ethanol azeotropic mixture in this study and pure ethanol in a previous study [11]. Such a property is undesirable when prepared membranes are intended to be applied in the ethanol dehydration process because high membrane swelling adversely affects their separation capacity. CS100, with the longest polymer chains and highest DD, facilitated the formation of porous structures and thus made the chitosan membrane swell more in the ethanol azeotropic mixture. On the other hand, the lower degree of swelling of the membrane made with CS30 is related to its relatively low DD, which affects the polymer structure and makes it more of a barrier for the ethanol azeotropic mixture.

The significant swelling of chitosan membranes in water shows their high affinity to water molecules, which is desirable in the membrane dehydration process, but excessive swelling influences the density and affects membrane separation properties. However, in ethanol-water pervaporation, the ethanol concentration in the separated mixture was high; therefore, membrane behaviour in 96% and pure ethanol is more important.

3.2. Separation Properties

From the three characterised chitosan materials, two series of membranes with different states before being placed in the membrane chamber were prepared. The first series consisted of membranes that, after being removed from the Petri dishes, were placed in deionised water and, before being placed in the apparatus, were immersed in ethanol. The second series contained analogous dry membranes which were directly placed in the membrane module. As can be seen from the results presented in Table 1, both the type of chitosan and the initial state of the membrane affect the transport and separation properties of chitosan membranes.

Table 1. Parameters obtained for three kinds of chitosan membranes in different initial states.

| Chitosan	Initial membrane state	d^a [μm]	J [kg/ m²·h]	β [-]	α [-]	PSI [kg/m²·h]
CS600	Wet	21.0 ± 2.0	1.70	1.10	1.52	0.17
	Dry	23.6 ± 2.1	3.23	2.37	2.62	4.41
CS30	Wet	21.4 ± 2.1	4.74	1.56	3.38	2.65
	Dry	26.3 ± 2.4	6.91	0.78	2.74	-1.49
CS100	Wet	20.6 ± 0.7	3.59	1.65	3.33	2.33
	Dry	30.2 ± 2.6	5.24	1.04	2.39	0.19

Note. ª Thickness of dried membranes after pervaporation.

The polymer structure of chitosan has three kinds of water: free water, not bound with polymer chain, freezable bound water, and bound water which remains in the polymer even after drying [15]. When the chitosan membrane was immersed in the ethanol solution, water molecules were partially removed from the polymer matrix. However, the remaining water plasticises the structure of the material and improves ethanol transport across the membrane during pervaporation. Therefore, a high ethanol content in the permeate and low separation factors were obtained. An increase in the polymer chain length increased both the membrane degree of swelling in water and the separation factor.

On the other hand, when pervaporation was carried out on dry membranes, material swelled when the feed began to circulate between the tank and the membrane chamber. Despite the increase in the swelling ratio in ethanol as the chitosan DD increased, the separation factor was highest for chitosan with the lowest molecular weight, probably due to the dense structure of the obtained membrane. Furthermore, permeate flux increased as the chitosan molecular weight increased, but for chitosan CS30, the greater number of acetyl groups in the polymer chain facilitates transport of alcohol through the membrane. Hence, the membrane made with CS40 had the greatest flux but the separation factor was <1.

Surprisingly, fluxes obtained for dry chitosan membranes were higher than for wet ones, despite the fact that transport of feed components across swelled membranes should be easier. To determine the reason for this phenomenon, diagrams of the permeate mass dependence on the duration of pervaporation were obtained (Figure 2).
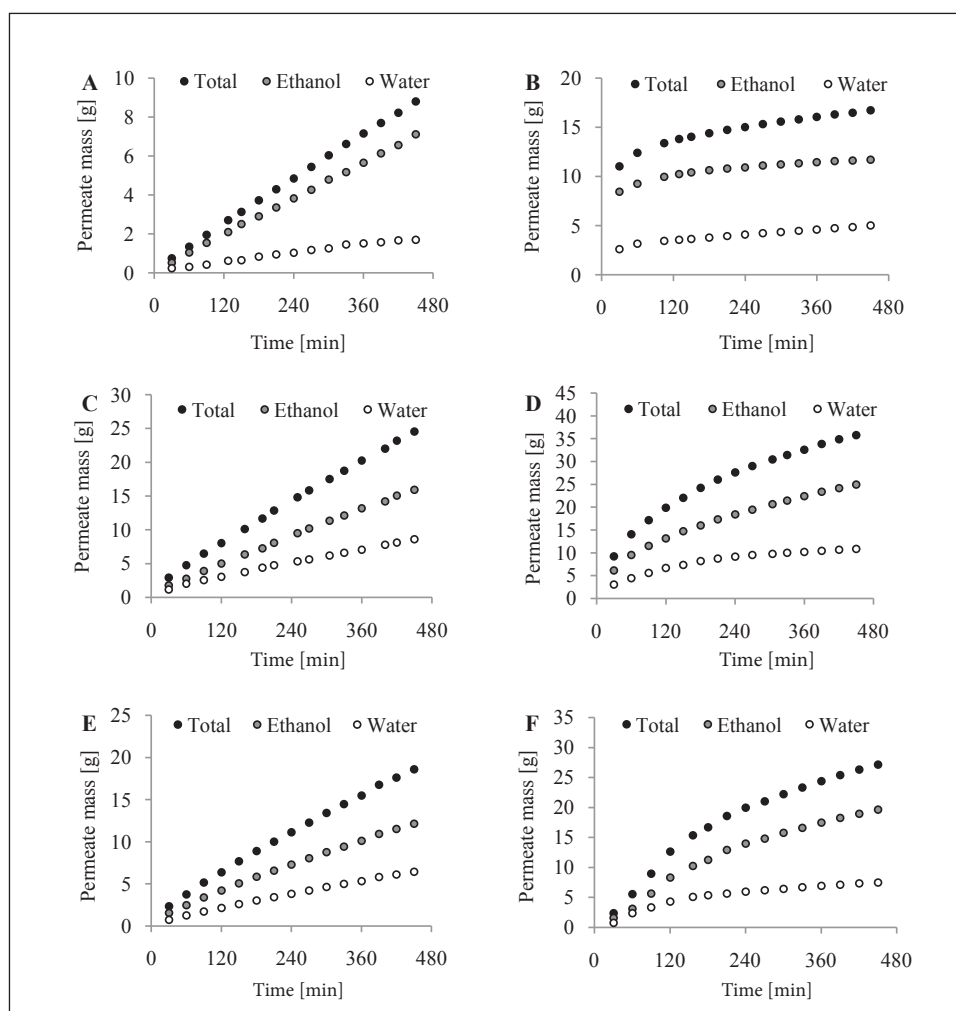
Figure 2. Relationship between the total permeate mass and pervaporation time with the participation of water and ethanol in permeate for membranes prepared from chitosan CS600 (A and B), CS30 (C and D), and CS100 (E and F). The graphs on the left side present measurements carried out on wet membranes, while the graphs on the right side present measurements obtained on dry membranes.

The course of the curves varied significantly depending on the initial state of the membrane. Wet chitosan membranes were stable from the beginning of the process because the content of water and ethanol in the permeate increased linearly, whereas for dry chitosan membranes, the curves were not linear and their course depended on the type of chitosan used. For the dry membrane prepared from CS600, during the first 30 min of measurement, there was a rapid increase in permeate mass. However, when the chitosan molecular weight increased, the mass of the first collected permeate sample decreased. For the CS100 membrane, the mass of the first permeate sample was similarly independent of the initial membrane state. Despite a high mass of the first permeate sample, the next permeate samples were decreased, a phenomenon associated with the membrane swelling process. Because the dry membrane was less of a barrier than the swollen membrane, the structure of the used material changed during the drying process.
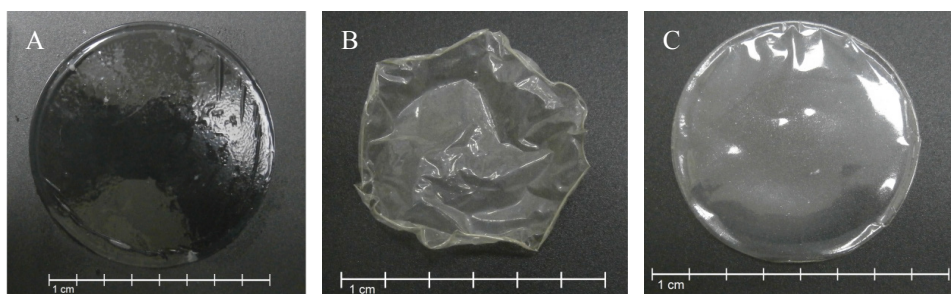
In non-cross-linked chitosan membranes stored in water, the polymer chains are loosely arranged and interconnected by hydrogen bonds (Figure 3B). Only a portion of the water that penetrates the structure is bound to the polymer chain. Such a spatial structure allows for relatively free diffusion of solvent molecules. When the chitosan membrane is dried in a standard way – by leaving the material to evaporate the solvent without additional interference – the material gradually gives away unbound and then weakly polymer-bound water molecules to the environment. When the water content decreases, the volume of the material begins to decrease and the distance between the polymer chains and simultaneous spatial reorganisation of polymer chains takes place (Figure 3A).
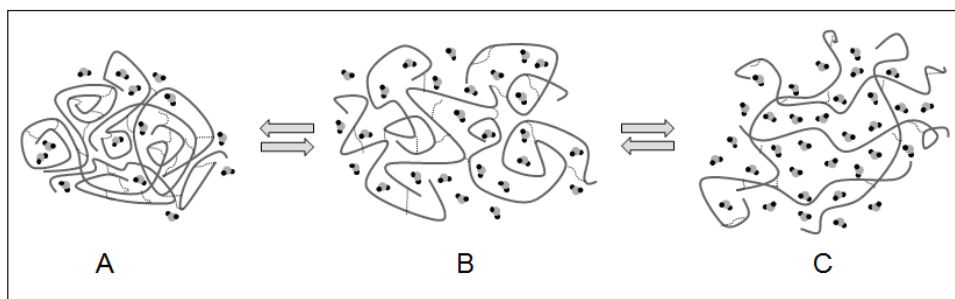
Figure 3. Schematic representation of the state of the polymer membrane network: dry membrane – dried in the standard way (A), swollen – wet (B), and dry – with reduced shrinkage (C).

The chains assume the location of hydroxyl groups, which facilitate the formation of hydrogen bonds with water molecules remaining in the membrane. If this kind of material were immersed in a concentrated alcohol solution, then its swelling would be limited not only by the low water content in the solution but also by intermolecular and intramolecular interactions between polymer chains. In effect, low permeability or lack of membrane transport could be observed. Unfortunately, the materials obtained in this way were not flat films, did not have a uniform thickness over the entire surface, and the surface area was reduced by >60%; therefore, they could not be used in the research (Figure 4B).

Drying the material in the implemented way significantly reduced the shrinkage of the material. The membrane area surface was reduced up to 40%, was flat, and had a much more uniform thickness than the membrane dried in the standard way (Figure 4C). During drying, the membrane could not contract freely in the preferred directions. To neutralise the stress arising in the membrane, polymer chains began stretching and straightening,

98 *Progress on Chemistry and Application of Chitin and its Derivatives, Volume XXVII, 2022, https://doi.org/10.15259/PCACD.27.007*

Figure 4. Photograph of CS600 chitosan membrane in the wet state (A), the dry state, dried in the standard way (B), and the dry state based on the procedure implemented in this study (C).

which causes the creation of free spaces in the polymer matrix, as shown in Figure 3C. If such a membrane is in contact with the ethanol-water azeotropic mixture, where there is relatively little water, the swelling process allows restoring the optimal structure before drying. The open structure with free spaces allows easy penetration of both components of the azeotropic mixture; therefore, at the beginning of the process, the membrane is not selective, and the composition of the permeate collected is similar to the feed composition. Continuing the process causes loosening of the polymer chains, which are stretched during drying. Greater mobility of the chains enables the re-formation of intermolecular and intramolecular hydrogen bonds and the permeate stream begins to gradually decrease until it becomes established and remains at a similar level.

The obtained result diverges from the literature data on the beneficial effect of loosening polymer chains on the permeability of membrane material [16-23]. However, in the present work dry membrane material had larger spaces between the chains than swollen membrane. In addition, just like the shrinkage of the material during drying was reduced, that small space in the membrane module limited material swelling; hence, there was a decrease in membrane permeability. Although the flux obtained during the 7.5 h measurement for the dry membrane was higher than for the wet membrane, the course of the permeate mass curves for both types of membranes allows us to conclude that if the process was carried out for a long enough time, then the permeate flux obtained for the wet membrane would be higher than for a dry membrane.

The time it would take for the permeate flux of wet membranes to be higher than for dry membranes depends on the chitosan used to form the polymer matrix. The time values, determined for individual chitosan membranes, are presented in Figure 5. The time in which the permeate mass growth curves for the wet and dry membranes intersect increased as the chitosan molecular weight increased. The times were 1191 min for CS600, 1302 min for CS30, and 2712 min for CS100.

Another important difference between wet and dry membranes is the time needed to stabilise membrane transport parameters (Figure 6). As mentioned previously, the wet membrane transport parameters were stable from the beginning of the process, but when each permeate sample was analysed, it turned out that for the CS600 and CS30 membranes, water and ethanol transport were not stable. Furthermore, after subjecting the CS600 membrane to six samples, the water content decreased when the ethanol content in the permeate sample increased and vice versa. On the other hand, for the CS30 membrane, both ethanol and water content in permeate samples increased or decreased simultaneously. This suggests that for the CS30 membrane, ethanol and water transport were associated
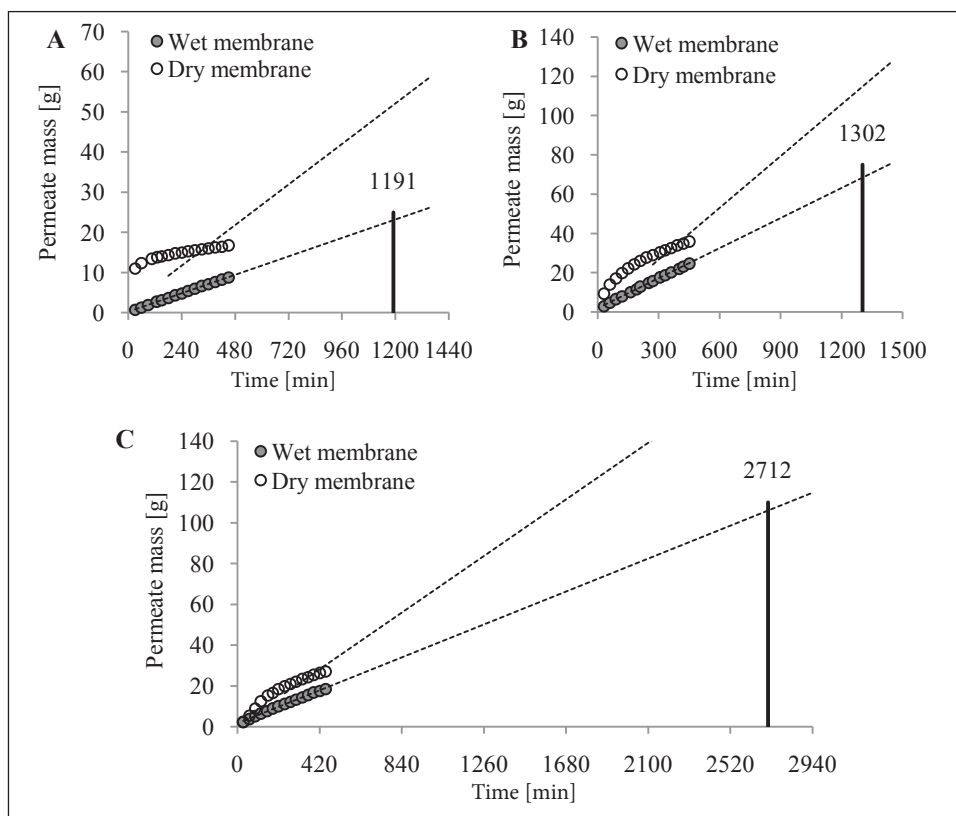
Figure 5. The time after which the permeate flux obtained for the wet membrane would exceed the permeate flux obtained for the dry membrane. The points of intersection are an extension of the straight lines of mass increment for empirically determined points. The graphs show the relationship between the wet and dry membranes prepared from chitosan CS600 (A), CS30 (B), and CS100 (C).

more strongly than in the CS600 membrane. On the other hand, the CS100 membrane was stable after the first collected permeate sample.

For dry chitosan membranes, differences in membrane stabilisation time were clearer and equal at 3 h for the CS600 membrane and at 4 h for both the CS30 and CS100 membranes. However, there was a linear decrease in the content of both components in consecutive permeate samples for the CS30 membrane (Figure 6D). This was the result of a low water concentration in the separated mixture and membrane low degree of swelling in ethanol.

The transport of feed components through the CS600 membrane during the first phase of the process was large and despite a low water concentration in the separated mixture, the membrane swelled and after 3 h of stabilisation, transport parameters were observed. However, it was only for water molecules because the ethanol content in the permeate samples decreased during pervaporation (Figure 6B). The obtained result was similar to the wet CS600 membrane, meaning that ethanol transport was not strongly associated with water molecules. Moreover, after 6.5 h, the water content in the permeate sample was higher than ethanol and the membrane separation properties had improved.
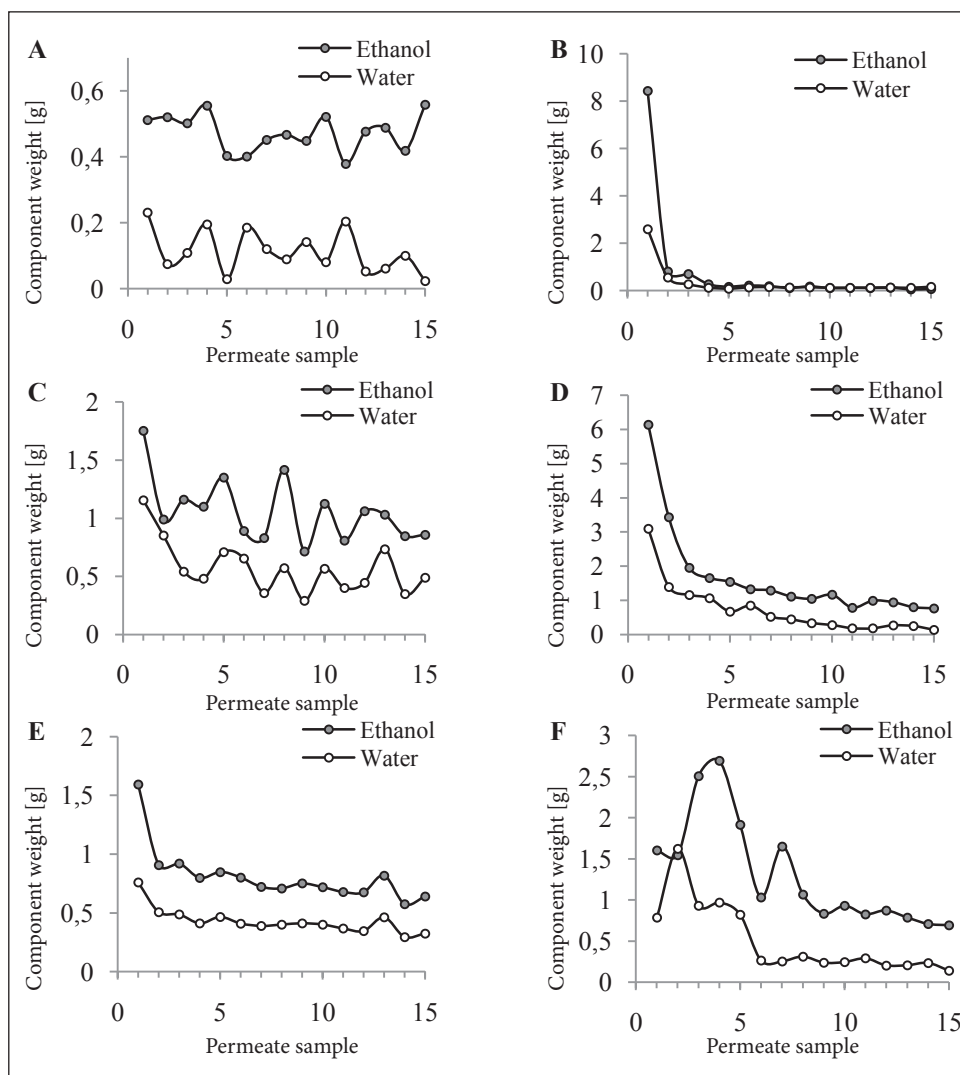
Figure 6. Composition of the collected permeate samples obtained for membranes prepared from chitosan CS600 (A and B), CS30 (C and D), and CS100 (E and F). The graphs on the left side present measurements carried out on wet membranes, while the graphs on the right side present measurements carried out on dry ones.

The dry CS100 membrane had the lowest permeability during the first phase because free spaces created during controlled drying of longer polymer chains were less effective, so the transport through such material was lower. On the other hand, swelling of the membrane in contact with the azeotropic mixture was difficult and required more time; therefore, the membrane stabilisation time was longer than for the wet CS100 membrane.

The transport parameters obtained for initially wet membranes differed from those obtained for initially dry ones (Table 2). For all chitosan membranes, the water permeability coefficient was higher than the ethanol permeability coefficient and reached higher values if the membrane was initially dry.

Wet chitosan membranes showed higher water solubility coefficients, whereas diffusion coefficients of individual components decreased as the chitosan molecular weight increased. The obtained values of diffusion coefficients for water were lower than for ethanol because water molecules saturated membranes before pervaporation and the chitosan matrix could not bind more water molecules from the feed solution. There was a lower water diffusion coefficient, a smaller plasticising effect, and greater membrane separation properties. Independently of the chitosan molecular weight, the sorption stage had the greatest impact on the selectivity coefficient for wet membranes. However, an increase in the chitosan molecular weight reduced the ethanol diffusion coefficient, which further improved the membrane separation properties.

Table 2. Transport parameters obtained for chitosan membranes in the initially wet and dry states.

		Chitosan					
		CS600		CS30		CS100	
	Transport parameter	**Water**	**EtOH**	**Water**	**EtOH**	**Water**	**EtOH**
Wet	Permeability coefficient, $P \cdot 10^6$ [cm$^3_{STP}$·cm/ cm^2·s·cmHg]	11.98	78.57	43.54	12.88	32.80	9.83
	Diffusion coefficient, $D \cdot 10^{11}$ [cm^2/s]	68.00	313.88	39.43	80.07	43.97	38.00
	Solubility coefficient, $S \cdot 10^{-4}$ [cm$^3_{STP}$/cm^3·cmHg]	1.76	0.25	11.04	1.61	7.47	2.59
Dry	Permeability coefficient, $P \cdot 10^6$ [cm$^3_{STP}$·cm/ cm^2·s·cmHg]	28.68	10.97	63,46	23.17	49.20	20.56
	Diffusion coefficient, $D \cdot 10^{11}$ [cm^2/s]	4.50	1.42	3.79	10.31	10.49	17.54
	Solubility coefficient, $S \cdot 10^{-4}$ [cm$^3_{STP}$/cm^3·cmHg]	63.72	76.88	167.13	22.46	46.90	11.72

Note. EtOH – ethanol.

The results for dry membranes showed that the selectivity of higher molecular weight chitosan (the CS30 and CS100 membranes) depends on the sorption stage. For the CS30 and CS100 membranes, the high value of the water solubility coefficient facilitates penetration of water molecules into the membrane material. Water acts as a polymer plasticiser that facilitates the diffusion of water as well as ethanol molecules. In the initial phase of pervaporation, the dry membrane 'supplements water deficiencies' by binding its molecules to the polymer chain and low water diffusion coefficient values were observed. Moreover, the ethanol diffusion coefficient increases as the chitosan molecular weight increases, which coincides with the ethanol swelling capacity exhibited by these materials.

In contrast to CS30 and CS100 membranes, the initial state of the CS600 membrane affected the membrane separation mechanism. In the case of the dry CS600 membrane, the process selectivity was determined by the diffusion stage. The dense membrane structure and low water content in the feed solution limit chitosan swelling. Therefore, water molecules that penetrated the membrane do not plasticise it enough to facilitate the transport of ethanol. Furthermore, a higher ethanol solubility coefficient allows the membrane to swell in a separated azeotropic mixture. In general, for dry chitosan

membranes the water solubility coefficient decreases as the chitosan DD increases. On the other hand, the ethanol solubility coefficient decreases as the chitosan molecular weight increases.

4. Conclusion

Based on the results presented in this article, the chitosan molecular weight and DD as well as the initial state of the membrane influence the separation properties of the chitosan membrane materials. The molecular weight has a greater effect on membrane swelling behaviour in water, whereas the DD influences membrane swelling in ethanol. However, the influence of molecular weight and DD on separation properties depends on the initial membrane state.

The initial state of the membrane influences the course of the permeate mass increment curves during pervaporation. The applied drying process of the membranes creates a space between the polymer chains and increases the permeability of the material at the beginning of the dewatering process. Based on the course of the permeate mass increase curves over time, it is possible to separate the conditioning stage during which swelling and relaxation of the polymer matrix take place and the stage in which the process parameters are stabilised. In the case of wet membranes, for which the permeate mass increment is linear over time, there is no conditioning step because the membranes are placed in the module in a swollen form. For wet membranes, the adsorption stage had the greatest impact on the selectivity coefficient, but an increase of chitosan molecular weight reduced the ethanol diffusion coefficient, which also improved the membrane separation properties.

The structure of chitosan membranes changed during the drying process, which increased the time of membrane transport stabilisation; however, water and ethanol content fluctuations in permeate were much lower than for membranes in a wet initial state. In addition, for dry chitosan membranes, the water solubility coefficient decreased when the chitosan DD increased, whereas the ethanol solubility coefficient decreased when the chitosan molecular weight increased. Moreover, the drying process of the CS600 membrane (made with the lowest molecular weight chitosan) changed the membrane separation mechanism and improved the membrane separation factor and selectivity coefficient.

The dry chitosan membranes showed better separation properties, which, unlike wet membranes, swelled under the influence of water present in the separated mixture. The dry CS600 membrane had the best properties, showing both the highest values of the separation coefficient and the pervaporative separation index among all the prepared membranes.

5. Acknowledgements

6. References

[1]   Rakoczy J, Kupiec K, Larwa T; (2008) Dehydration of distillery spirit to obtain fuel bioethanol. Czas Tech 105 1-Ch, 115-124.
[2]   Hwang KT, Kim JT, Jung ST, Cho GS, Park HJ; (2003) Properties of chitosan-based biopolymer films with various degrees of deacetylation and molecular weights. J Appl Polym Sci 89, 3476-3484. **DOI**:10.1002/app.12561
[3]   Hsu SH, Whu SW, Tsai CL, Wu YH, Chen HW, Hsieh KH; (2004) Chitosan as scaffold materials: effects of molecular weight and degree of deacetylation. J Polym Re 11, 141-147. **DOI**:10.1023/B:JPOL.0000031080.70010.0b

[4] Cao W, Jing D, Li J, Gong Y, Zhao N, Zhang X; (2005) Effects of the degree of deacetylation on the physicochemical properties and Schwann cell affinity of chitosan films. J Biomater Appl 20, 157-177. **DOI**:10.1177/0885328205049897

[5] Foster LJR, Ho S, Hook J, Basuki M, Marçal H; (2015) Chitosan as a biomaterial: Influence of degree of deacetylation on its physiochemical, material and biological properties, PLoS One 10, e0135153. **DOI**:10.1371/journal.pone.0135153

[6] Chen RH, Hwa HD; (1996) Effect of molecular weight of chitosan with the same degree of deacetylation on the thermal, mechanical, and permeability properties of the prepared membrane. Carbohydr Polym 29, 353-358. **DOI**:10.1016/S0144-8617(96)00007-0

[7] Kam HM, Khor E, Lim LY; (1999) Storage of partially deacetylated chitosan films. J Biomed Mater Res 48, 881-888. **DOI**:10.1002/(SICI)1097-4636(1999) 48:6<881::AID-JBM18>3.0.CO;2-2

[8] Szymańska E, Winnicka K; (2015) Stability of chitosan - a challenge for pharmaceutical and biomedical applications. Mar Drugs 13, 1819-1846. **DOI**:10.3390/md13041819

[9] Mima S, Miya M, Iwamoto R, Yoshikawa S; (1983) Highly deacetylated chitosan and its properties. J Appl Polym Sci 28, 1909-1917. **DOI**:10.1002/app.1983.070280607

[10] Chen RH, Lin JH, Yang MH; (1994) Relationships between the chain flexibilities of chitosan molecules and the physical properties of their casted films. Carbohydr Polym 24, 41-46. **DOI**:10.1016/0144-8617(94)90115-5

[11] Gnus M; (2020) Influence of chitosan molecular weight and degree of deacetylation on membrane physicochemical and separation properties in ethanol dehydration by the vapour permeation process. Prog Chem Appl Chitin Deriv 25, 79-93. **DOI**:10.15259/PCACD.25.006

[12] Gnus M, Dudek G, Turczyn R; (2018) The influence of filler type on the separation properties of mixed-matrix membranes. Chem Pap 72, 1095-1105. **DOI**:10.1007/ s11696-017-0363-9

[13] Qin C, Du Y, Zong L, Zeng F, Liu Y, Zhou B; (2003) Effect of hemicellulase on the molecular weight and structure of chitosan. Polym Degrad Stab 80, 435-441. **DOI**:10.1016/S0141-3910(03)00027-2

[14] Uragami T, Saito T, Miyata T; (2015) Pervaporative dehydration characteristics of an ethanol/water azeotrope through various chitosan membranes. Carbohydr Polym 120, 1-6. **DOI**:10.1016/j.carbpol.2014.11.032

[15] Ostrowska-Czubenko J, Pieróg M, Gierszewska-Drużyńska M; (2011) State of water in noncrosslinked and crosslinked hydrogel chitosan membranes–DSC studies. Prog Chem Appl Chitin Deriv 16, 147-156

[16] Li BB, Xu ZL, Alsalhy Qusay F, R. Li; (2006) Chitosan-poly (vinyl alcohol)/ poly (acrylonitrile) (CS-PVA/PAN) composite pervaporation membranes for the separation of ethanol-water solutions. Desalination 193, 171-181. **DOI**:10.1016/j. desal.2005.08.021

[17] Devi DA, Smitha B, Sridhar S, Aminabhavi TM; (2005) Pervaporation separation of isopropanol/water mixtures through crosslinked chitosan membranes. J Memb Sci 262, 91-99. **DOI**:10.1016/j.memsci.2005.03.051

[18] Uragami T, Matsuda T, Okuno H, Miyata T; (1994) Structure of chemically modified chitosan membranes and their characteristics of permeation and separation of aqueous ethanol solutions. J Memb Sci 88, 243-251. **DOI**:10.1016/0376-7388(94)87010-1

[19] Wang X, Shen Z, Zhang F; (1998) Pervaporation separation of water/alcohol mixtures through hydroxypropylated chitosan membranes. J Appl Polym Sci 69, 2035-2041. **DOI**:10.1002/(SICI)1097-4628(19980906)69:10<2035::AID-APP15>3.0.CO;2-0

[20]   Yang D, Li J, Jiang Z, Lu L, Chen X; (2009) Chitosan/TiO$_2$ nanocomposite pervaporation membranes for ethanol dehydration. Chem Eng Sci 64, 3130-3137. **DOI**:10.1016/j.ces.2009.03.042

[21]   Zhao Q, Qian J, An Q, Gao C, Gui Z, Jin H; (2009) Synthesis and characterization of soluble chitosan/sodium carboxymethyl cellulose polyelectrolyte complexes and the pervaporation dehydration of their homogeneous membranes. J Memb Sci 333, 68-78. **DOI**:10.1016/j.memsci.2009.02.001

[22]   Varghese JG, Kittur AA, Rachipudi PS, Kariduraganavar MY; (2010) Synthesis, characterization and pervaporation performance of chitosan-g-polyaniline membranes for the dehydration of isopropanol, J Memb Sci 364, 111-121. **DOI**:10.1016/j.memsci.2010.08.007

[23]   Sunitha K, Satyanarayana SV, Sridhar S; (2012) Phosphorylated chitosan membranes for the separation of ethanol – water mixtures by pervaporation. Carbohydr Polym. 87, 1569-1574. **DOI**:10.1016/j.carbpol.2011.09.054