VAPOUR PERMEATION STUDY OF WATER AND ETHANOL THROUGH CROSSLINKED CHITOSAN AND ALGINATE MEMBRANES

Roman Turczyn*, Małgorzata Gnus, Gabriela Dudek, Artur Tórz, Dorota Łącka, Anna Strzelewicz, Mieczysław Łapkowski

Faculty of Chemistry, Silesian University of Technology
ul. Akademicka 2A, 44-100 Gliwice, Poland
e-mail: roman.turczyn@polsl.pl

Abstract
A vapour permeation of water and ethanol through homogenous chitosan and alginate membranes was investigated. The influence of the polymer matrix and crosslinking agents, and measurement protocol on the transport properties were discussed. The conducted experiments showed the greater separation factor, better stability and resistant to solvents for chemically crosslinked membranes. On the other hand, stronger association of the matrix, than the physical, caused decrease of vapour fluxes.

Keywords – vapour permeation, chitosan, alginate, crosslinking agents

Received: 11.05.2015
Accepted: 03.06.2015
1. Introduction

Membrane separation is one of the most important separation techniques from the economic and environment safety point of view [1-4]. Vapour permeation can be treated as an interesting technical alternative to the pervaporation separation [5]. Feed mixture is in a vapour state, so the species just have to permeate through a non-porous permselective membrane. This technique allows to separate near-boiling point or azeotropic mixtures like in case of dehydration of ethanol. Many different types of membranes have been tested. Still new effort to obtain higher efficiency of ethanol/water separation [6-10]. This process is very common due to ethanol is one of the most important substances used in chemical industry, e.g. solvent, fuel and reagent [11].

In this paper, we focus on membranes prepared from naturally originated polymers – chitosan and alginate. Due to the excessive swelling in aqueous solutions, membranes prepared from these polymers posed a lack of mechanical strength and stability. This disadvantage could be overcome by chemical or physical crosslinking. We compare the properties of crosslinked alginate and chitosan membranes. The influence of crosslinking agent nature and crosslinking parameters are discussed based on the evaluated transport parameters, i.e. diffusion coefficient, permeation coefficient and solubility coefficient.

2. Materials and Methods

2.1 Preparation of membrane

All membranes were prepared by common solution casting and solvent evaporation technique [12-17]. The previously prepared 3 wt.% chitosan solution in 1 vol.% acetic acid was cast into a 16 cm diameter Petri dish and left until solvent evaporation at 40 °C. Next, chitosan membranes were immersed in a crosslinking solution, and subsequently washed with distilled water, immersed in 2 wt.% sodium hydroxide solution. After taken off, membranes were again washed with distilled water until neutral pH and dried at room temperature.

Alginate membranes were prepared in a similar manner. The previously prepared 1.5 wt.% sodium alginate solution was casted into a Petri dish and left until solvent evaporation at 37 °C. Next, alginate membranes were immersed into the solution of selected crosslinking agent for certain time, then washed with distilled water to clean off an excess of the crosslinking agent. In case of alginate membranes, ethanol were used to support the removal them from a Petri dish. Next, membranes were dried at room temperature. Details about crosslinking protocol for prepared membranes is gathered in Table 1.

2.2. Experimental setup for vapour permeation

To study the permeation of water and ethanol vapours through prepared membranes the special permeation vessel was applied. The investigated mixture (8.5 or 6 cm³) was placed into a top-opened, aluminium, cylindrical vessel presented in Fig. 1. The top of the cell (1) was covered with membrane (4 cm in diameter) (2) and hermetically fixed with a tightly screwed aluminium ring (3). Because the membranes are hydrophilic, to avoid the influence of the vapour
Table 1 Experimental parameters of the chitosan and alginate membranes crosslinking process.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Crosslinking agent</th>
<th>Time of crosslinking [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHSA</td>
<td>0.5 M sulphuric acid</td>
<td>30</td>
</tr>
<tr>
<td>CHGA</td>
<td>1.25 % glutaraldehyde solution</td>
<td>5</td>
</tr>
<tr>
<td>Alginate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALPA</td>
<td>3.5 % phosphoric acid in 90% isopropanol solution</td>
<td>120</td>
</tr>
<tr>
<td>ALCa</td>
<td>2.5 % calcium chloride solution</td>
<td>120</td>
</tr>
</tbody>
</table>

absorption on the air environment, the measuring vessel was placed into a desiccator. The flux of permeate was determined based on the estimated weight loss of the measuring vessel over time using analytical balance. The weight loss was measured in fixed time periods at room temperature. The measurements were performed for pure substances, i.e. distilled water and ethanol (p.a. 99.8 %), using six different membranes obtained from one large cast membrane. The determined fluxes were an average of six measurements.

Figure 1. Scheme of the measuring vessel: (1) – cylindrical body of the vessel; (2) – investigated membrane; (3) – fixing ring.

All measurements of vapour permeability for crosslinked chitosan membranes performed on the swollen membranes are labelled with "_A". In this case 8.5 cm$^3$ of given solvent was poured into measuring vessel placed into a desiccator. Measurements denoted with "_B" were performed using membranes without previous contact with liquid, and the measuring vessel were filled with 6 cm$^3$ of investigated solvent. During the measurement, desiccator was purged using dry air with flow rate of at least 50 cm$^3$/min. Water vapour permeation experiments labelled with "_C" were conducted like measurements labelled
"_B", excepting the membranes was previously used in ethanol vapour experiments.

2.3 Degree of swelling

The swelling test was determined by weight method. A specimen of membrane (4 cm²) was immersed in distilled water or ethanol for 24 h. Weight change of the analysed membranes was calculated based on the measurements carried out before and after swelling experiment, using analytical balance. Degree of swelling was calculated using following equation:

$$DS = \frac{W_S - W_D}{W_D} \cdot 100 \%$$  (1)

where: $W_S$ is the weight of the swollen membrane; $W_D$ is the weight of the dried membrane samples.

3. Results and Discussion

For investigation on the influence of polymer matrix and crosslinking agents on the vapour permeation of water and ethanol, four different membranes were prepared. Physically or chemically crosslinked chitosan and alginate were used as a material for membranes. Based on the values of the gathered transport parameters, vapour permeation properties of polysaccharide membranes were determined against pure water and ethanol, and crosslinking agent. The calculated parameters were collected in Table 2.

Table 2 Calculated transport characteristic of prepared chitosan and alginate membranes with different agents for pure water and ethanol.

<table>
<thead>
<tr>
<th></th>
<th>Diffusion coefficient, $D \cdot 10^{10}$ [cm²/s]</th>
<th>Solubility coefficient, $S \cdot 10^3$ [g/Pa·cm³]</th>
<th>Permeation coefficient, $P \cdot 10^{14}$ [g/Pa·cm·s]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2O$</td>
<td>EtOH</td>
<td>$H_2O$</td>
</tr>
<tr>
<td>CHSA_A</td>
<td>0.27±0.07</td>
<td>0.23±0.06</td>
<td>0.82±0.24</td>
</tr>
<tr>
<td>CHGA_A</td>
<td>5.43±0.63</td>
<td>2.98±0.29</td>
<td>0.41±0.03</td>
</tr>
<tr>
<td>CHGA_B</td>
<td>22.9±0.63</td>
<td>4.43±0.29</td>
<td>4.76±0.03</td>
</tr>
<tr>
<td>ALPA_B</td>
<td>5.10±0.82</td>
<td>3.57±0.17</td>
<td>2.12±0.35</td>
</tr>
<tr>
<td>ALCa_B</td>
<td>7.49±0.96</td>
<td>4.71±0.12</td>
<td>1.54±0.03</td>
</tr>
<tr>
<td>ALCa_C</td>
<td>4.13±0.38</td>
<td>-</td>
<td>3.97±0.16</td>
</tr>
</tbody>
</table>

Use of the crosslinking agent changes hydrophilic-hydrophobic properties of prepared membranes. Crosslinking reaction results in the formation of new bonds – chemical crosslinking, or Coulomb forces – physical crosslinking [18] which can modify polymer molecules' conformation, reducing existing free volume of the membrane matrix. During crosslinking the content of the available free carboxyl groups in alginate or amino groups in chitosan diminishes.

For ALPA membrane permeation and solubility coefficients were greater for ethanol, however, obtained value of flux for water was 16.5 times greater...
Vapour permeation study of water and ethanol through crosslinked chitosan and alginate membranes

than that of ethanol. This means that for ALPA membrane, in a model of diffusion-solubility transport, diffusion dominates [14].

In calcium ionic crosslinked alginate membranes the interaction of calcium ions with the carboxyl acid groups of alginate creates a unique amorphous molecular network structure consisting of physical tie-points made by association of calcium ions with the molecules. These tie-points are different from chemical crosslinks as they are formed by aggregation of many Ca\(^{2+}\) and obtained complex introduced noncrystalline physical crosslinks of the molecular network [19]. While the pure water was tested, the amorphous region of calcium ion crosslinked alginate membrane is more swollen, and this area makes the polymer matrix more flexible. Therefore, the water molecules are able to pass through the membrane easily. During the process of ethanol vapour permeation, a significant decrease in their flux values was observed, and membranes became more dense and rigid. Probably, after first contact during ethanol vapour permeation, formation of a crystalline phase may occur, which made hindrance for the vapour transport.

The experiments showed that the chemically crosslinked alginate membranes are more resistant to solvents that pass through, and therefore, were more stable and their possible separation efficiency was greater. On the other hand, stronger than the physical, association of the matrix resulting in lower yields of observed fluxes.

Due to chemical structure of polymers with a large number of hydroxyl groups and the possibilities of creating hydrogen bond interaction with water, both chitosan and alginate, show more preferential sorption and diffusion of water though the barrier membrane which is also confirmed by the results of swelling degree (Fig. 2). In case of swelling in pure ethanol, experimental results showed that all prepared membranes did not display noticeable changes of solvent uptake.

Comparing the influence of crosslinking agent nature it can be seen, that hydrophobic glutaraldehyde introduced into chitosan matrix decrease their potential to water and resulting degree of swelling was 93% in contrast to sulphuric (VI) anion where swelling ratio equal to 126%. This trend is similar to that obtained in [14]. Whereas alginate membranes, despite different crosslinking agents, have very close behaviour in both solvents, what may be associated with a similar interaction between crosslinkers and polymer matrix.

On the other hand, the water sorption of non-crosslinked alginate and chitosan membranes for ethanol-water mixture have been tested by Moon et al [20]. They showed that amount of water absorbed in membrane increases with water content in the mixture, but regardless of the content of water in the mixture, alginate always shows much higher water selectivity than chitosan.
R. Turczyn, M. Gnus, G. Dudek, A. Törz, D. Łącka, A. Strzelewicz, M. Łapkowski

Progress on Chemistry and Application of Chitin and its Derivatives, Volume XX, 2015
DOI: 10.15259/PCACD.20.28

Figure 2. Degree of swelling in water and ethanol for chitosan and alginate membranes with different cross-linking agents.

4. Conclusions

In this paper, homogenous chitosan, and alginate membranes crosslinked by different crosslinking agents were prepared. For chitosan membranes sulphuric (VI) acid (CHSA) and glutaraldehyde (CHGA) were used as crosslinkers. Alginate membranes were crosslinked by phosphoric acid (ALPA) and calcium chloride (ALCa). Influence of the crosslinking modification on the efficiency of ethanol and water vapour permeation process was studied. The experiment showed that the chemical crosslinking agents, comparing to physical one, used to crosslinking chitosan/alginate membranes give more resistant membranes to solvents. Moreover, they were more stable, and their separation factor was greater. It was also observed that the transport properties changed after adding hydrophobic or hydrophilic crosslinking agents. In case of a hydrophobic glutaraldehyde, the decrease of water transport was noticed, and finally, the degree of swelling was smaller in contrast to the hydrophilic crosslinking agent. Comparing chitosan and alginate membranes we observed that, generally, degree of swelling in water was smaller in case of chitosan membranes.

The obtained results for pure solvents give promising conditions for separation of ethanol-water mixture. Both chitosan and alginate membranes show more preferential sorption and diffusion of water. Based on the literature data it can be assumed that the increase of water content in the mixture, which leads to the swelling of the polymer matrix, can make easier diffusion of water.

5. Acknowledgements

The authors would like to thank The National Centre for Research and Development for providing financial support under the project INNOTECH-K2/IN2/7/181844/NCBR/13.
6. References