Sorption and pervaporation study of methanol/dimethyl carbonate mixture with poly(etheretherketone) (PEEK-WC) membrane

Wenqi Li[a], Francesco Galiano[b*], Julien Estager[c], Jean-Christophe M. Monbaliu[d], Damien Debecker[e], Alberto Figoli[b*], Patricia Luis[a*]

[a] Materials & Process Engineering (iMMC-IMAP), Université catholique de Louvain, Place Sainte Barbe 2, 1348 Louvain-la-Neuve, Belgium

[b] Institute on Membrane Technology, National Research Council (ITM-CNR), University of Calabria, Pietro Bucci 17/C, 87036 Rende (CS), Italy

[c] Certech, Centre de ressources technologiques en chimie, Rue Jules Bordet, Zone Industrielle C, 7180 Seneffe, Belgium

[d] Center for Integrated Technology and Organic Synthesis, Department of Chemistry, University of Liège, B-4000 Liège (Sart Tilman), Belgium

[e] Institute of Condensed Matter and Nanoscience (IMCN), Université catholique de Louvain, Place Louis Pasteur, 1, box L4.01.09, 1348 Louvain la-Neuve, Belgium

* Tel: +32 16 322348; Fax: +32 16 322991; Email: patricia.luis@uclouvain.be; a.figoli@itm.cnr.it; f.galiano@itm.cnr.it

1. Introduction

Dimethyl carbonate (DMC) is considered as green chemical due to its biodegradability and low toxicity, being widely applied in the chemical industry.[1] As a low toxic intermediate, it can be used as a substitute in the pharmaceutical industry to replace more toxic solvents such as dimethyl sulfate, or in the production of important thermoplastics polycarbonate materials to replace phosgene.[2] Furthermore, it finds applications as a solvent in painting and coating industries and it is used as an electrolyte carrier for Li-ion cells.[3,4] In the literature, different synthetic routes of DMC are reported. One of them follows a phosgene-based route to produce DMC. However, phosgene is a toxic raw material and the complementary use of NaOH during the reaction requires a high capital equipment investment for preventing corrosion.[5] DMC can be also produced by the transesterification reaction of cyclic carbonate and methanol, such as ethylene carbonate[6–9] or can be synthesized from methanol oxidative carbonation by using copper chloride as a catalyst.[10] DMC synthesis from alcoholysis of urea is an attractive chemical route since urea is widely available at low cost as a waste.[11,12] This reaction proceeds through two successive steps: 1) urea reacts with

methanol to produce methyl carbamate; 2) methylcarbamate reacts with methanol to produce the final product DMC. In addition, DMC can be obtained from direct reaction of methanol and carbon dioxide (methanol carboxylation route) with the possibility of using various catalysts.[13–15] Consequently, methanol is present in the different synthetic routes of DMC. In addition, the use of DMC as a reagent also leads to the formation of methanol as a by-product in the synthesis of glycerol carbonate - a valuable intermediate chemical - *via* transesterification reaction of biobased glycerol.[16–24] Therefore, the separation of DMC and methanol is of great importance in the chemical industry but it remains very challenging as these two compounds form an azeotrope (at 30/70 wt% DMC/methanol concentration). In the literature, several alternative approaches have been proposed such as extractive distillation,[25] membrane processes[26,27] or the use of ionic liquids as entrainers.[28]

Membrane separation has many advantages compared to other separation processes. Pervaporation is one of the most promising membrane separation technologies due to its low energy consumption and low environment impact. This process has significant advantages over the distillation for the separation of azeotropic mixtures, of heat sensitive compounds and of low concentrated pollutants from aqueous wastes.[29] Different polymeric materials have been investigated in pervaporation for the separation of DMC/methanol mixtures, but their application at an industrial level is still limited. Modified poly ether ether ketone (poly(oxa-p-phenilene-3,3-phthalido-p-phenylene-oxy-phenylene) (PEEK-WC: WC refers to cardo group) is a polymer containing a spirolacton group with good thermal stability, mechanical property and high resistance to chemicals due to its high glass transition temperature (225 °C).[30,31] Due to these properties, PEEK-WC membranes find wide applications in different fields such as in biomedical engineering due to its low affinity to proteins[32] and in fuel cell applications due to its high proton conductivity and its low cost comparing to Nafion membranes.[32] In pervaporation, the performance of PEEK-WC membranes has been investigated for the separation of methanol and MTBE.[31] A high separation factor (above 250) was obtained at low concentration of methanol (1 wt%). In the application of dehydration of acetic acid, PEEK-WC membranes can achieve good separation with a value of 103 as separation factor at 50 °C for a concentration of 90 wt% of acetic acid.[33] In this work, a detailed study on sorption and pervaporation for DMC/methanol mixtures

with PEEK-WC membranes is presented at different concentrations and temperatures. The coupling phenomenon during the permeation was investigated as well. The performance of the membrane was evaluated in terms of flux, separation factor, permeance and selectivity.

2. Materials and methods

2.1 Materials

Dimethyl carbonate (ReagentPlus®, 99%) and methanol (purity 99.8%), were purchased from Sigma-Aldrich and used without further purification. Chloroform (anhydrous, ≥99%, containing 0.5-1.0% ethanol as stabilizer) was obtained from Sigma-Aldrich and used without further purification. The polymer (poly(oxa-p-phenilene-3,3-phthalido-p-phenylene-oxy-phenylene), namely PEEK-WC, was purchased from Chanchung Institute of applied chemistry (China).

2.2 Membrane preparation

PEEK-WC was dissolved in chloroform by magnetically stirring overnight up to its complete dissolution at room temperature[31]. The solution was then casted on a glass plate using a manual casting knife (thickness 250 µm). After solvent evaporation, the casted film was immersed in a coagulation bath containing distilled water to detach the obtained dense membranes. Then, the membranes obtained were dried in an oven at 40 °C for 24 hours.

2.3 Membrane characterization

2.3.1 Contact angle measurement

Wettability expresses how easily a liquid can spread on a solid surface, relating to the intermolecular forces. It is determined by contact angle measurements. Contact angle (θ) is obtained by measuring the angle between the solid-liquid interface and the liquid-vapor interface. By convention, when $\theta < 90°$, the membrane is defined as hydrophilic and hydrophobic if $\theta > 90°$. The contact angle of the membrane surface was measured by an optical instrument (Nordtest srl, G-I, Italy) at room temperature and the measurements were repeated three times. A water droplet was dropped on the membrane surface and the contact angle was measured immediately.

2.3.2 Mechanical test

Mechanical tests were performed using a Zwick/Roell testing machine single column model Z2.5,

equipped with a 50 N maximum load cell (BTC-FR2.5TN-D09, Germany). Each membrane sample (1 cm x 5 cm) was stretched unidirectionally at the constant rate of 5 mm/min until its break.

2.3.3 Scanning electron microscopy (SEM) analysis

The morphology of the prepared membranes (top, bottom and cross-section) was evaluated by SEM (Zeiss, EVO MA10). Before the analyses, all the samples were sputter coated with a thin layer of gold (Quorum Q150 RS) to make them conductive.

2.4 Swelling degree experiments

In order to estimate the degree of swelling, three membrane pieces were immersed and weighed in pure solvents as well as in 0.1, 0.3, 0.5, 0.7, and 0.9 molar fraction of methanol in MeOH/DMC solutions at room temperature (25 °C) for 7 days so that the membrane and solution reached swelling equilibrium. After achieving swelling equilibrium, the membranes were taken out from the solution. The excess of liquid on the membrane surface was removed immediately by using a tissue paper. After cleaning, the membrane was weighed on a high precision balance (Mettler-Toledo, AE200, Belgium) with a precision of +/- 0.0001 g. The swelling degree of the membrane was then calculated by the following equation[34]:

$$SD = \frac{m_w - m_d}{m_d} \times 100\% \quad (1)$$

where m is the mass of membrane (g); subscripts *w* and *d* refer to the membrane after sorption (wet) and before sorption (dry), respectively.

2.5 Evaluation of coupling effects

Hansen solubility parameters play an important role in the analysis of the interactions between the membrane polymer material and solvents. As the solubility parameters of pure components and their mixtures are completely different. A pure component rejected by membrane can present in the permeate when it is one of the components in the mixture as feed due to the change of solubility property and results in coupling effects.[35] Therefore, the variation of solubility parameters caused by different composition in the mixture is not negligible.

According to Hansen,[36] the distance of the pure/mixture solvents to the center of the polymer

115 solubility sphere can be calculated by the following equation:

$$R_a = \left[4(\delta_{Ds} - \delta_{Dp})^2 + (\delta_{Ps} - \delta_{Pp})^2 + (\delta_{Hs} - \delta_{Hp})^2\right]^{1/2} \quad (2)$$

116 where R_a is the distance between the solvents and the center of solubility sphere of polymer
117 (MPa$^{1/2}$), and δ is the Hansen solubility parameters. D, P and H, are the Hansen components:
118 dispersion, polar and hydrogen bonding component, respectively; s and p are the solvent and
119 polymer, respectively.

120 The Hansen solubility parameters of mixture were calculated by equation (13):[37]

$$\overline{\delta_k} = \sum_i \phi_i \delta_{ki} \quad (3)$$

121 the subscripts k indicates the D, P and H Hansen components. ϕ_i is the volume fraction of the
122 pure components in the mixture.

123 2.6 Pervaporation experiments

124 The pervaporation experiments were performed using a pervaporation membrane cell produced
125 by DeltaE s.r.l., Italy. The scheme of the experimental set-up is presented in Figure 1. The detailed
126 description of the set-up is reported elsewhere.[38]

127 The feed solution (around 100 mL) was poured in a stainless steel feed tank with an inner diameter
128 of 89 mm. When the experiment started, the system was run for two hours in order to achieve
129 quasi static steady state before a sample of the permeate was collected. An overhead stirrer was
130 installed with a rotation speed of 40 rpm in order to avoid concentration and temperature
131 polarization on the surface of the membrane. A heating circulator was employed to maintain the
132 experimental temperature of the feed solution at 30, 40, 50 or 60 °C (+/- 2 °C). The membrane was
133 contacted with different composition of binary mixtures methanol/DMC. The feed compositions
134 of 0.1, 0.3, 0.5, 0.7, 0.9 mole fraction in methanol were studied. The PEEK-WC membrane was
135 immersed in the feed solution for 24 hours before starting the experiments. The permeate was
136 collected every 60 minutes and the composition of the permeate was analyzed by an Abbe 60 type
137 direct reading refractometer (Bellingham Stanley Ltd., UK) at 25 °C.

138 The mass of permeate was weighed over time with a precision of 10^{-4} g balance. Then, the

transmembrane total flux J (kg/m²·h) was calculated by the following equation:

$$J = \frac{w}{\Delta t \times A} \quad (4)$$

where *A* is the membrane effective area (m²), Δt is the permeate collecting time (h) and w is the weight of permeate (kg). The partial flux of each component (j_i: kg/m²·h) was determined by the following equation:

$$j_i = J \times y_i \quad (5)$$

where y_i is molar fraction of component *i* in the permeate.

Then, the permeance ($\frac{P_i}{l}$) was calculated as follows[39]:

$$\frac{P_i}{l} = \frac{j_i}{(x_i \times \gamma_i \times P_i^0 - y_i \times P_p)} \quad (6)$$

Aspen Plus was used to calculate vapor pressure P_i^0 (atm) and activity coefficients.[40] Non-random two-liquid method (NTRL) was employed to calculate the activity coefficients (γ_i) of methanol and DMC in the binary mixture methanol/DMC at different temperatures and different concentrations. x_i and y_i are the molar fraction of component *i* in the feed and permeate, respectively. P_p is the vacuum pressure at the permeate side. The permeance was obtained from the partial molar flux (j_i) divided by the term of driving force. As a result, the impact of driving force on the permeation was eliminated. The unit of permeance is expressed in GPU ($1\ \mathrm{GPU} = 1 \times 10^{-6}\ \mathrm{cm^3\ (STP)/(cm^2\ s\ cmHg)} = 7.5005 \times 10^{-12}\ \mathrm{m\ s^{-1}\ Pa^{-1}}$).

The separation factor (β) was calculated by the following equation:

$$\beta_{i/j} = \frac{y_i/y_j}{x_i/x_j} \quad (7)$$

where the subscript indicates the components *i* and *j* in the permeate (y_i, y_j) and feed (x_i, x_j) solutions, respectively.

The selectivity (α) of the membrane is the ratio of permeances of component *i* and *j* in the mixture:

$$\alpha_{i/j} = \frac{P_i/l}{P_j/l} = \frac{P_i}{P_j} \quad (8)$$

From equation 8, it can be seen that if the value of selectivity ($\alpha_{i/j}$) is larger than 1, component *i* is more favorable to permeate through the membrane than component *j*.

3. Results and discussion

3.1 membrane characterization *via* contact angle, mechanical test and SEM analysis

PEEK-WC membranes exhibited a water contact angle of 84.96±2.28. This result indicates that the PEEK-WC membrane was slightly hydrophilic. Therefore, a polar component can permeate through the membrane easier than a non-polar component.

Mechanical test results showed that the average Young's modulus of the PEEK-WC membrane was 1147.71 ± 34.9 N/mm^2 with an elongation at break of 10.6% ± 4.6%. The average maximum stress was 47.76 ± 8.28 N/mm^2. If compared to the Young's modulus and the maximum stress of polyvinyl alcohol (PVA) (170-360 N/mm^2 and 6.4 ± 0.5 N/mm^2, respectively) and chitosan membranes (4.5-5.89 5 N/mm^2 and 2.43-7 N/mm^2, respectively), PEEK-WC membrane shows good mechanical features.[41,42,43,44]

SEM analysis confirmed the dense nature of the prepared membranes. As observed in Figure 2a, 2b and 2c, the prepared membrane is homogeneous and no pore is present in the membrane surface and cross section. For pervaporation separation, the transport is based on a solution-diffusion mechanism, therefore, a dense membrane is required.

3.2 Swelling degree measurement

The swelling degree of the membrane for different concentrations of methanol/DMC solutions is shown in Figure 3. A decrease in swelling degree was observed when the concentration of methanol was increased in the binary mixture. The values of swelling degree of PEEK-WC in pure methanol are in agreement with the literature,[31] showing values of 5%-7%. One interesting observation is that the PEEK-WC membrane is more favorable to absorb DMC than methanol. For pure DMC, the swelling degree can reach 17% and for high concentrations of DMC (0.9 molar fraction of DMC), the swelling degree is still above 15%. The swelling effect may have negative influence on the membrane separation performance. An excessive membrane swelling leads to

polymer plasticization and the polymer chain spacing increases resulting in reducing selectivity severely.[45]

3.3 Coupling effects

Hansen solubility parameters of PEEK-WC, methanol, DMC and their mixtures are shown in table 1. There are several different approaches to estimate solubility parameters of PEEK-WC that will lead to different results.

In the work of Zereshki et al., it is stated that the solubility parameters derived from Hoy method can be more realistic than other methods for the study of the separation of methanol/MTBE mixtures by using PEEK-WC membranes.[31] The three dimensional solubility vector distance (δ_t) between PEEK-WC polymer and methanol/DMC was calculated and shown in table 2. From table 2, it can be observed that the method applied by Hoy is not able to describe the phenomena observed in the swelling degree of methanol/DMC mixtures since pure methanol and DMC have a similar distance (8.3 methanol and 8.9 DMC, respectively) to the polymer solubility center. This is in contradiction with the results obtained with the swelling degree since the latter increases with the increase of the concentration of DMC in the mixture. Noteworthy, the solubility parameters derived from the other methods can better explain this behavior as the lower the distance polymer/solvent is, the higher the compatibility between them is. Therefore, it can be speculated that the coupling effect is more likely to occur at low concentration of methanol.

3.4 Pervaporation performance

Figure 4 shows the impact of concentrations and temperatures on the permeation flux and separation factor. The results show that the temperature, as expected, plays a crucial role on the permeation flux. With the increase of the temperature, the flux increases. In the pervaporation process, the vacuum pressure at the permeate side was less than 5 mbar, therefore, the driving force term $\left(x_i \times \gamma^i \times P_i^{\circ} - y_i \times P_p\right)$ in equation (6), $y_i \times P_p$ is close to 0. As a result, the driving force depends on the activity coefficient, on the initial concentration of feed and on the vapour pressure of the components. The activity coefficient and the vapour pressure are both temperature dependent. In both factors, the variation of vapour pressures of methanol and DMC are more sensitive to the temperature change than their activity coefficients. With an

increase of temperature, the vapour pressure of methanol and DMC are increasing dramatically, leading to an increase of the driving force. As a result, the flux increases by increasing the temperature.[46] In addition, temperature also shows an impact on the separation factor particularly at high concentration of DMC (0.9). The separation factor decreases with the increase of the temperature. High temperature can lead to the expansion and relaxation of the polymer chains and to the formation of more free volume promoting the indiscriminate transportation of molecules through the membrane.[47,48] As a result, the separation factor decreases.

Regarding the concentration effect, both transmembrane flux and separation factor are concentration dependent. In general, lower concentration of methanol in the binary mixture leads to higher transmembrane flux and separation factor. This phenomenon could be interpreted by the variation of activity of methanol and DMC. Figure 5 shows the variation of activity of methanol and DMC in the mixture. The activity of methanol in the mixture decreases with increasing methanol concentration. Similar observations were reported elsewhere.[31]

In the analysis of Hansen solubility, it is shown that the solubility vector distance (δ_t in Table 2) increases with increasing methanol concentration (except for the method used by Hoy[49]). The concentration effect on the flux follows this trend. A larger distance between the polymer and solvent implies a lower the affinity between them. Therefore, the membrane flux decreases with the increase of methanol concentration. The Hansen solubility parameters give a good prediction of this phenomenon.

3.5 Membrane performance

The permeance and selectivity are used to describe the performance of membrane in order to eliminate the impact of the operating conditions. Figure 6 and 7 show the permeance of methanol and DMC and the selectivity at different temperatures and concentrations.

An interesting phenomenon was observed by comparing the permeance behavior of methanol and DMC with respect to their concentrations. In Figure 6a and 6b, the permeance of DMC increased while increasing of methanol concentration. However, the permeance of methanol showed an opposite trend: a higher concentration of DMC in the binary mixture led to a higher permeance of methanol. From the experiments of swelling degree, it was found that the membrane was more

prone to sorb DMC than methanol. However, a preferential sorption does not give a preferential permeation at high concentration of DMC. The polarity indexes of methanol and DMC are 0.762 and 0.232, respectively.[4] Due to the higher polarity of methanol, the hydrophilic membranes can favour the permeation of methanol (instead of DMC) from the binary mixture due to the significant difference of polarity between these two components. In addition, methanol can easily diffuse through the membrane due to its smaller molecular size when compared with DMC.[50]

Besides, the intermolecular attractions are affected by the functional groups which contribute to dipole-dipole attractions and hydrogen bonds. From the molecular structure of PEEK-WC, DMC and methanol (Figure 8), it can be seen that the polymer bears a ketone group which is an organic group where a carbonyl group (C=O) is bonded to two carbon atoms of the carbon backbone. Carbonyl groups are polar and can generate dipole-dipole attraction with carbonyl group (C=O) as well as hydrogen bonding (-OH group).[51,52] In studying the interactions between PEEK-WC and the two solvents, it is necessary to consider that the carbonyl group of PEEK-WC polymer generates not only dipole-dipole attractions with DMC (as DMC has a carbonyl group as well) but also hydrogen bonding with methanol (-OH group). In the interaction between molecules, DMC and methanol contains a carbonyl and a hydroxyl group, respectively. Consequently, both molecules undergo intermolecular interactions due to hydrogen bonding.

In Figure 6, the permeance of DMC decreases with the decrease of the molar fraction of methanol. At low concentration of methanol, the amount of hydroxyl group from methanol is much less than the carbonyl group from PEEK-WC polymer and DMC. The major competition is between carbonyl group from PEEK-WC and DMC to interact with methanol. DMC prefers to form cis-trans clusters in the liquids and half of cis-trans molecules are clustered, hence the permeation of DMC becomes difficult due to this effect and the intermolecular interaction of hydrogen bonding is usually stronger than dipole-dipole attraction.[53] Therefore, methanol is more prone to interact with PEEK-WC membrane due to hydrogen bonding formation in comparison to DMC because the interaction between PEEK membrane and DMC is dipole-dipole attraction. As a result, methanol molecules have more opportunity to occupy the carbonyl site of PEEK-WC than DMC and, therefore, to diffuse through the membrane.

With the increase of methanol concentration, the carbonyl groups of DMC can be surrounded by

the methyl group of methanol due to the intermolecular attraction between the carbonyl oxygen and hydrogen atoms because the carbonyl groups are more favorable to be surrounded by the methyl groups of methanol.[53] Drag effect can exist in the permeation behavior as DMC is surrounded by methanol. Consequently, a strong drag effect becomes more dominant when more methanol is present in the mixture. Therefore, the permeance of DMC increases with an increase of the concentration of methanol in the mixture.

The result of selectivity shows that both concentration and temperature have a great influence on the membrane performance. When the concentration of methanol was larger than 50 mol%, the selectivity was smaller than 1, (90% methanol: selectivity 0.25-0.35; 70% methanol: selectivity 0.65-0.88). This indicates that the membrane permeates DMC due to the strong drag effect caused by the high concentration of methanol. When the concentration of methanol was 50 mol%, the selectivity was near to 1. On the contrary, when the concentration of methanol was less than 50 mol%, the selectivity could achieve the values of 3.5, showing that the membrane prefers to permeate methanol instead of DMC due to the higher polarity of the alcohol respect to the carbonate.

In table 3, a literature comparison of different membranes regarding the pervaporation of methanol/DMC mixtures is given. If compared to these other membranes, the PEEK-WC one can have a good separation performance at low concentration of methanol equal to 0.1 molar fraction (3.8 wt% methanol) and at low temperature (30°C) with a separation factor of 13.4. This separation performance is better than any other membranes tested under the same conditions. This makes the process feasible when a large excess of DMC, in methanol/DMC mixtures, is encountered. This kind of composition can be found, for example, in the case of the transesterification reaction of glycerol and DMC, an excess of DMC is introduced to produce glycerol carbonate and methanol as a byproduct. In the final product mixture, a high concentration of DMC is present in the mixture with a low concentration of methanol.[17]

5. Conclusions

PEEK-WC membranes were prepared and studied for the pervaporation separation of a binary mixture of methanol/DMC at different conditions. In the membrane swelling experiment, the results showed that the membrane can be swollen by both of these chemicals, but this

phenomenon is more significant for DMC than for methanol. The swelling degree increases with the increase of the DMC concentration in the DMC/methanol mixture. The transmembrane flux increases with the increase of temperature, but decreases with methanol concentration mainly due the hydrophilicity of the membrane which can promote the diffusion of the more polar compound (methanol) of the binary mixture. The molecular structure has a strong impact on the membrane performance. A higher concentration of methanol can lead to a strong drag effect and to a subsequent decrease of the selectivity. Even if the transmembrane flux is not extraordinary high in comparison to the data reported in literature, the separation factor (13.5) exhibits a better performance than other membranes at low concentration of methanol (0.1 molar fraction) and at low temperature (30 °C). Moreover, the membrane showed excellent mechanical properties during the overall experimental period. Therefore, PEEK-WC membranes can be of interest to be applied in pervaporation at industrial level for breaking the azeotrope of methanol and DMC.

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Reference:

1. Tundo, P., Aricò, F., Rosamilia, A. E., Grego, S. & Rossi, L. Dimethyl Carbonate: Green Solvent and Ambident Reagent. *Green Chem. React.* 213–232 doi:10.1007/978-1-4020-8457-7_10
2. Ono, Y. Dimethyl carbonate for environmentally benign reactions. *Catal. Today* **35,** 15–25 (1997).
3. Shiao, H. Ž. A., Chua, D., Lin, H., Slane, S. & Salomon, M. Low temperature electrolytes for Li-ion PVDF cells. *J. Power Sources* **87,** 167–173 (2000).
4. Pyo, S. H., Park, J. H., Chang, T. S. & Hatti-Kaul, R. Dimethyl carbonate as a green chemical. *Curr. Opin. Green Sustain. Chem.* **5,** 61–66 (2017).
5. Aresta, M. & Galatola, M. Life cycle analysis applied to the assessment of the environmental impact of alternative synthetic processes. The dimethylcarbonate case: part 1. *J. Clean. Prod.* **7,** 181–193 (1999).
6. Kumar, P., Kaur, R., Verma, S., Srivastava, V. C. & Mishra, I. M. The preparation and efficacy of SrO/CeO2catalysts for the production of dimethyl carbonate by transesterification of ethylene carbonate. *Fuel* **220,** 706–716 (2018).

7. Zheng, H., Hong, Y., Xu, J., Xue, B. & Li, Y. X. Transesterification of ethylene carbonate to dimethyl carbonate catalyzed by CeO2materials with various morphologies. *Catal. Commun.* **106,** 6–10 (2018).
8. Gandara-Loe, J., Jacobo-Azuara, A., Silvestre-Albero, J., Sepúlveda-Escribano, A. & Ramos-Fernández, E. V. Layered double hydroxides as base catalysts for the synthesis of dimethyl carbonate. *Catal. Today* **296,** 254–261 (2017).
9. Du, G. F. *et al.* N-heterocyclic carbene catalyzed synthesis of dimethyl carbonate via transesterification of ethylene carbonate with methanol. *J. Saudi Chem. Soc.* **19,** 112–115 (2015).
10. Romano, U., Tesel, R., Massi Mauri, M. & Rebora, P. Synthesis of Dimethyl Carbonate from Methanol, Carbon Monoxide, and Oxygen Catalyzed by Copper Compounds. *Ind. Eng. Chem. Prod. Res. Dev.* **19,** (1980).
11. Hou, Z. *et al.* High-yield synthesis of dimethyl carbonate from the direct alcoholysis of urea in supercritical methanol. *Chem. Eng. J.* **236,** 415–418 (2014).
12. Wu, X. *et al.* Synthesis of dimethyl carbonate by urea alcoholysis over Zn/Al bi-functional catalysts. *Appl. Catal. A Gen.* **473,** 13–20 (2014).
13. Wu, X. L., Meng, Y. Z., Xiao, M. & Lu, Y. X. Direct synthesis of dimethyl carbonate (DMC) using Cu-Ni/VSO as catalyst. *J. Mol. Catal. A Chem.* **249,** 93–97 (2006).
14. Jiang, C. *et al.* Synthesis of dimethyl carbonate from methanol and carbon dioxide in the presence of polyoxometalates under mild conditions. *Appl. Catal. A Gen.* **256,** 203–212 (2003).
15. Aresta, M. *et al.* Cerium(IV)oxide modification by inclusion of a hetero-atom: A strategy for producing efficient and robust nano-catalysts for methanol carboxylation. *Catal. Today* **137,** 125–131 (2008).
16. Ilham, Z. & Saka, S. Esterification of glycerol from biodiesel production to glycerol carbonate in non-catalytic supercritical dimethyl carbonate. *Springerplus* **5,** 923 (2016).
17. Ramesh, S. & Debecker, D. P. Room temperature synthesis of glycerol carbonate catalyzed by spray dried sodium aluminate microspheres. *Catal. Commun.* **97,** 102–105 (2017).
18. Stefanus, F. *et al.* Applied Catalysis A : General CaO-catalyzed synthesis of glycerol carbonate from glycerol and dimethyl carbonate : Isolation and characterization of an active Ca species. *"Applied Catal. A, Gen.* **401,** 220–225 (2011).
19. Okoye, P. U., Abdullah, A. Z. & Hameed, B. H. Journal of the Taiwan Institute of Chemical Engineers Glycerol carbonate synthesis from glycerol and dimethyl carbonate using trisodium phosphate. **68,** 51–58 (2016).
20. Hu, K., Wang, H., Liu, Y. & Yang, C. KNO3/CaO as cost-effective heterogeneous catalyst for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate. *J. Ind. Eng. Chem.* **28,** 334–343 (2015).
21. Malyaadri, M., Jagadeeswaraiah, K., Prasad, P. S. S. & Lingaiah, N. Applied Catalysis A : General Synthesis of glycerol carbonate by transesterification of glycerol with dimethyl carbonate over Mg / Al / Zr catalysts. *"Applied Catal. A, Gen.* **401,** 153–157 (2011).
22. José R. Ochoa-Gómez; Olga Gómez-Jiménez-Aberasturi; *et al.* Applied Catalysis A : General Synthesis of glycerol carbonate from glycerol and dimethyl carbonate by transesterification : Catalyst screening and reaction optimization. *Appl. Catal. A Gen.* **366,** 315–324 (2009).
23. Stefanus, F. *et al.* Applied Catalysis B : Environmental Synthesis of glycerol carbonate from the transesterification of dimethyl carbonate with glycerol using DABCO and DABCO-anchored

Merrifield resin. *"Applied Catal. B, Environ.* **165,** 642–650 (2015).
24. Bai, R., Wang, S., Mei, F., Li, T. & Li, G. Journal of Industrial and Engineering Chemistry Synthesis of glycerol carbonate from glycerol and dimethyl carbonate catalyzed by KF modified hydroxyapatite. *J. Ind. Eng. Chem.* **17,** 777–781 (2011).
25. Liu, W., Wong, D. S., Wang, S. & Hsu, H. Journal of the Taiwan Institute of Chemical Engineers Effect of mass transfer on the design of an extractive distillation process for separating DMC and methanol. *J. Taiwan Inst. Chem. Eng.* **60,** 205–212 (2016).
26. Wang, L., Li, J., Lin, Y. & Chen, C. Separation of dimethyl carbonate / methanol mixtures by pervaporation with poly (acrylic acid)/ poly (vinyl alcohol) blend membranes. *J. Memb. Sci.* **305,** 238–246 (2007).
27. Won, W., Feng, X. & Lawless, D. Separation of dimethyl carbonate / methanol / water mixtures by pervaporation using crosslinked chitosan membranes. *Sep. Purif. Technol.* **31,** 129–140 (2003).
28. Zhang, Z. *et al.* Separation of methanol dimethyl carbonate azeotropic mixture using ionic liquids as entrainers. *Fluid Phase Equilib.* **435,** 98–103 (2017).
29. Smitha, B., Suhanya, D., Sridhar, S. & Ramakrishna, M. Separation of organic-organic mixtures by pervaporation - A review. *J. Memb. Sci.* **241,** 1–21 (2004).
30. Gordano, A., Clarizia, G., Torchia, A., Trotta, F. & Drioli, E. New membranes from PEEK-WC and its derivatives. *Desalination* **145,** 47–52 (2002).
31. Zereshki, S. *et al.* Pervaporation separation of MeOH/MTBE mixtures with modified PEEK membrane: Effect of operating conditions. *J. Memb. Sci.* **371,** 1–9 (2011).
32. De Bartolo, L. *et al.* Novel PEEK-WC membranes with low plasma protein affinity related to surface free energy parameters. *J. Mater. Sci. Mater. Med.* **15,** 877–883 (2004).
33. Chen, J. H., Liu, Q. L., Zhu, A. M., Fang, J. & Zhang, Q. G. Dehydration of acetic acid using sulfonation cardo polyetherketone (SPEK-C) membranes. *J. Memb. Sci.* **308,** 171–179 (2008).
34. Kuila, S. B. & Ray, S. K. Separation of isopropyl alcohol – water mixtures by pervaporation using copolymer membrane : Analysis of sorption and permeation. *Chem. Eng. Res. Des.* **91,** 377–388 (2012).
35. Li, W. & Luis, P. Understanding coupling effects in pervaporation of multi-component mixtures. *Sep. Purif. Technol.* **197,** 95–106 (2018).
36. Hansen, C. M. 50 Years with solubility parameters — past and future. *Prog. Org. Coat.* **51,** 77–84 (2004).
37. Barton, A. F. M. Solubility Parameters. *Chem. Rev.* **75,** 731–753 (1975).
38. Castro-Muñoz, R., Galiano, F., Fíla, V., Drioli, E. & Figoli, A. Matrimid® 5218 dense membrane for the separation of azeotropic MeOH-MTBE mixtures by pervaporation. *Sep. Purif. Technol.* **199,** 27–36 (2018).
39. Luis, P., Degrève, J. & der Bruggen, B. Van. Separation of methanol-n-butyl acetate mixtures by pervaporation: Potential of 10 commercial membranes. *J. Memb. Sci.* **429,** 1–12 (2013).
40. Esteban, J., Ladero, M., Molinero, L. & García-ochoa, F. Chemical Engineering Research and Design Liquid – liquid equilibria for the ternary systems DMC – methanol – glycerol , DMC – glycerol carbonate – glycerol and the quaternary system DMC – methanol – glycerol carbonate – glycerol at catalytic reacting temp. *Chem. Eng. Res. Des.* **92,** 2797–2805 (2014).
41. Hemeda, O. M., Hemeda, D. M. & Said, M. Z. Some Physical Properties of Pure and Doped Polyvinyl Alcohol under Applied Stress. *Mech. Time-Dependent Mater.* **7,** 251–268 (2003).

42. Kienzle-Sterzer, C. a., Rodriguez-Sanchez, D. & Rha, C. Mechanical Properties of Chitosan Films: Effect of Solvent Acid. *Die Makromol. Chemie* **183,** 1353–1359 (1982).
43. Mohammad Mahdi Dadfar, S., Kavoosi, G. & Mohammad Ali Dadfar, S. Investigation of mechanical properties, antibacterial features, and water vapor permeability of polyvinyl alcohol thin films reinforced by glutaraldehyde and multiwalled carbon nanotube. *Polym. Compos.* **35,** 1736–1743 (2014).
44. Le, H. R., Qu, S., Mackay, R. E. & Rothwell, R. Fabrication and mechanical properties of chitosan composite membrane containing hydroxyapatite particles. *J. Adv. Ceram.* **1,** 66–71 (2012).
45. Cao, S., Shi, Y. & Chen, G. Permeation behaviour in cellulose triacetate dense membrane during pervaporation separation of methanol/methyl tert-□butyl ether mixture. *Polym. Int.* **215,** 209–215 (2000).
46. Luis, P. & Van Der Bruggen, B. The driving force as key element to evaluate the pervaporation performance of multicomponent mixtures. *Sep. Purif. Technol.* **148,** 94–102 (2015).
47. Burshe, M. C., Sawant, S. B. & Pangarkar, V. G. Dehydration of Glycerine-Water Mixtures by Pervaporation. *J. Am. Oil Chem. Soc.* **76,** 209–214 (1999).
48. Guo, W. F., Chung, T. & Matsuura, T. Pervaporation study on the dehydration of aqueous butanol solutions : a comparison of flux vs . permeance , separation factor vs . selectivity. *J. Memb. Sci.* **245,** 199–210 (2004).
49. Hoy, K. L. Solubility parameter as a design parameter for water-borne polymers and coatings. *J. Coat. Fabr.* **19,** 53–67 (1989).
50. Smuleac, V., Wu, J., Nemser, S., Majumdar, S. & Bhattacharyya, D. Novel perfluorinated polymer-based pervaporation membranes for the separation of solvent/water mixtures. *J. Memb. Sci.* **352,** 41–49 (2010).
51. Schuster, P. Studies on hydrogen bonding: The interaction between carbonyl and hydroxyl groups. *Int. J. Quantum Chem.* **3,** 851–871 (1969).
52. Cheong, W. J., Keum, Y. I. & Ko, J. H. The hydroxyl group-solvent and carbonyl group-solvent specific interactions for some selected solutes including positional isomers in acetonitrile/water mixed solvents monitored by HPLC. *Bull. Korean Chem. Soc.* **23,** 65–70 (2002).
53. Reddy, S. K. & Balasubramanian, S. Liquid dimethyl carbonate: A quantum chemical and molecular dynamics study. *J. Phys. Chem. B* **116,** 14892–14902 (2012).

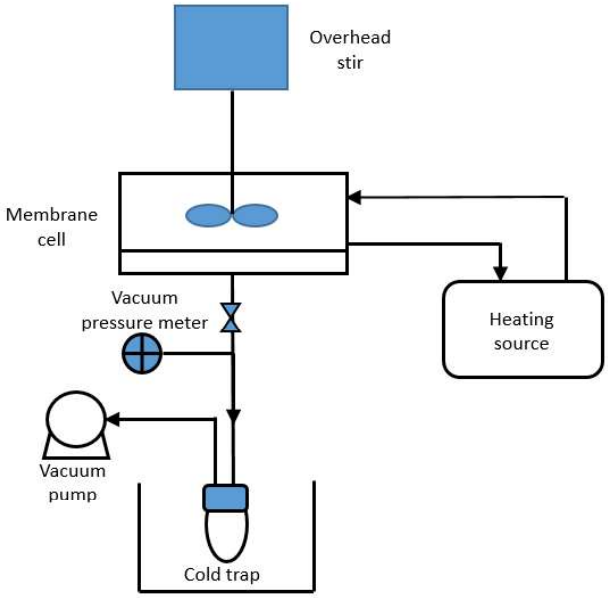
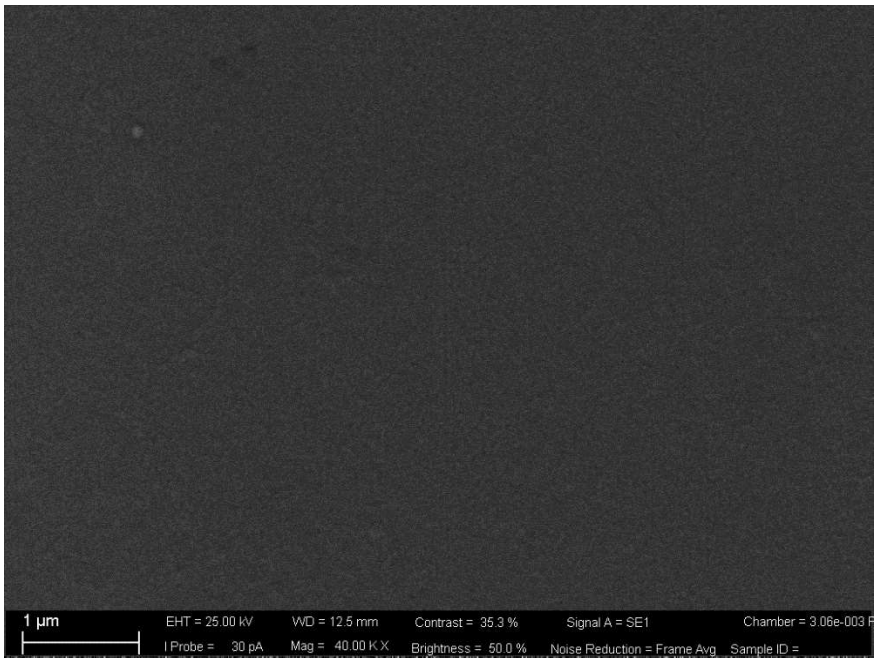
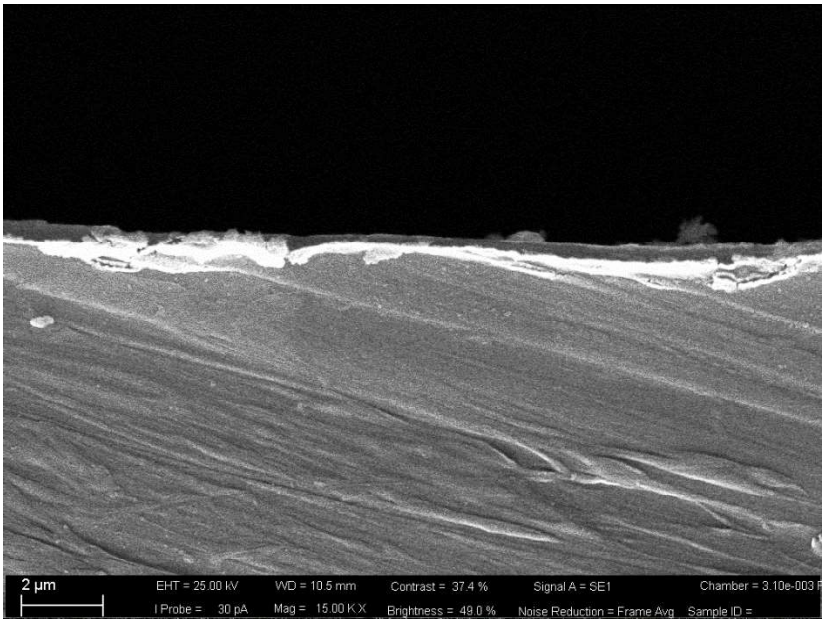


Figure 1. Scheme of the PV experimental set-up



(a)



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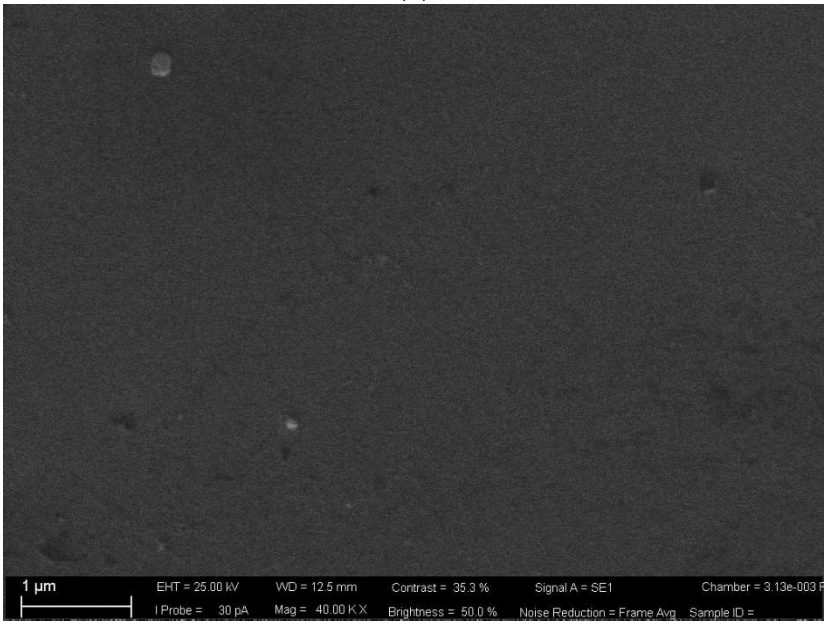


(c)

Figure 2. SEM image of PEEK-WC membrane. Top surface of the membrane (a) with magnification 40.00 KX; cross section (b) with magnification 15.00 KX; and bottom surface (c) with magnification 40.00 KX

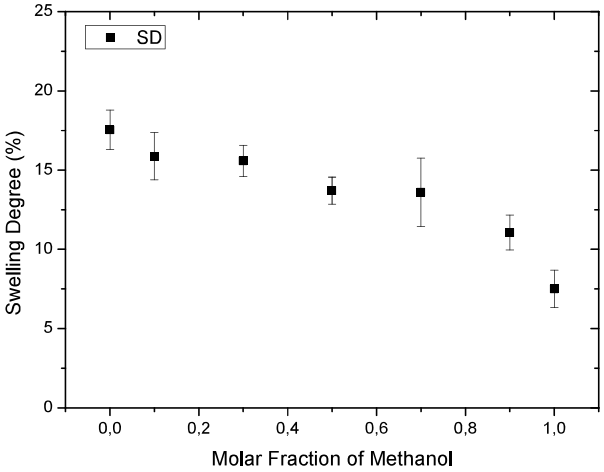


Figure 3. Swelling degree in different methanol/DMC mixtures.

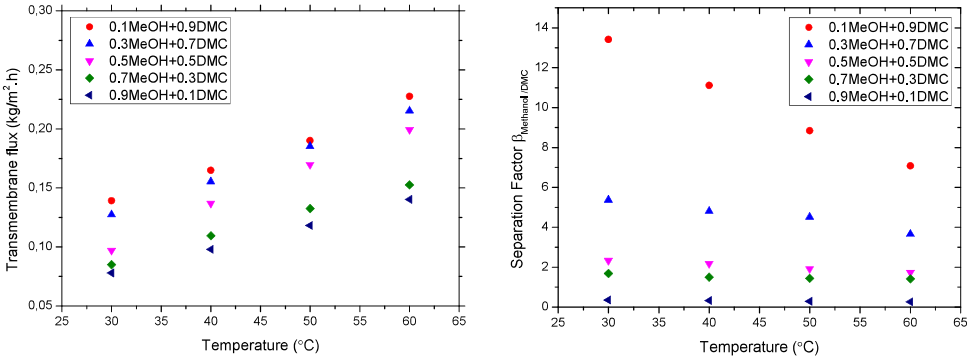


Figure 4. The effect of concentration and temperature on transmembrane flux and separation factor

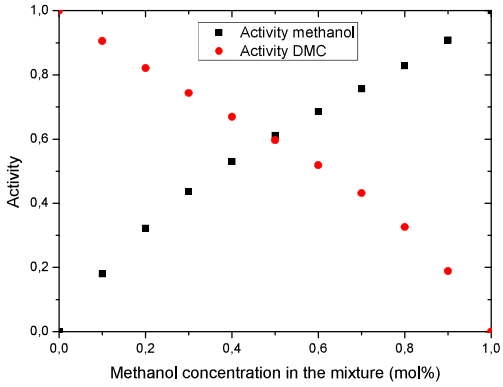
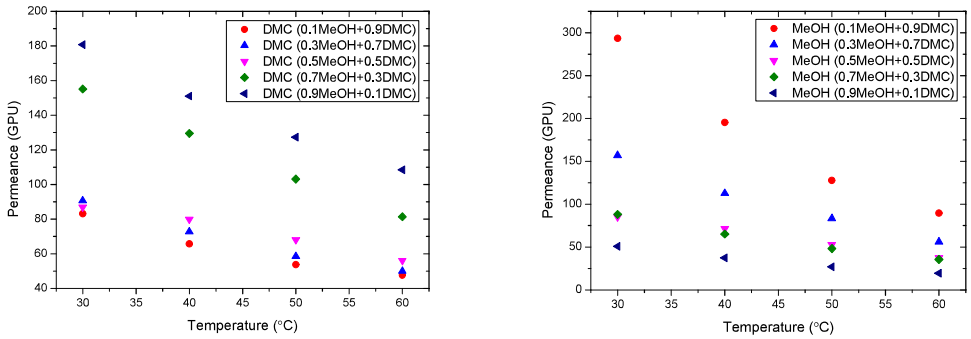


Figure 5. Variation of activity of methanol and DMC in their binary mixture



(a) (b)

Figure 6. Permeance of DMC (a) and methanol (b) at different temperatures and concentrations

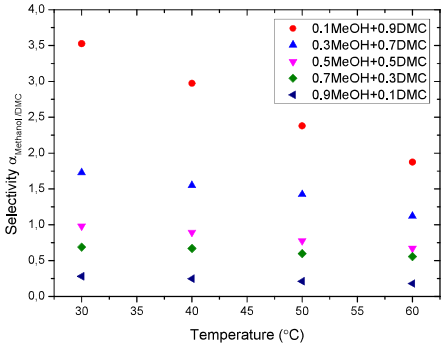
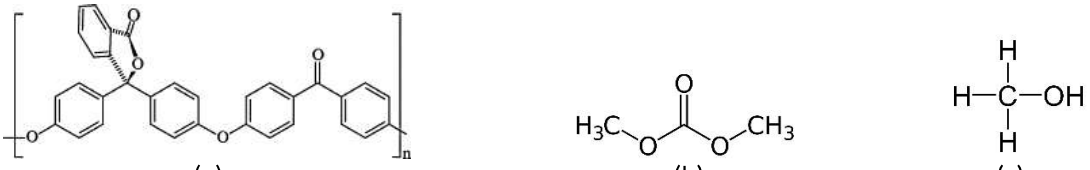


Figure 7. Selectivity of PEEK-WC membrane in the separation of DMC/methanol at different concentrations and temperatures



(a) (b) (c)

Figure 8. Molecular structure of (a) PEEK-WC, (b) DMC and (c) methanol

Table 1. Hansen solubility parameters of pure methanol, DMC and PEEK-WC at different concentrations

Material	Methods	δ_D	δ_P	δ_H	δ_t
Methanol		15.1	12.3	22.3	29.6
Dimethyl carbonate		15.5	3.9	9.7	18.7
PEEK-WC	Yamamoto[46]	19.2	8.3	3.9	21.3
	Stefanis-Panayiotou[47]	25.5	-8	5.6	27.3
	Van Krevelen[48]	18.9	2.8	6.2	20.1
	Hoy[49]	16.5	11	14.6	24.6
Mixture					
0,1 MeOH + 0,9 DMC		15.5	4.3	10.3	19.1
0,3 MeOH + 0,7 DMC		15.4	5.3	11.9	20.2
0,5 MeOH + 0,5 DMC		15.4	6.6	13.8	21.7
0,7 MeOH + 0,3 DMC		15.3	8.3	16.4	23.9
0,9 MeOH + 0,1 DMC		15.2	10.7	19.9	27.3

Table 2. Solubility vector distance (δ_t) of different estimation methods of Hansen solubility parameters of PEEK-WC

Material	Yamamoto	Stefanis-Panayiotou	Van Krevelen	Hoy
Methanol	20.5	33.5	20.2	8.3
Dimethyl carbonate	10.4	23.6	7.7	8.9
Mixture				
0,1 MeOH + 0,9 DMC	10.6	24.0	8.1	8.2
0,3 MeOH + 0,7 DMC	11.4	24.9	9.3	6.6
0,5 MeOH + 0,5 DMC	12.6	26.3	11.1	5.0
0,7 MeOH + 0,3 DMC	14.7	28.3	13.6	4.0
0,9 MeOH + 0,1 DMC	18.1	31.3	17.5	6.0

Table 3.Comparison of pervaporation performances of methanol/DMC separation membranes in literatures

Membrane material	Feed Methanol concentration (wt%)	Temperature (℃)	Flux ($g/m^2 \cdot h$)	Separation Factor	Permeance (GPU)	Selectivity	Ref.
Chitosan/silica	30-70	30-50	850-1265	29-49	-	-	58
Poly(vinyl alcohol)	40-70	50-40	154-510	2.8-37	-	-	59
Nano-Silica/ polydimethylsiloxane	70	40	702	3.97	-	-	60
PDMS/PVDF	72	40	487.2	3.95	~$1X10^4$ – $8.4X10^4$ DMC ~$2X10^3$-$1.7X10^4$ MeOH	-	61
Silicotungstic acid hydrate/Chitosan	10-70	30-60	1163-1500	52-67.3	-	-	62
Chitosan hollow fiber membrane	10-90	20-50	150-500	4-24	~50-100 DMC ~720-1200 MeOH	14-17	63
Poly(acrylic acid)/poly(vinyl alcohol)	10-90	40-80	3000	1.8-13	~20-200 DMC ~80-180 MeOH	~0.2-5.8	26
Crosslinked chitosan	6-70	25-55	30-500	10-90	-	-	27
PDMS and PTMSP	9.1-80.3	40	7.2-828	1.8-4.2	~700-1800 DMC ~70-177 MeOH	-	64
PEEK-WC	3.8-96.2	30-50	78-227	0.25-13.4	~48-180 DMC ~20-293 MeOH	~0.2-3.5	This work