**Graphene oxide – filled polyimide membranes in pervaporative separation of
azeotropic Methanol–MTBE mixtures**

Roberto Castro-Muñoz^{a,b,c}, Francesco Galiano^a, Óscar de la Iglesia^d, Vlastimil Fíla^b,
Carlos Téllez^c, Joaquín Coronas^{c*}, Alberto Figoli^{a*}

(a) Institute on Membrane Technology, ITM-CNR, c/o University of Calabria
Via P. Bucci 17c, 87030 Rende (CS), Italy
E-mail: a.figoli@itm.cnr.it

(b) University of Chemistry and Technology Prague
Technická 5, 166 28 Prague 6, Czech Republic.

(c) Chemical and Environmental Engineering Department, Instituto de Nanociencia
de Aragón (INA) and Instituto de Ciencia de Materiales de Aragón (ICMA),
Universidad de Zaragoza-CSIC, 50018 Zaragoza, Spain.
E-mail: coronas@unizar.es

(d) Centro Universitario de la Defensa Zaragoza,
Academia General Militar, 50090 Zaragoza, Spain

Abstract

Graphene oxide (GO)-polyimide mixed matrix membranes (MMMs) were produced using chloroform by solvent evaporation. The membranes have been used, for the first time, in pervaporation (PV) for the separation of azeotropic methanol (MeOH)- methyl *tert*-butyl ether (MTBE) mixtures (14.3 and 85.7%, respectively). The effect of the GO

loading in the PV process was investigated. The PV experiments were carried out at different feed operating temperatures (25–45 °C). Furthermore, an analysis of the PV process through the Arrhenius relationship has been given. The feed temperature (in the range of 25–45 °C) affected the permeation of both components producing an increase in total permeate flux; however, separation factor was compromised. Indeed, the best permeate fluxes (ca. 0.091 kg m⁻² h⁻¹) of the MMMs (containing 4 wt.-% GO) were found at 45 °C, while the best separation factor ($\alpha=28$) was found at 1.0 wt.-% GO at 25 °C. In addition, the membranes were characterized by TGA, SEM, DSC, solvent uptake and mechanical test (Young's modulus). Finally, the performance of the GO-polyimide membranes was compared with other polymeric and MMMs membranes at the azeotropic conditions.

Keywords: Pervaporation; Matrimid® 5218; Graphene oxide, Methanol (MeOH); Methyl *tert*-butyl ether (MTBE)

Nomenclature

PV: pervaporation

MeOH : methanol

MTBE: methyl *tert*-butyl ether

CA: cellulose acetate

PVP: poly(N-vinyl-2-pyrrolidone)

PVA: poly(vinyl alcohol)

PLA: poly(lactic acid)

50 PES-C: polyarylethersulfone with cardo
51 EVAc: poly(ethylene-co-vinyl acetate)
52 PEEKWC: poly(ether ether ketone)
53 PAMHEMA: 2-hydroxyethyl methacrylate
54 J: permeate flux
55 α : separation factor
56 SEM: Scanning electron microscopy
57 DSC: Differential scanning calorimetry
58 TGA: Thermo-gravimetric analysis
59 DS: Degree of swelling

60

61 1. Introduction

62 Pervaporation (PV) technology is well known as the merging of permeation and
63 evaporation processes. This membrane-based process is able to separate organic-
64 organic mixtures formed by close-boiling compounds (R. Castro-Muñoz, De La Iglesia,
65 Fila, Téllez, & Coronas, 2018; Luis & Van Der Bruggen, 2015). For instance, ~~m~~Methanol
66 (MeOH)- methyl *tert*-butyl ether (MTBE) is one of the most explored organic-organic
67 mixture due to the fact that this separation comprises the purification of MTBE, which is
68 a common octane enhancer in the production of lead-free gasoline. Even though MTBE
69 use has been banned in some countries (e.g. USA) as a consequence of its effects on
70 groundwater contamination, it is still produced and used in European and Asian
71 countries in order to meet the growing demand of fuel worldwide production (M.
72 Winterberg, E. Schulte-Korne, U. Peters, 2010). MeOH, on the other side, is used as a

73 fuel, as well as in the production of several chemicals. Typically, MeOH is able to react
74 with isobutylene, producing MTBE; however, minimum boiling azeotrope (14.3% MeOH
75 and 85.7% MTBE) is produced ([Sridhar, Smitha, & Shaik, 2017](#)). Within the MTBE
76 production, the presence of methanol is a drawback to produce a highly pure MTBE.
77 Methanol removal is generally performed by means of conventional distillation
78 technology. Nevertheless, distillation requires high-energy consumption to reach high-
79 pressure steam and thus carry out the separation. At this point, PV has proven to be
80 more energy efficient and lower cost process, which makes attractive such technology
81 for a possible replacement of the conventional distillation. To date, several types of
82 hydrophilic polymers have been proposed in preparing membranes aiming this
83 pervaporation separation, such as poly(lactic acid) (PLA) ([F. Galiano et al., 2018](#);
84 [Zereshki, Figoli, Madaeni, Simone, & Drioli, 2010](#)), cellulose acetate (CA) ([Cao, Shi, &
85 Chen, 2000](#)), poly(vinyl alcohol) (PVA) ([Khatinzadeh, Mahdyaifar, & Mehdizadeh, 2017](#);
86 [Peivasti, Madandar, & Mohammadi, 2008](#); [Rhim & Kim, 1999](#)), CA-poly(N-vinyl-2-
87 pyrrolidone) (PVP) blend ([Wu et al., 2008](#)), polyarylethersulfone with cardo (PES-C)
88 ([Han, Zhang, Zhu, & Liu, 2013](#)), poly(ethylene-co-vinyl acetate) (EVAc) ([Gozzelino &
89 Malucelli, 2004](#)), modified poly(ether ether ketone) (PEEKWC) ([Zereshki et al., 2011](#)),
90 PVA-CA blend ([Zhou, Gen, Han, Zhu, & Lin, 2013](#)), cross-linked 2-hydroxyethyl
91 methacrylate (PAMHEMA) ([Ray & Ray, 2006](#)), acrylic acid plasma polymerized poly(3-
92 hydroxybutyrate) ([Villegas, Romero, Parentis, Vidaurre, & Gottifredi, 2016](#)). Recently,
93 we proposed a commercial polyimide (Matrimid® 5218), which has been mainly
94 explored for gas separation applications ([R. Castro-Muñoz & Fila, 2018](#); [R. Castro-
95 Muñoz, Martin-Gil, Ahmad, & Fila, 2018](#)), to separate the MeOH from MTBE ([R. Castro-](#)

96 [Muñoz, Galiano, Fíla, Drioli, & Figoli, 2018a](#)). This is due to the fact that it displays good
97 chemical resistance, excellent thermal stability, mechanical performances and a
98 hydrophilic nature as well. Within this framework, our research was oriented to
99 investigate, for the first time, a possible improvement of MeOH selectivity of this
100 polyimide by incorporating a highly hydrophilic material, like graphene oxide (GO), into
101 its polymer matrix. It has been stated that GO displays highly oxygenated groups having
102 hydroxyl and epoxy functional groups on its basal planes. Furthermore, carbonyl and
103 carboxyl groups are located at the sheet edges. These functional groups indeed provide
104 a high hydrophilic profile to the material ([Singh et al., 2011](#)). Thereby, our aim was to
105 analyze the effect of GO filled into Matrimid® 5218 in the PV separation of azeotropic
106 MeOH-MTBE mixtures. The effect of operating temperature on total permeate flux and
107 separation factor was studied by doubling the GO content (at 1.0, 2.0, and 4.0 wt.%) in
108 the mixed matrix membranes (MMMs). In addition, the pure membrane and its MMMs
109 were characterized by differential scanning calorimetry (DSC), thermogravimetric
110 analysis (TGA), scanning electron microscopy (SEM), degree of swelling (uptake) and
111 mechanical properties.

112

113

114 **2. Materials and methods**

115 **2.1. Materials**

116 The commercial polyimide (Matrimid® 5218, molecular weight= 80,000) was kindly
117 supplied by Huntsman (Everberg, Belgium). The solvents, chloroform (CHCl₃, b.p. 61
118 °C, >99.9 %), methyl *tert*-butyl ether (MTBE) (99.7%), methanol (99.8%), were

purchased from Sigma-Aldrich (St. Louis, USA) and used without any further purification.

2.2. GO synthesis

The graphene oxide (GO) was synthesized using the procedure described by Castarlenas et al. (2017), in which Hummers' method (Hummers & Offeman, 1958) was followed. Firstly, the graphite ~~was~~ oxidized by a treatment using KMnO_4 and NaNO_3 in concentrated H_2SO_4 . In a round bottom flask, sodium nitrate (1.5 g) was dissolved in 70 mL of concentrated sulfuric acid. The dispersion was stirred at room temperature up to the NaNO_3 was completely dissolved (about 5-10 min). After this, graphite (3.0 g) (with a particle size of ca. of 5 μm , supplied by Richard Anton KG) was added to the solution under gently stirring during 30 min to facilitate a homogeneous suspension. Afterward, KMnO_4 (9.0 g) was slowly added to the suspension to skip the increase of the flask temperature due to the heat generated during the redox reaction. Once KMnO_4 addition was over, the temperature of the solution was gradually raised to 35 °C and then maintained under stirring for 30 min. To facilitate the control of the exothermic reaction, an ice bath was placed under the glass balloon. A brownish gray paste was formed. Then, using a Pasteur pipette, deionized water (140 mL) was slowly added to the slurry because of the smoke production was very fast. Once the deionized water was added, the suspension was kept under stirring overnight at 95 °C. Moreover, deionized water (500 mL) was added and then followed by H_2O_2 (20 mL) to reduce the residual permanganate. The round bottom flask was kept under stirring at 95 °C during 3 h. The resulting mixture was filtered and washed by means of 10 wt.% aqueous HCl solution. Finally, GO was centrifuged (10000 rpm, 15 min) and washed with water 4 times,

reaching a neutral pH. The product was dried at 80 °C overnight, obtaining a light brown solid (4.2 g).

Comentado [JC1]: Todo esto es casi igual al paper del JMS. Si llega a publicarse puede ser un problema porque Elsevier suele pasar una máquina para detectar autoplagio y a veces en base a eso rechazan papers sin revisar. Puede irse tranquilamente al SI dejando esas referencias.

2.3. Mixed matrix membrane preparation

Matrimid® 5218 was dried overnight in oven at 120 °C in order to remove any possible trace of moisture. Matrimid® 5218 MMMs were prepared by the dense-casting method and solvent evaporation (Roberto Castro-Muñoz, Fíla, & Dung, 2017). The dope solutions (10 wt.%) were prepared by dispersing the GO into the right chloroform amount. The GO loading for the MMMs was varied at 1, 2 and 4 wt.%. The GO solutions were stirred mixed and stirred for 24 h at room temperature. After this, a sonication period was applied for 15 min. Then, the precise amount of polymer was gradually added into the GO solutions. The final dope solutions were stirred for 24 h at room temperature, and then sonicated for 15 min. A glass plate was used for solution casting. The fabricated membranes were dried at room temperature for 24 h. Lately, they were peeled off from the glass plate, then dried at 50 °C under vacuum for 48 h. Finally, the membranes were stored in a desiccator up to be characterized and tested. The final thickness of the membranes was $64\pm 3.6\text{ }\mu\text{m}$ (measured with digital micrometer Mitutoyo with an accuracy of 1 μm).

2.4. Membrane characterization

2.4.1. Scanning electron microscopy (SEM)

The morphological structure of the pure Matrimid® 5218 and its mixed matrix membranes was observed by scanning electron microscopy (SEM). Membrane surface

165 and cross-section images were recorded by a scanning electron microscope (Zeiss
166 EVO, MA100, Assing, Italy). The membrane samples were attached to SEM carbon
167 stubs with a diameter of 1" using two-sided adhesive tape. The specimens were coated
168 through a sputtering process with gold (Au). The corresponding images were captured
169 at suitable magnification. The cross-sections were obtained by cryogenic fracture
170 immersion of the samples in liquid N₂.

171

172 2.4.2. Differential scanning calorimetry (DSC)

173 Differential scanning calorimetry (DSC) for T_g determination was recorded by SENSYS
174 Evo-TG-DSC calorimeter (Setaram Inc, USA). In general, the T_g routine was performed
175 at 30-450 °C in Pt crucibles (sample around 10 mg); argon as carrier gas (20 mL min⁻¹),
176 and a rate of 20° C min⁻¹. The T_g determination was done in triplicate.

177

178 2.4.2.1. Thermo-gravimetric analysis (TGA)

179 Thermal gGravimetric aAnalysis (TGA) using a Linseis (STA 700LT, Germany) was
180 recorded to investigate the thermal properties. The analysis was performed by placing
181 the sample (around 10 mg) in an alumina crucible. TGA analysis was carried out
182 heating up the sample to 700 °C with a heating rate of 20 °C min⁻¹ under nitrogen flow
183 of 20 mL min⁻¹. Temperature was hold at 700 °C for 30 min, and then cooled down to 50
184 °C at 20 °C min⁻¹.

185

186 2.4.2.2. Degree of swelling (DS)

-The degree of swelling (DS) of the Matrimid membrane and its GO-MMMs was measured for the azeotropic mixture (14.3% MeOH and 85.7% MTBE). We followed the previously reported procedure (R. Castro-Muñoz, Galiano, et al., 2018a), which basically consists on weighing three small membrane pieces (1x5 cm). Afterward, they were immersed in the azeotropic mixture at 30 °C for 48 h. The wet membranes were quickly wiped with tissue paper to remove the excess free liquid on their surface, being immediately weighed with a digital balance (Gibertini, Crystal 500, Italy, Crystal 500, Gibertini Elettronica srl, Milan, Italy). At this point, the DS was calculated using the following Eq. (1):

$$DS(\%) = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

where W_w and W_d are the weights of the membranes in wet and dry states, respectively.

2.4.2.3. Mechanical properties

Mechanical properties of the pure Matrimid membrane and its MMMs were measured by means of a Zwick/Roell Z2.5 test unit (BTC-FR2.5TN-D09, Germany). Measurements were normally carried out at room temperature (25 °C) using membrane samples of 1x5 cm. The samples were extended at the constant elongation rate of 5 mm·min⁻¹ until their break. In particular, Young's modulus data were recorded. For each membrane, four samples were analyzed, reporting the average and standard deviation. In addition, Young's modulus was also carried out on all the tested membranes after soaking them in a MeOH-MTBE solution (14.3-85.7 wt.%) at 25 °C for 1 week.

2.4.3. Pervaporation performance

The PV experiments were carried out in a laboratory-scale setup, which has been reported in previous studies (R. Castro-Muñoz, Galiano, et al., 2018a) (see Figure S1).

To evaluate the PV performance, an azeotropic MeOH-MTBE (14.3-85.7 wt.%, respectively) feed solution (250 mL) was placed in the feed tank. The feed operating temperature (at 25, 35, 45 °C) was controlled (accuracy of 0.01 °C) by using a thermo digital circulating bath (Neslab RTE-201, USA). The vacuum pressure on permeate side was set (at 0.0538 m bar) and controlled through a RV5 two-stage vacuum pump (Edwards, UK).

The membrane, (membrane area of 9.6 cm²) was placed on a porous support within the membrane cell. Once the running test has been started, the permeated vapor was condensed and collected in a glass trap, which was located in a liquid nitrogen condenser. Until reach the steady-state, the permeates were collected and weighted during 4 h. Thereby, the total permeate flux (J) was calculated according to the following Eq. (2):

$$J = \frac{Q}{A \cdot t} \quad (2)$$

where Q is the weight of the permeate (kg), A is the membrane area (m²) and t is the operating time (h). The partial flux (J_i) for component i was calculated by multiplying its weight fraction (y_i) in the collected permeate sample by the total permeate flux (J), as Eq. (3) describes:

$$J_i = y_i \cdot J \quad (3)$$

The separation factor (α) or MeOH selectivity was determined based on Eq. 4:

$$\alpha = \frac{y_{MeOH} / y_{MTBE}}{X_{MeOH} / X_{MTBE}} \quad (4)$$

where y and x are the weight fractions of the components in the permeate and feed, respectively. The permeate composition of each sample was determined by an Abbe 60 type direct reading refractometer (Bellingham+Stanley Ltd., UK) at 25 °C. The J and α values are the averages of more than two runs to ensure the accuracy of the results.

Comentado [JC2]: Mencionar el calibrado previo...

3. Results and discussion

3.1. Membrane characterization

3.1.1. DSC (T_g), TGA, and SEM

The glass transition (T_g) temperature for pure Matrimid® membranes is around 310.14 ± 0.22 °C, which has been well documented in literature (Dorosti, Omidkhah, & Abedini, 2014; Loloie, Mahsa, 2015). In the MMMs, such property tended to increase by increasing GO content (from 339.8 ± 1.4 at 1 wt% to 348.3 ± 0.2 at 4 wt%), as Table 1 reports. This trend was also reported by (Li et al., 2015). Generally, the T_g is related to the polymer chain rigidification at the filler-polymer interface. In other words, the T_g provides information about any possible interaction between both phases. In this regard, it has been reported that the GO sheets, which have two sides, can strongly interact with the polymer matrix (e.g. polyimides) by their both sides (Li et al., 2015).

Table 1. T_g values of the pure Matrimid® membrane and its GO-MMMs.

To investigate the effect of the GO on the thermal stability of the polyimide MMMs, the TGA profile was evaluated which can be seen in **Figure 1**. Firstly, for the pristine polyimide membrane, it can be seen that a ~10% weight loss starting from 50 up to 270 °C was observed. This weight loss is commonly attributed to the presence of residual solvent or guest molecules (Ordoñez, Balkus, Ferraris, & Musselman, 2010). After this, the pure polyimide membrane presented acceptable thermal stability from 300 up to reach ~470 °C. A decomposition temperature was noticed at ~520 °C (Martin-Gil et al., 2017), followed by a degradation step up to 650 °C with a ~50% weight loss, which is normally attributed to the decomposition of the polymer chains. The MMMs had a similar decomposition profile representing of such two major weight loss steps as well; however, it was noticed that MMMs started to be decomposed at a higher temperature, which was increased with increasing the GO content. At this point, the enhanced thermal stability may indicate a possible strong interfacial polymer-GO interaction (Li et al., 2015) being also consistent with the barrier effect of the filler to the gases involved in the membrane degradation.

Figure 1. TGA profile under N₂ of Matrimid® membrane and its GO-MMMs.

Con formato: Subíndice

Figure 2 shows the surface and cross-section SEM images of the MMMs. The pure polyimide membrane showed a uniform and smooth surface characteristic without signs of plastic deformation, which is common for dense polymeric membranes (Yanfeng Zhang, Musselman, Ferraris, & Balkus, 2008). Such uniform and smooth surface was

slightly lost by incorporating the GO, as **Figure 2** shows. It seems like the roughness of the membranes increased by increasing the filler content.

On the other hand, a crater-like pattern can be observed in pure polyimide cross-section view which has been already documented ([R. Castro-Muñoz, Galiano, Fila, Drioli, & Figoli, 2018b](#); [Yanfeng Zhang et al., 2008](#)). This crater-like pattern is typically generated during deformation by the freeze fracture ([Dorosti et al., 2014](#)). It can be noticed that such crater-like pattern was strongly increased by increasing the filler loading into the MMMs. Unfortunately, the GO flakes were not clearly visible in the cross-sectional views. This was also reported by [Melicchio & Favvas \(2018\)](#), who stated a possible homogeneous dispersion of the filler into the polyimide, which could be in agreement according to the observable non-agglomeration.

Figure 2. Membrane surface and cross-section SEM images of GO-Matrimid® MMMs.

3.1.2. Uptake determination and mechanical properties

The calculated uptake values are represented in **Figure 3**. The typical uptake of the pure polyimide is around 4.4 wt. % at the azeotropic concentration (14.3/85.7 wt. % MeOH-MTBE). Basically, a decreasing trend of uptake was noted with the increase of GO loading, displaying the lowest uptake value (MMMs containing 4 wt. % GO) around $\approx$ 2.329 wt. %. This tendency has been reported during the filling of GO into hydrophilic chitosan membranes ([Qian, Li, Wang, & Ji, 2018](#)). Basically, the decrease in uptake degree is associated to the strong GO-polymer interactions which, besides reducing the

availability of hydrophilic groups, could restrict the mobility of the polyimide chains and decrease even more the free volume of the polymer (in terms of MeOH-MTBE uptake). GO has proven, as multi-walled carbon nanotubes, to suppress the swelling degree of other polymers, like PVA membranes (Choi, Jegal, Kim, & Choi, 2008). Therefore, GO tends to provide a better stability to the polyimide against the swelling phenomenon in contact with the organic feed solution. Moreover, the results of the relatively low values of uptake prove the solvent resistance of the pristine and its MMMs

Figure 3. Uptake of Matrimid® membrane and its GO-MMMs at the azeotropic MeOH-MTBE (14.3/85.7 wt.%) concentrations (at 30°C).

When dealing with the stability of MMMs in PV separations, the mechanical properties, like Young's modulus, are commonly evaluated before and after exposure to the organic-organic mixture, as. **Table 2** reports. In pristine polyimide membrane, no appreciable variations on the properties were observed when soaking the membrane. This result can indicate the stability of the polyimide itself towards this organic-organic solution. In the MMMs, before soaking, Young's modulus was enhanced by adding low content of GO (1 wt.-%). Indeed, the improvement on mechanical properties by incorporation of GO into other polymers has been reported (Y. Zhang, Shen, Hou, Sutrisna, & Chen, 2017), where a good interfacial compatibility between GO and polymers is suggested. It has been stated that polymers can interact with the carboxylic groups of GO forming amide groups (J. Ma, Ping, & Dong, 2017). On the other hand,

Comentado [JC3]: Pero esto puede contradecirse con la disminución del módulo de Young que se ve a continuación, que sugiere que el material se hace menos rígido.... Pienso que el Go es más flexible que otros fillers. Yo me quedaría con el argumento de que se reducen los grupos hidrófilos. Aunque con esto hay que tener cuidado, es cierto que el MTBE u el Meo son polares, pero al hablar de grupos hidrófilos parece que se está pensando solo en wáter uptake, y no es el caso. En cuanto al free volumen, tiene sentido al menos en términos de MTBE-MeOH, que es lo que se observa

Comentado [JC4]: Falta el comentario general de cómo y porqué el módulo de Young disminuye con la carga... En general suele ser al revés (por lo menos con MOFs y zeolitas), por ejemplo: Mixed matrix membranes for gas separation by combination of silica MCM-41 and MOF NH2-MIL-53(Al) in glassy polymers Si no es así en GO, es porque la carga no es tan alta y el GO es más flexible que estos otros rellenos?

321 the incorporation of GO at higher loading was responsible of a decrease in membranes
322 mechanical properties. ~~Unfortunately, t~~The exposure of the MMMs into the azeotropic
323 mixture abruptly provoked the decrease of Young's modulus.

324

325

326 **Table 2.** Young's modulus measurements of the Matrimid® membrane and its GO-
327 MMMs before and after exposure to MeOH-MTBE solution (composition 14.3:85.7
328 wt.%).

329

330 3.2. Pervaporation tests

331 3.2.1. Effect of feed temperature and filler loading

332 **Figure 4** displays the effect of feed temperature, as well as GO loading into the MMMs,
333 on total permeate flux at specific vacuum pressure (data available in [supplementary](#)
334 [material](#), **Table S1**). Firstly, an increase in the total permeation rate was observed with
335 double increasing the GO loading. This trend is usually noticed during the embedding of
336 inorganic materials into polymer membranes, which may be a result of the free volume
337 increase as well as the possible interfacial selective gaps between GO laminates and
338 polyimide matrix, while the highly hydrophilic nature of the filler can also produce an
339 increase in the permeation rates by preferential adsorption of the more polar compound
340 (e.g. methanol).

341

Comentado [JC5]: Parece que faltaría algo aquí:

1) Pienso que no tiene que ser malo que el módulo disminuya al estar las membranas húmedas. Esto no implica ni que se disuelvan ni que se rompan.

2) Entiendo que se hacen más flexibles. Pero esto puedes matizarlo con la impresión que daban las membranas al sacarlas de la mezcla, etc.

Pero si damos a entender que es malo ("unfortunately") se sugiere que las membranas nos sirven, etc.

Comentado [JC6]: Quizá podamos dar aquí los momentos dipolares o las permitividades del metanol y MTBE para reforzar el argumento)

Figure 4. Total permeate flux as a function of the GO loading at different operating temperatures (14.3/85.7 wt.% MeOH/MTBE, pressure: 5.4×10^{-2} mbar). The curves are only guides to the eye.

Furthermore, an increase on total permeation rate was observed with temperature increase (in the range of 25-45 °C). Typically, the polymer chains tend to be more flexible at higher temperatures promoting the sorption ability of the components, leading to the increase of permeating compounds through the intermolecular distances of the polymeric matrix. Moreover, the MMMs displayed a higher permeate flux than the unfilled membrane (see **Figure 4** and **Table S1**). ~~In theory, t~~his is attributed to the enhancement of sorption and diffusion of the membranes containing GO, which are selective toward polar molecules.

The effect of the temperature on total permeate flux can be analyzed by using the so-called Arrhenius relationship (Eq. 5) (R. Castro-Muñoz, Galiano, et al., 2018a), as follows:

$$J = J_o \cdot \exp \left(-\frac{E_p}{R \cdot T} \right) \quad (5)$$

Where J_o is the pre-exponential factor, E_a is the apparent activation energy for permeation (for the total mixture and each component) and $R \cdot T$ is the common energy term. The linearization of the Eq. (5) through logarithmic laws allows the plotting of **Figure S2**, which displays the total fluxes as a function of the reciprocal of temperature

at azeotropic conditions. The figure confirms that an Arrhenius relationship exists between total fluxes and operating temperature. i.e. the total flux tends to increase with the increase of the temperature. Furthermore, the apparent activation energy (E_a), which can be calculated as the slope of the curve (**Figure S2**), and using the Eq. (5), can provide an idea on the relationship between the total flux and the GO content. From **Table 3**, it can be seen that the E_a values for total flux gradually decrease with the increase of filler loading, e.g. 15.1 in the pristine polyimide membranes to 9.7 kJ/mol in the MMMs-4 wt.% GO. In this regard, the E_a decrease towards methanol was more influenced than the one for MTBE in the range of handled temperatures. This means that the presence of GO contributed to reduce the energy needed for the components to permeate across the membranes (Constantino, Faria, Ribeiro, Loureiro, & Rodrigues, 2017); similar behavior was recently reported by Qian et al. (2018) during the PV application of polar molecules (e.g. water) through chitosan-GO membranes.

377

378

Table 3. Apparent activation energies for total permeate, MeOH and MTBE partial fluxes of the GO-MMMs at different GO loadings (Data obtained from **Figures S2-S4**).

381

Regarding the selectivity, the separation factor values decreased by embedding the GO into the polymer matrix, as **Figure 5** shows. It is likely that the incorporation of GO was not enough to compensate the distortion in the polyimide chains that it caused creating non selective pores (but still hydrophilic, see **Tables S3 and S4**). The decrease in separation efficiency can also be affected by the inorganic material preparation.

According to [Hung et al. \(2014\)](#), it is extremely challenging to form highly ordered and precise GO laminates. For instance, it has been stated that the repulsive electrostatic interactions produced by negatively charged carboxyl groups might usually create some out-of-order accumulation (i.e. wrinkles). Also, a large number of nonselective defects (basic plane holes) derived from the strong oxidization of Hummers method may penalize the membrane separation performance ([Huang, Liu, & Jin, 2017](#)). Finally, the distribution of functional groups in the surface of the GO sheets can be random, contributing to the heterogeneous distribution of polar sites along the composite membrane.

Figure 5. Separation factor as a function of the GO loading at different operating temperatures (14.3–85.7 wt.% MeOH–MTBE). The curves are only guides to the eye.

Furthermore, the decrease in separation factor was observed when the feed temperature was increased. Generally, ~~in fact,~~ the thermal motion of the polymeric chains facilitates the diffusion of larger molecules (like MTBE) through the membrane causing a decrease in membrane separation factor. This typical trend has been reported with other hydrophilic-based membranes based on PLA ([Zereshki et al., 2010](#)), PEEKWC ([Zereshki et al., 2011](#)), PVA ([Peivasti et al., 2008](#)), EVAc ([Gozzelino & Malucelli, 2004](#)) CA-(PVP) blend ([Wu et al., 2008](#)) used for the MeOH-MTBE separations. In addition, the decrease in separation factor is in agreement with the fact

Comentado [JC7]: Poner aquí los diámetros cinéticos de las dos moléculas para ilustrar lo que se dice

that activation energy values for MTBE are always larger than for methanol (see **Table 3**). The absence of negative values for the activation energy data reveals that the permeation of the species presented in these MMMs is less governed by the adsorption (Constantino et al., 2017).

3.2.2. Performance comparison of GO-polyimide MMMs with other polymeric membranes

The PV performance of polymeric and MMMs for any organic-organic separation, like MeOH-MTBE, through PV technology, depends directly on their properties (e.g. materials, nature, structure, thickness), physicochemical properties and concentration of the compounds contained in the mixture, as well as the operating conditions (e.g. temperature, vacuum pressure, feed flow rate and so on) (Francesco Galiano, Falbo, & Figoli, 2016). All the aforementioned information makes difficult to make a fair comparison of PV data with works where different conditions have been applied (Figoli, Santoro, Galiano, & Basile, 2015). However, a comparison of the performance of GO-polyimide MMMs with other polymeric and MMMs membranes used for the same separation at close azeotropic conditions, is provided in **Table 4**.

Table 4. Comparison of GO-MMMs performance with some pure polymeric and MMMs at close MeOH-MTBE azeotropic conditions.

The best performance, in terms of permeate flux, of the GO-polyimide membranes was achieved with 4 wt.% GO, which displayed values of total flux of about $0.091 \text{ kg m}^{-2} \text{ h}^{-1}$

Comentado [JC8]: Para evitar confusioines (con el exponente 10^3) poner en todas las tablsas y figuras $\text{g m}^{-2} \text{ h}^{-1}$

433 with a separation factor around 9. Considering the permeate fluxes, these hydrophilic
 434 MMMs displayed relatively better performance than other reported membranes, as
 435 PEEKWC ($0.068 \text{ kg m}^{-2} \text{ h}^{-1}$) and cross-linked PVA ($0.036 \text{ kg m}^{-2} \text{ h}^{-1}$), but lower
 436 performance respect to other polymers which showed highly permeability values, such
 437 as PVA-CA blend, PLA, PVA, PVA-CA blend, acrylic acid plasma polymerized poly(3-
 438 hydroxybutyrate), and cross-linked PAMHEMA (see **Table 4**). However, some of these
 439 highly permeable polymers did not offer high separation factor values, e.g. PLA ($\alpha=5$),
 440 acrylic acid plasma polymerized poly(3-hydroxybutyrate) ($\alpha=3$); where GO-polyimide
 441 membranes (4 wt.%) offered better MeOH separation factor than those polymeric
 442 materials.
 443 On the other hand, the GO-polyimide MMMs found their best MeOH selectivity ($\alpha=28$)
 444 containing 1.0 wt. % GO. This separation factor is comparable with a PVA membrane
 445 ($\alpha=25$). On the contrary, these GO-polyimide MMMs (1.0 wt.% GO) did not overcome
 446 the MeOH selectivity for chemically modified membranes including such as cross-linked
 447 PVA, cross-linked PAMHEMA, or blended materials (e.g. PVA-CA, CA-PVP).
 448 To date, some other MMMs have been tested for this organic-organic separation, e.g.
 449 polyamide filled with Al_2O_3 (Kopeck, Meller, Kujawski, & Kujawa, 2013), CA filled with
 450 HZSM5 (X. Ma et al., 2008), sulfonated polyarylethersufone filled with $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]_n$
 451 (Han et al., 2014), and CA filled with ZnO (Wang, Yang, Luo, & Dai, 2009), which have
 452 easily overcome the separation performance of the GO-polyimide MMMs. While, the
 453 separation factor value of GO-polyimide MMMs 1.0 wt.% ($\alpha=28$) can be comparable just
 454 with MMMs based on polyamide filled with Al_2O_3 ($\alpha=20$).

455

456

457 **4. Conclusions**

458 ~~In this study,~~ GO-polyimide mixed matrix membranes have been successfully prepared
459 and tested for the PV separation of MeOH-MTBE azeotropic mixture. The effect of
460 operating temperature has been evaluated. In this regard, all MMMs displayed an
461 enhanced total permeate flux compared to the unfilled polyimide membrane. In fact, the
462 temperature dependency (in the range of 25-45 °C) of the total permeate flux was
463 corroborated by the Arrhenius relationship. Interestingly, it was found that the increase
464 of handled feed temperature determined not only the higher MeOH permeation, but also
465 promoted the MTBE permeation, which provoked the loose of the MeOH selectivity.
466 Thereby, the MMMs found their best separation factor at the lower operating
467 temperature and lower GO loading, whereas their best total flux was found at the
468 highest filler loading and operating temperature. The results showed that the
469 performance of the GO-polyimide membranes, related to the PV separation of MeOH-
470 MTBE mixture, are comparable with the ones observed for other polymers. When
471 dealing with the comparison to other reported MMMs, our MMMs cannot overcome such
472 separation performance; however, it is important to consider that really low filler loading
473 was embedded (1-4 wt.%), while most of the reported MMMs reached to incorporate
474 between 10-30 wt.%. Finally, based on the results obtained, it is possible to conclude
475 that GO-polyimide membranes have the potentiality to be used in PV for the separation
476 of MeOH/MTBE azeotropic mixture. Moreover, this study can be considered as starting
477 point for using ~~such GO-polymeric~~ membranes in the separation of other
478 organic/organic mixtures.

479

480 **Acknowledgments**

481 R. Castro-Muñoz acknowledges the European Commission - Education, Audiovisual
482 and Culture Executive Agency (EACEA) for his PhD scholarship under the program:
483 Erasmus Mundus Doctorate in Membrane Engineering – EUDIME (FPA No 2011-0014,
484 Edition V, <http://eudime.unical.it>). Financial support from the Spanish MINECO and
485 FEDER (MAT2016-77290-R), the Aragón Government (T43-17R) and the ESF is also
486 gratefully acknowledged.

References

- Cao, S., Shi, Y., & Chen, G. (2000). Influence of acetylation degree of cellulose acetate on pervaporation properties for MeOH / MTBE mixture, *165*, 89–97.
- Castarlenas, S., Téllez, C., & Coronas, J. (2017). Gas separation with mixed matrix membranes obtained from MOF UiO-66-graphite oxide hybrids. *Journal of Membrane Science*, *526*(November 2016), 205–211.
<https://doi.org/10.1016/j.memsci.2016.12.041>
- Castro-Muñoz, R., De La Iglesia, Ó., Fila, V., Téllez, C., & Coronas, J. (2018). Pervaporation-assisted esterification reactions by means of mixed matrix membranes. *Industrial and Engineering Chemistry Research* *10.1021/acs.iecr.8b01564*. <https://doi.org/10.1021/acs.iecr.8b01564>
- Castro-Muñoz, R., & Fila, V. (2018). Progress on incorporating zeolites in matrimid® 5218 mixed matrix membranes towards gas separation. *Membranes* *10.3390/membranes8020030*, *8*(2). <https://doi.org/10.3390/membranes8020030>
- Castro-Muñoz, R., Fila, V., & Dung, C. T. (2017). Mixed Matrix Membranes Based on PIMs for Gas Permeation: Principles, Synthesis, and Current Status. *Chemical Engineering Communications*, *204*(3), 295–309.
<https://doi.org/10.1080/00986445.2016.1273832>
- Castro-Muñoz, R., Galiano, F., Fila, V., Drioli, E., & Figoli, A. (2018a). Matrimid®5218 dense membrane for the separation of azeotropic MeOH-MTBE mixtures by pervaporation. *Separation and Purification Technology*, *199*, 27–36.
<https://doi.org/10.1016/j.seppur.2018.01.045>
- Castro-Muñoz, R., Galiano, F., Fila, V., Drioli, E., & Figoli, A. (2018b). Matrimid ® 5218

510 dense membrane for the separation of azeotropic MeOH- MTBE mixtures by
 511 pervaporation. *Separation and Purification Technology*, 199(November 2017), 27–
 512 36. <https://doi.org/10.1016/j.seppur.2018.01.045>

513 Castro-Muñoz, R., Martín-Gil, V., Ahmad, M. Z., & Fila, V. (2018). Matrimid® 5218 in
 514 preparation of membranes for gas separation - current state-of-the-art. *Chemical*
 515 *Engineering Communications*, 205, 161–196.
 516 <https://doi.org/http://dx.doi.org/10.1080/00986445.2017.1378647>

517 Constantino, D. S. M., Faria, R. P. V., Ribeiro, A. M., Loureiro, J. M., & Rodrigues, A. E.
 518 (2017). Performance Evaluation of Pervaporation Technology for Process
 519 Intensification of Butyl Acrylate Synthesis. *Industrial and Engineering Chemistry*
 520 *Research*, 56(45), 13064–13074. <https://doi.org/10.1021/acs.iecr.7b01328>

521 Dorosti, F., Omidkhah, M., & Abedini, R. (2014). Fabrication and characterization of
 522 Matrimid/MIL-53 mixed matrix membrane for CO₂/CH₄ separation. *Chemical*
 523 *Engineering Research and Design*, 92(11), 2439–2448.
 524 <https://doi.org/10.1016/j.cherd.2014.02.018>

525 Figoli, A., Santoro, S., Galiano, F., & Basile, A. (2015). Pervaporation membranes:
 526 preparation, characterization, and application. In A. Basile, A. Figoli, & M. Khayet
 527 (Eds.), *Pervaporation, vapour permeation and membrane distillation* (First edit, pp.
 528 281–304). Cambridge UK: Elsevier Ltd.

529 Galiano, F., Falbo, F., & Figoli, A. (2016). Polymeric Pervaporation Membranes :
 530 Organic-Organic Separation. In O. Visakh & P. Nazarenko (Eds.), *Nanostructured*
 531 *Polymer Membranes*, (pp. 281–304). Massachusetts, United States: Scrivener
 532 Publishing LLC.

533 Galiano, F., Ghanim, A. H., Rashid, K. T., Marino, T., Simone, S., Alsahy, Q. F., &
 534 Figoli, A. (2018). Preparation and characterization of green polylactic acid (PLA)
 535 membranes for organic/organic separation by pervaporation. *Clean Technologies*
 536 *and Environmental Policy*, 1–12. [https://doi.org/https://doi.org/10.1007/s10098-018-](https://doi.org/https://doi.org/10.1007/s10098-018-1621-4)
 537 1621-4
 538 Gozzelino, G., & Malucelli, G. (2004). Permeation of methanol / methyl- t -butyl ether
 539 mixtures through poly (ethylene-co-vinyl acetate) films, 235, 35–44.
 540 <https://doi.org/10.1016/j.colsurfa.2004.01.004>
 541 Han, G. L., Zhang, Q. G., Zhu, A. M., & Liu, Q. L. (2013). Pervaporation separation of
 542 methanol/methyl tert-butyl ether mixtures using polyarylethersulfone with cardo
 543 membranes. *Separation and Purification Technology*, 107, 211–218.
 544 <https://doi.org/10.1016/j.seppur.2013.01.039>
 545 Han, G. L., Zhou, K., Lai, A. N., Zhang, Q. G., Zhu, A. M., & Lin, Q. (2014). [Cu 2 (bdc
 546) 2 (bpy)] n / SPES-C mixed matrix membranes for separation of methanol /
 547 methyl tert-butyl ether mixtures. *Journal of Membrane Science*, 454, 36–43.
 548 <https://doi.org/10.1016/j.memsci.2013.11.049>
 549 Huang, K., Liu, G., & Jin, W. (2017). Vapor transport in graphene oxide laminates and
 550 their application in pervaporation. *Current Opinion in Chemical Engineering*, 16,
 551 56–64. <https://doi.org/10.1016/j.coche.2017.04.009>
 552 Hummers, W. S., & Offeman, R. E. (1958). Preparation of Graphitic Oxide. *Journal of*
 553 *the American Chemical Society*, 80(6), 1339. <https://doi.org/10.1021/ja01539a017>
 554 Hung, W. S., An, Q. F., De Guzman, M., Lin, H. Y., Huang, S. H., Liu, W. R., ... Lai, J.
 555 Y. (2014). Pressure-assisted self-assembly technique for fabricating composite

membranes consisting of highly ordered selective laminate layers of amphiphilic graphene oxide. *Carbon*, 68, 670–677.
<https://doi.org/10.1016/j.carbon.2013.11.048>

Choi, J. H., Jegal, J., Kim, W. N., & Choi, H. S. (2008). Incorporation of Multiwalled Carbon Nanotubes into Poly(vinyl alcohol) Membranes for Use in the Pervaporation of Water/Ethanol Mixtures. *Journal of Applied Polymer Science*, 111, 2186–2193.

Khatinzadeh, G., Mahdizarfar, M., & Mehdizadeh, A. (2017). Pervaporation (PV) Separation of Methanol / Methyl Tert-butyl Ether Mixtures in Low Permeate Pressure Conditions, 7(2), 43–48.

Kopec, R., Meller, M., Kujawski, W., & Kujawa, J. (2013). Polyamide-6 based pervaporation membranes for organic-organic separation. *Separation and Purification Technology*, 110, 63–73. <https://doi.org/10.1016/j.seppur.2013.03.007>

Li, X., Ma, L., Zhang, H., Wang, S., Jiang, Z., Guo, R., ... Wang, B. (2015). Synergistic effect of combining carbon nanotubes and graphene oxide in mixed matrix membranes for efficient CO₂ separation. *Journal of Membrane Science*, 479, 1–10.
<https://doi.org/10.1016/j.memsci.2015.01.014>

Loloei, Mahsa, et al. (2015). Improved CO₂ separation performance of Matrimid®5218 membrane by addition of low molecular weight polyethylene glycol. *Greenhouse Gases: Science and Technology*, 5, 1–15. <https://doi.org/10.1002/ghg>

Luis, P., & Van Der Bruggen, B. (2015). The driving force as key element to evaluate the pervaporation performance of multicomponent mixtures. *Separation and Purification Technology*, 148, 94–102. <https://doi.org/10.1016/j.seppur.2015.05.006>

M. Winterberg, E. Schulte-Korne, U. Peters, F. N. (2010). Methyl Tert-Butyl Ether. In

579 *Ullmann's Encyclopedia of Industrial Chemistry* (pp. 413–454). Wiley-VCH,
580 Weinheim. <https://doi.org/10.1002/14356007.a16>

581 Ma, J., Ping, D., & Dong, X. (2017). Recent Developments of Graphene Oxide-Based
582 Membranes : A Review. *Membranes*, 7, 1–29.
583 <https://doi.org/10.3390/membranes7030052>

584 Ma, X., Hu, C., Guo, R., Fang, X., Wu, H., & Jiang, Z. (2008). HZSM5-filled cellulose
585 acetate membranes for pervaporation separation of methanol/MTBE mixtures.
586 *Separation and Purification Technology*, 59(1), 34–42.
587 <https://doi.org/10.1016/j.seppur.2007.05.023>

588 Martin-Gil, V., Lopez, A., Hrabanek, P., Mallada, R., Vankelecom, I. F. J., & Fila, V.
589 (2017). Study of different titanosilicate (TS-1 and ETS-10) as fillers for Mixed Matrix
590 Membranes for CO₂/CH₄ gas separation applications. *Journal of Membrane*
591 *Science*, 523(December 2015), 24–35.
592 <https://doi.org/10.1016/j.memsci.2016.09.041>

593 Melicchio, A., & Favvas, E. P. (2018). Preparation and characterization of graphene
594 oxide as a candidate filler material for the preparation of mixed matrix polyimide
595 membranes. *Surface & Coatings Technology*, 349(June), 1058–1068.
596 <https://doi.org/10.1016/j.surfcoat.2018.06.082>

597 Ordoñez, M. J. C., Balkus, K. J., Ferraris, J. P., & Musselman, I. H. (2010). Molecular
598 sieving realized with ZIF-8/Matrimid?? mixed-matrix membranes. *Journal of*
599 *Membrane Science*, 361(1–2), 28–37.
600 <https://doi.org/10.1016/j.memsci.2010.06.017>

601 Peivasti, M., Madandar, A., & Mohammadi, T. (2008). Effect of operating conditions on

pervaporation of methanol / methyl tert -butyl ether mixtures, 47, 1069–1074.
<https://doi.org/10.1016/j.cep.2007.08.005>

Qian, X., Li, N., Wang, Q., & Ji, S. (2018). Chitosan/graphene oxide mixed matrix membrane with enhanced water permeability for high-salinity water desalination by pervaporation. *Desalination*, 438(March), 83–96.
<https://doi.org/10.1016/j.desal.2018.03.031>

Ray, S., & Ray, S. K. (2006). Synthesis of highly methanol selective membranes for separation of methyl tertiary butyl ether (MTBE)– methanol mixtures by pervaporation, 278, 279–289. <https://doi.org/10.1016/j.memsci.2005.11.011>

Rhim, J., & Kim, Y. (1999). Pervaporation Separation of MTBE – Methanol Mixtures Using Cross-linked PVA Membranes, (August), 1699–1707.

Singh, V., Joung, D., Zhai, L., Das, S., Khondaker, S. I., & Seal, S. (2011). Graphene based materials: Past, present and future. *Progress in Materials Science*, 56(8), 1178–1271. <https://doi.org/10.1016/j.pmatsci.2011.03.003>

Sridhar, S., Smitha, B., & Shaik, A. (2017). Pervaporation - Based Separation of Methanol / MTBE Mixtures — A Review, 2119(August).
<https://doi.org/10.1081/SPM-200054949>

Villegas, M., Romero, A. I., Parentis, M. L., Vidaurre, E. F. C., & Gottifredi, J. C. (2016). Chemical Engineering Research and Design Acrylic acid plasma polymerized poly (3-hydroxybutyrate) membranes for methanol / MTBE separation by pervaporation. *Chemical Engineering Research and Design*, 109, 234–248.
<https://doi.org/10.1016/j.cherd.2016.01.018>

Wang, Y., Yang, L., Luo, G., & Dai, Y. (2009). Preparation of cellulose acetate

625 membrane filled with metal oxide particles for the pervaporation separation of
 626 methanol / methyl tert -butyl ether mixtures. *Chemical Engineering Journal*, 146, 6–
 627 10. <https://doi.org/10.1016/j.cej.2008.05.009>

628 Wu, H., Fang, X., Zhang, X., Jiang, Z., Li, B., & Ma, X. (2008). Cellulose acetate – poly (
 629 N-vinyl-2-pyrrolidone) blend membrane for pervaporation separation of methanol /
 630 MTBE mixtures, 64, 183–191. <https://doi.org/10.1016/j.seppur.2008.09.013>

631 Zereszki, S., Figoli, A., Madaeni, S. S., Simone, S., & Drioli, E. (2010). Pervaporation
 632 Separation of Methanol / Methyl tert -Butyl Ether with Poly (lactic acid)
 633 Membranes. *Journal of Applied Polymer Science*, 118, 1364–1371.
 634 <https://doi.org/10.1002/app>

635 Zereszki, S., Figoli, A., Madaeni, S. S., Simone, S., Esmailinezhad, M., & Drioli, E.
 636 (2011). Pervaporation separation of MeOH / MTBE mixtures with modified PEEK
 637 membrane : Effect of operating conditions. *Journal of Membrane Science*, 371(1–
 638 2), 1–9. <https://doi.org/10.1016/j.memsci.2010.11.068>

639 Zhang, Y., Musselman, I. H., Ferraris, J. P., & Balkus, K. J. (2008). Gas permeability
 640 properties of mixed-matrix matrimid membranes containing a carbon aerogel: A
 641 material with both micropores and mesopores. *Industrial and Engineering*
 642 *Chemistry Research*, 47(8), 2794–2802. <https://doi.org/10.1021/ie0713689>

643 Zhang, Y., Shen, Q., Hou, J., Sutrisna, P., & Chen, V. (2017). Shear-aligned graphene
 644 oxide laminate/Pebax ultrathin composite hollow fiber membranes using a facile
 645 dip-coating approach. *Journal of Materials Chemistry A*, 5, 7732–7737.
 646 <https://doi.org/10.1039/c6ta10395b>

647 Zhou, K., Gen, Q., Han, G. L., Zhu, A. M., & Lin, Q. (2013). Pervaporation of water –

648 ethanol and methanol – MTBE mixtures using poly (vinyl alcohol)/ cellulose
649 acetate blended membranes. *Journal of Membrane Science*, 448, 93–101.
650 <https://doi.org/10.1016/j.memsci.2013.08.005>
651
652

Figure 1. TGA profile under N₂ of Matrimid® membrane and its GO-MMMs.

Con formato: Subíndice

Figure 2. Membrane surface and cross-section SEM images of GO-Matrimid® MMMs.

657

Figure 3. Uptake of Matrimid® membrane and its GO-MMMs at the azeotropic MeOH-MTBE concentration (at 30°C)

658

659

Comentado [JC9]: en estas figuras frente a la carga:
1) Aumentar el tamaño de los puntos y el grosor de las barras de error
2)2) que la escala vaya de -0.2 hasta 4.2 para que los puntos y las barras no estén encima de los ejes, etc.

660 **Figure 4.** Total permeate flux as a function of the GO loading at different operating temperatures (14.3: 85.7 wt.% MeOH-
661 MTBE, pressure: 5.4×10^{-2} mbar). The curves are only guides to the eye.

Comentado [JC10]: 1) Aumentar el tamaño de los puntos y el grosor de las barras de error
2) que la escala vaya de -0.2 hasta 4.2 para que los puntos y las barras no estén encima de los ejes, etc.
3) Lo dicho: Para evitar confusiones pondría en todas partes g·m⁻²·h⁻¹

664 **Figure 5.** Separation factor as a function of the GO loading at different operating temperatures (14.3: 85.7 wt.% MeOH-
665 MTBE). The curves are only guides to the eye.

Comentado [JC11]: 1) Aumentar el tamaño de los puntos y el grosor de las barras de error
2) que la escala vaya de -0.2 hasta 4.2 para que los puntos y las barras no estén encima de los ejes, etc.
3) Lo dicho: Para evitar confusiones pondría en todas partes g·m-2·h-1

Table 1. T_g values of the pure Matrimid® membrane and its GO-MMMs.

<i>Membrane</i>	<i>T_g (°C)</i>
Pure Matrimid membrane	310.14±0.22
1 wt.% GO	339.78±1.44
2 wt.% GO	346.765±0.106
4 wt.% GO	348.325±0.24

Data represents the means ± standard deviation with 3-4 replicates for each test.

684

685 **Table 2.** Young’s modulus measurements of the Matrimid® membrane and its GO-MMMs before and after exposure to
686 MeOH-MTBE solution (composition 14.3:85.7 wt.%).

687

688

689

690

691

692

693

694

695

696

697

698

699

700

Sample:	Before	After
	Young’s modulus (N/mm ²)	Young’s modulus (N/mm ²)
Pure Matrimid membrane	1100±137	1024±159
1 wt.% GO	1153±121	358±64
2 wt.% GO	1080±124	234±35
4 wt.% GO	942±28	206±36

Data represents the means ± standard deviation with 3-4 replicates for each test.

Table 3. Apparent activation energies for total permeate, methanol and MTBE partial fluxes of the GO-MMMs at different GO loadings (Data obtained from **Figures S2-S4**).

GO loading (wt.%)	Activation energy values		
	(kJ/mol)		
	Total	Methanol	MTBE
0	15.1	10.7	13.3
1	10.4	8.8	13.2
2	9.7	8.3	9.7
4	9.7	7.0	9.6

Table 4. Comparison of GO-MMMs performance with some pure polymeric and MMMs at close azeotropic conditions.

Membrane material	Filler loading:	Concentration of MeOH-MTBE mixture	Operating conditions	J (kg m ⁻² h ⁻¹)	Separation factor (α)	Reference:
GO-polyimide	4 wt. %	14.3 wt. % MeOH 85.7 wt. % MTBE	45 °C, 0.0538 mbar	0.091	9.0	This work
PEEKWC	-	15 wt. % MeOH 85 wt. % MTBE	40 °C, 6.1 mbar	0.068	10	(Zereshki et al., 2011)
PVA	-	30 wt. % MeOH 70 wt. % MTBE	45 °C, 15 mbar	0.900	25	(Peivasti et al., 2008)
PLA	-	15 wt. % MeOH 85 wt. % MTBE	30 °C, 6 mbar	0.620	5	(Zereshki et al., 2010)
CA-PVP blend	-	20 wt. % MeOH 80 wt. % MTBE	45 °C, 3 mbar	0.225	340	(Wu et al., 2008)
PVA-CA blend	-	15 wt. % MeOH 85 wt. % MTBE	45 °C, 17 mbar	796*	1427	(Zhou et al., 2013)
Acrylic acid plasma polymerized poly(3-hydroxybutyrate)	-	20 wt. % MeOH 80 wt. % MTBE	45 °C, 1.3 mbar	11*	3	(Villegas et al., 2016)

Cross-linked PVA	-	20 wt.% MeOH	50 °C, 0.4 mbar	0.036	1230	(Rhim & Kim, 1999)
		80 wt.% MTBE				
Cross-linked PAMHEMA	-	11 wt.% MeOH	50 °C, 1.33 mbar	0.140	150	(Ray & Ray, 2006)
		89 wt.% MTBE				
Polyamide filled with Al ₂ O ₃	10 wt. %	50 wt.% MeOH	30 °C	15*	20	(Kopeck et al., 2013)
		50 wt.% MTBE				
CA filled with HZSM5	0.5 wt. %	20 wt.% MeOH	40 °C, 3.3 mbar	4.2*	150	(X. Ma et al., 2008)
		80 wt.% MTBE				
Sulfonated polyarylethersulfone with cardo filled with [Cu ₂ (bdc) ₂ (bpy)] _n	30 wt. %	15 wt.% MeOH	40 °C, 6 mbar	0.28	2300	(Han et al., 2014)
		85 wt.% MTBE				
CA filled with ZnO	10 wt. %	31 wt.% MeOH	40 °C, 5 mbar	2*	400	(Wang et al., 2009)
		69 wt.% MTBE				

* Normalized flux by thickness.