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Pebax[®] 1041 supported membranes with carbon nanotubes prepared via phase inversion for CO₂/N₂ separation

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This work shows the preparation of Pebax[®] 1041 films from solutions in DMAc and water-DMAc emulsions, meaning an alternative to those prepared by extrusion that can be found in the literature. These membranes were tested in post-combustion CO₂ capture, in the separation of a 15/85 (v/v) CO₂/N₂ mixture. Self-supported membranes of Pebax[®] 1041 were prepared by solvent evaporation and phase inversion. The characterization of these films defined the intrinsic properties of this polymer in terms of chemical structure, crystallinity, thermal stability and gas separation performance (CO₂ permeability of 30 Barrer with a CO₂/N₂ selectivity of 21 at 35°C and 3 bar feed pressure). Supported Pebax[®] 1041 membranes were also developed to decrease the Pebax[®] thickness (in the 1.5–10 µm range), reaching a higher permeance. These membranes were prepared by a phase inversion process consisting of the precipitation of a Pebax[®] 1041/DMAc solution in water and dispersing it to form a stable emulsion that was drop-cast on PSF asymmetric supports. Once dried, the polymer formed a dense continuous layer. The phase inversion methodology is “greener” than solvent evaporation since dimethylacetamide is not released as toxic vapours during membrane preparation. The amount drop-cast led to a different selective layer thickness, which was enhanced by the dispersion of MWCNTs in the polymer emulsion. The properties of the Pebax[®] selective layer were studied by thermogravimetry and measuring the contact angle of the membrane surface, and the optimal CO₂/N₂ selectivity (22.6) was obtained with a CO₂ permeance of 3.0 GPU.

Introduction

With the Energy Roadmap 2050, the European Union has set the target of reducing the CO₂ emissions by at least 80–95% with a less than 8 percentage efficiency loss.¹ The major CO₂ emissions are related to power generation in fossil fuel plants and certain manufacturing plants such as those producing cement and steel, and capture technologies are necessary to reduce these emissions, reaching the desired target. Post-combustion CO₂ capture is the simplest technology to implement, since it can be easily adapted to already existing industrial facilities. Within this specific technology, the separation based on chemical absorption with amine aqueous solutions is the most widely used because of its high performance. However, besides their potential toxicity, absorption with amines shows some drawbacks in the regeneration of the CO₂-laden solvent, because of the high heat requirements and energy consumption and the evaporation losses of water during the process.² Membrane technology can mean an alternative with a number of benefits over other gas separation processes. The gas separation with membranes does

not require a phase change, with the corresponding lower operation cost. Besides, membrane modules build compact systems and can operate under steady-state conditions.³

The separation of CO₂ from post-combustion exhaust gases consists basically in the separation of a CO₂/N₂ mixture. Working with polymers with excellent transport parameters for this binary mixture is essential to fabricate productive membranes. Merkel et. al. have reported that the performance of Polaris[™] membranes, with a CO₂ permeance greater than 1000 GPU and a CO₂/N₂ selectivity of 50, can reach a CO₂ capture in the flue gas of 90%, with an estimated use of about 16% of plant energy at a cost as low as \$23/ton CO₂.⁴ Poly(ether-block-amide) copolymers (commercialized under the trademark Pebax[®]) have promising features for gas separation. These polymers combine linear chains of rigid polyamide (PA6 or PA12) with flexible, CO₂-philic polyether oxide (PEO) or poly(tetramethylene oxide) (PTMO) segments, building crystalline/amorphous structures that show the properties of both thermoplastics and rubbers. It is believed that the hard amide block provides the mechanical strength, whereas gas selective transport occurs primarily through the soft ether block.⁵ The transport properties through Pebax[®] films depend on the volume fraction of the PA and PEO/PTMO blocks, the PA crystallinity, the density and availability for interactions with polar groups, the block nature and the length and organization of the polymer chains in the films.⁶ Our research group published recently the influence of the casting solution concentration in the preparation of Pebax[®] 1657 membranes, showing a gas

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separation performance of 100 Barrer of CO₂ with a CO₂/N₂ selectivity of 35.⁷ Khosravi et. al.⁸ also studied the effect of functional group ratio in PEBAX copolymer on propylene/propane separation for facilitated olefin transport membranes.

The membranes in this work were prepared with an specific grade, Pebax[®] 1041, consisting of 75 wt% of PA12 and 25 wt% of PTMO.⁹ This Pebax[®] grade is specially developed for food uses because its excellent barrier properties to bacteria. Although information in the literature about this polymer is scarce, membranes prepared by extrusion with this Pebax[®] grade have also been developed for different applications, such as nanofiltration,¹⁰ dermal therapeutic systems¹¹ and pervaporation.¹² When tested for gas separation, they showed a CO₂ permeability of 23.3 Barrer with an ideal CO₂/N₂ selectivity of 33.3, at 25 °C operating temperature and 4 bar feed pressure.¹³ In a different work, 39.7 Barrer CO₂ permeability with a CO₂/CH₄ selectivity of 11 and a H₂S permeability of 175 Barrer with a H₂S/CH₄ selectivity of 49 was observed, operating at 35 °C and under 10 atm feed pressure.¹⁴ Offord et. al.¹⁵ also tested extruded Pebax[®] 1041 films for CO₂/N₂ separation at 35 °C and under feed pressures between ca. 1 and 5 atm, reaching a CO₂ permeability of 40 Barrer with a CO₂/N₂ selectivity of 22. As usual, the mechanism of this gas separation can be explained by the solution-diffusion model.¹⁶

Here we show the preparation of Pebax[®] 1041 membranes following the phase inversion route, forming emulsions of precipitated polymer that were drop-cast on polysulfone (PSF) asymmetric supports. This technique has already been used with several polymers to prepare supports¹⁷ but never before for Pebax[®]-type polymers to the best of our knowledge, although Wahab and Sunarti¹⁸ explored this possibility. The development of new methodologies of membrane preparation is of paramount importance to obtain the best of recent discovered polymers whose performances could be enhanced by preparing supported membranes with selective skin layers. The prepared membranes were tested for the separation of CO₂/N₂ mixtures and their gas separation performance is

discussed and compared to that of self-supported dense membranes.

Results and discussion

Pebax[®] 1041 self-supported membranes

The cross-section of the Pebax[®] 1041 self-supported membranes can be seen in the SEM images of Fig. 1. Fig. 1a shows the section of a membrane prepared by solvent evaporation from a casting solution of 5 wt% of Pebax[®] 1041 in DMAc, while Fig. 1b-c show those of the membranes prepared by phase inversion from casting solutions of 2, 5 and 10 wt% of Pebax[®] 1041 in DMAc, respectively. It can be seen that in all cases the resulting membranes had a dense morphology. Since high porosity is always obtained when preparing membranes via phase inversion, these pores may have collapsed during the drying stage. Despite rinsing the films changing solvents to others of lower polarity (from water to MeOH and n-hexane), the porosity of the Pebax[®] membranes collapsed during the drying, resulting in a dense symmetric structure. Noteworthy, the thickness of the membranes was independent of the concentration of polymer in the casting solution (between 2 and 10 wt%), showing regular value of 33±5 μm when the volume of the casting solution was accordingly adjusted. In wet state (just after the phase inversion and before drying), the membranes showed a thickness of 1 mm. This means that the membrane thickness diminished by 66% during the drying stage, which is in agreement with the collapse of porosity. Importantly, a phase inversion methodology means a greener alternative than solvent evaporation. In the former the DMAc, in which Pebax[®] 1041 is dissolved, remains absorbed in the coagulation bath of water during the membrane preparation, while in the solvent evaporation technique toxic vapors of DMAc are generated.

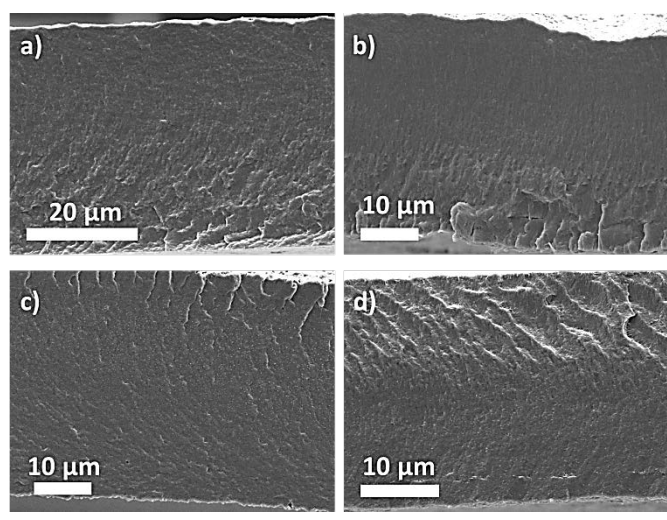


Fig. 1. SEM images of the cross sections of self-supported Pebax[®] 1041 membranes prepared by solvent evaporation from 5 wt% polymer solutions in DMAc (a), and phase inversion from 2 (b), 5 (c) and 10 wt% polymer solutions in DMAc (d).

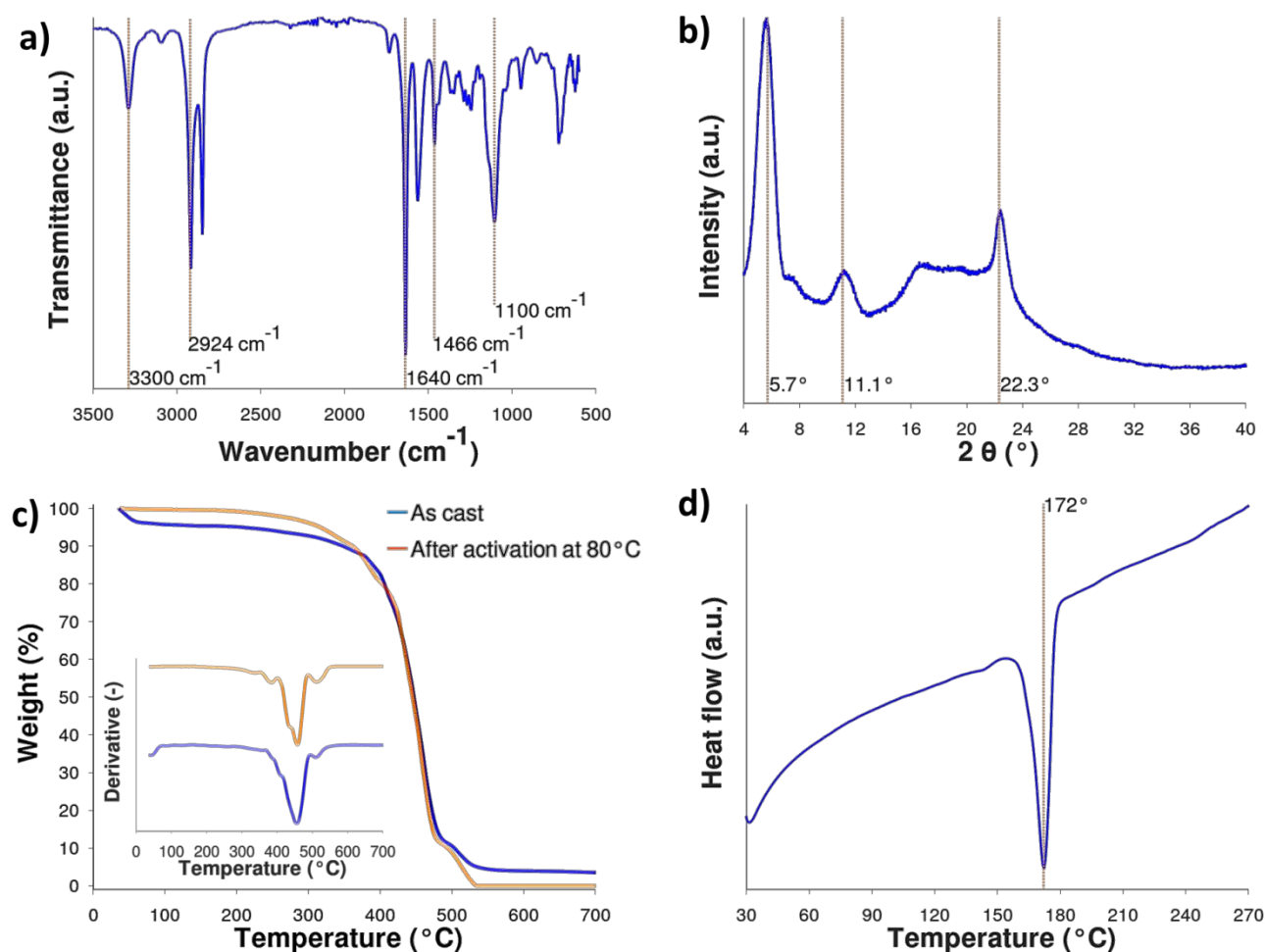


Fig. 2. Characterization of self-supported Pebax® 1041 membranes prepared by phase inversion from 5 wt% polymer solutions in DMAC: FTIR (a), XRD (b), TGA curves and derivatives (inset) in flowing air (c) and DSC analysis in N₂ atmosphere (d).

Several characterization techniques were used to inquire into the properties of the self-supported Pebax® 1041 membranes prepared by phase inversion. The chemical structure of the membranes is studied in the FTIR spectra in Fig.

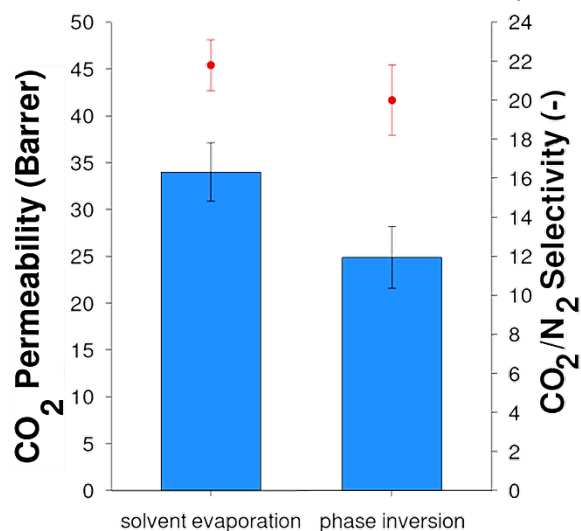


Fig. 3. Gas separation performance of the self-supported Pebax® 1041 membranes prepared from 5 wt% polymer solutions for the CO₂/N₂ mixture at 35 °C and 3 bar feed pressure. Bars stand for permeability and scatters for selectivity.

2a. Vibrations corresponding to the segments of polyamide are visible in the peak at 3300 cm⁻¹, related to the –N–H– linkages, and in the peak at 1640 cm⁻¹, assigned to the H–N–C=O group.¹⁹ Regarding the soft segment part of PTMO, the peak at 1100 cm⁻¹ is attributed to the stretching vibration of the C–O–C ether group.²⁰ Finally, the IR spectrum shows two peaks at 1466 and 2924 cm⁻¹, which correspond to the stretching and bending vibrations of the aliphatic –C–H bond.²¹ Since Pebax® 1041 is a semicrystalline copolymer an XRD analysis was also conducted. The diffractogram in Fig. 2b exhibits three characteristic peaks at 5.7°, 11.1° and 22.3° 2θ values consistent with both crystalline and amorphous PTMO and PA12 phases.²² The thermal stability of the membranes was studied by TGA and the results can be seen in Fig. 2c. The membrane degradation occurs in three steps. The first step (up to 100 °C) is due to the loss of the residual solvent and adsorbed water. The second step (from 350 to 490 °C) corresponds to the major polymer thermal degradation. Eventually, the third step over 490 °C shows the carbonization of the degraded chains. It can be seen that after treating the membranes at 80 °C the first step corresponding to the water loss disappeared, proving the right activation of the membranes. Besides, the lack of a degradation step at 150 °C means that all the DMAC was removed during the

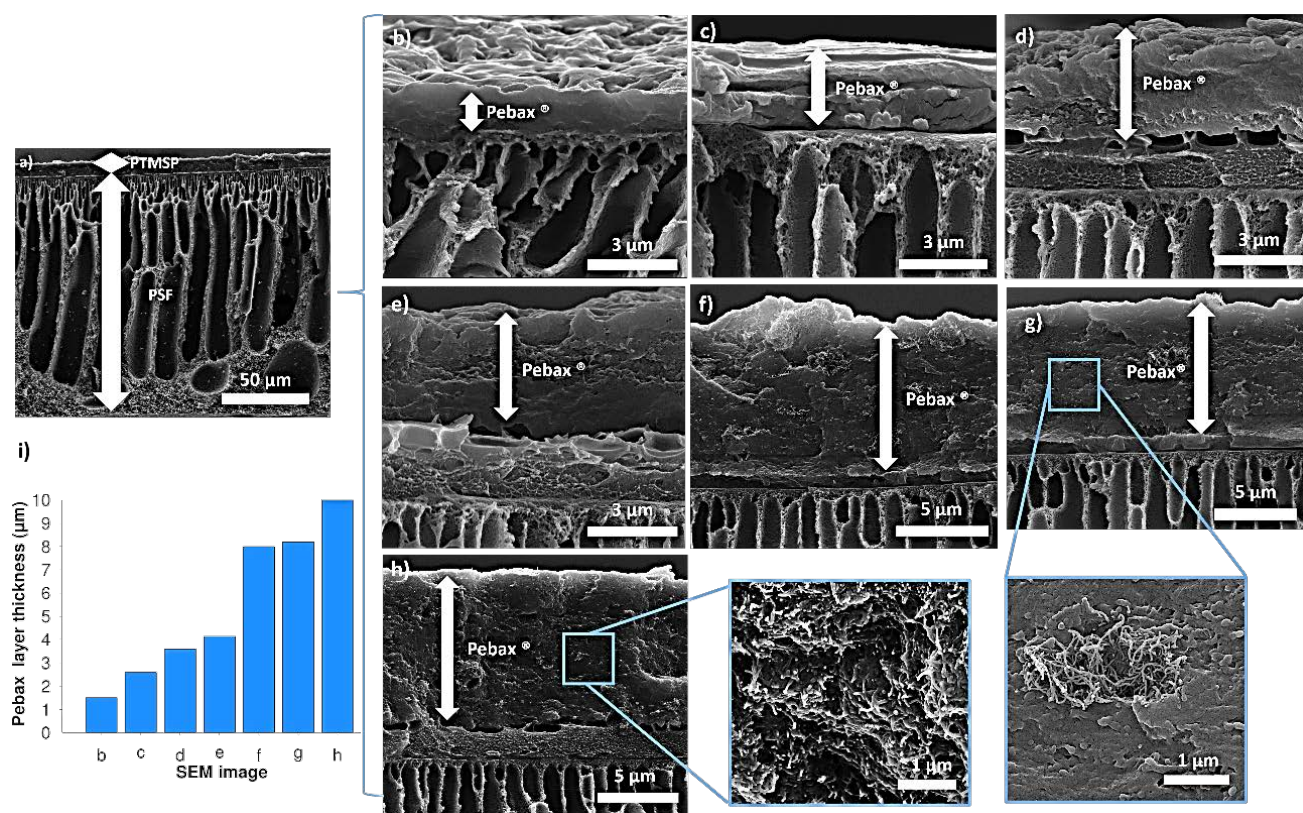


Fig. 4. SEM images of the cross-section of the PSF supports coated with a PTMSP gutter layer (a), bare Pebax® 1041 supported membranes with different Pebax® thicknesses: 1.5 μm (b), 2.6 μm (c), 3.6 μm (d), 4.1 μm (e) and 8.0 μm (f) and Pebax® 1041 supported membranes containing MWCNTs, also with different Pebax® thicknesses: 8.2 μm (g) and 10 μm (h). A graph showing the thickness of the Pebax® 1041 layer for the different volumes is also included (i).

phase inversion process. Finally, the thermal properties of the Pebax® 1041 membranes were further investigated by DSC (see Fig. 2d). The membranes show one endothermic peak at 172 °C, corresponding to the fusion of the crystalline fraction of PA12.²³ The fusion of PTMO cannot be seen because it occurs below room temperature.

Both self-supported Pebax® 1041 membranes prepared by solvent evaporation and phase inversion were tested for the separation of CO₂/N₂ mixtures (15/85 v/v proportion) at 35 °C and 3 bar of feed pressure. The results in Fig. 3 show that the gas separation performance of both kinds of membranes was similar, with CO₂ permeabilities between 25 and 35 Barrer (corresponding to a CO₂ permeance of 0.6 GPU) and a CO₂/N₂ selectivity around 21.

Pebax® 1041 supported membranes

After the successful preparation of self-supported Pebax® 1041 membranes, supported membranes were developed to decrease the thickness of the Pebax® selective layer in an attempt that should lead to higher permeances in the gas separation tests. However, the thickness of the Pebax® 1041 membranes was difficult to reduce following the previous phase inversion technique. Firstly, the polymer casting solution formed immediately a viscous gel upon cooling down. This made impossible to manipulate the as made polymer solution for the fabrication of the thin layers. Secondly, the use of DMAc in the casting solution damaged the PSF supports. For that reasons a different methodology was approached to prepare

the desired supported membranes. Once Pebax® 1041 was dissolved in DMAc, the polymer was precipitated in DI water and emulsified. This Pebax® 1041 emulsion was used for the preparation of the membranes by drop-casting, as shown below.

Pebax® 1041 supported membranes were prepared by drop-casting on PSF asymmetric supports previously coated with a gutter layer of PTMSP (Fig. 4a). Several amounts of Pebax® emulsion in DI water (0.5 wt%, verified by TGA) from 400 to 2400 μL were deposited. With 400 μL the selective Pebax® 1041 layer had a thickness of 1.5 μm (see Fig. 4b) and this thickness raised gradually with the amount cast up to the maximal value of 10 μm (as shown in Fig. 4h). In order to increase the performance of the Pebax® selective layer, MWCNTs were dispersed in the polymeric emulsion. Fig. 4 shows a comparison between two analogous supported membranes: one membrane prepared with the bare polymeric Pebax® 1041 emulsion (Fig. 4f) and another prepared with the emulsion containing MWCNTs (Fig. 4g), which are visible in the magnification. Both membranes have a similar selective layer thickness (8.0 and 8.2 μm, respectively), which will help to elucidate the influence of the MWCNTs in the gas separation performance of the membranes. In comparison with other fillers typically dispersed in polymeric phases, such as metal-organic frameworks (MOFs) or covalent organic frameworks (COFs),²⁴ the use of MWCNTs means a reduction in the amount of material dispersed, since only a 1 wt% loading is necessary.

This diminishes the cost for membrane preparation, resulting in more economical composites.

The thermal stability of the different membranes prepared was also tested by thermogravimetry. According to the TGA results shown in Fig. 5, Pebax® 1041 losses 86.5 % of its weight in the temperature interval between 400 and 490 °C, while PSF does not show any weight change in this range. Therefore, TGA results can be used to quantify the amount of Pebax® deposited on each kind of supported membrane, considering the weight loss within this temperature interval. The values in Table 1 reveal that the amount of Pebax® 1041 in the different supported membranes is comprehended between 9.3 and 26 % of the total weight of the composite. As expected, such amount increased following the same tendency as the thickness of the selective layer observed in Fig. 4.

Contact angle measurements were also performed with this kind of membranes to test the hydrophilicity/hydrophobicity of their surface. According to Fig. 6 and Fig. S1, the PSF support has a contact angle of 70° and it rose up to 83° after being coated with PTMSP. The contact angle of Pebax® 1041 is 74°, a value which, although smaller than that of PTMSP (83°), would explain the compatibility between both polymers. Regarding the supported Pebax® membranes, most contact angles are

comprehended between 73° and 77°, similar to the contact angle of self-supported Pebax® 1041 (74°). This means that the surface is well coated by the Pebax® selective layer. The only exception is the membrane prepared with 1.5 µm of Pebax® layer, whose contact angle is 84°. This suggests that the amount of Pebax® was not sufficient to cover all the surface of the support and the properties of PTMSP dominated the contact angle observation carried out. The oscillating values of contact angle are due to the fact that the Pebax® layer was prepared from a polymeric emulsion and the surface of the layer is not completely smooth. In any event and despite the heterogeneity of the surface, the contact angle decreases as a function of the thickness of the membrane. Finally, the surface of supported Pebax® 1041 membranes with and without MWCNTs can be seen in the SEM images of Figure S2. Both membranes have a heterogeneous surface with high roughness, which is due to the fact that the Pebax® layer was prepared by drop casting from a polymeric emulsion. Moreover, the incorporation of MWCNTs did not seem to alter the surface of the membranes since both images show similar texture. The XRD patterns of these two membranes are also provided in Figure S3.

The gas separation performance of the Pebax® 1041 supported membranes is represented in Fig. 7. It can be seen that the PSF supports coated with PTMSP had a CO₂ permeance of 41.4±1.0 GPU with an almost negligible CO₂/N₂ selectivity (2.7±1.2). A selectivity value over the unity assesses the right distribution of PTMSP over the PSF support since porous PSF has no separation capacity itself. As the amount of Pebax® deposited increased from 400 to 2400 µL (i.e. as the thickness of the Pebax® selective layer increased from 1.4 to 8.0 µm), the CO₂ permeance followed the opposite tendency, decreasing from 19.0±5.2 to 2.7±0.4 GPU, respectively. The result is logic due to the new resistance added to the composite membrane. On the contrary, the CO₂/N₂ selectivity increased as the thickness of the Pebax® layer became higher, reaching a maximal value of 17.4±0.4. The selectivity obtained was near that of the self-supported membranes prepared by phase inversion (21 according to the results in Fig. 3). This high selectivity result together with the continuity in the Pebax® layer, with no visible interruptions or holes in the SEM images of Fig. 2, may claim that, at the studied conditions, 8.0 µm was the minimal thickness necessary to build a defect-free Pebax® selective layer.

When MWCNTs were added to the composites maintaining a similar thickness of the Pebax® layer (8.2 µm, according to the SEM images of Fig. 4), the CO₂ permeance raised slightly to 3.0±0.1 GPU and, at the same time, the CO₂/N₂ selectivity increased to 22.6±0.6, reaching a slightly higher value than that obtained with the self-supported membranes (see Fig. 3). Increasing the thickness of the selective layer to 10 µm reduced the CO₂ permeance to 2.2±0.0 GPU and resulted in a CO₂/N₂ selectivity of 23.4±0.5, similar to the previous membrane in statistical terms. Apparently, the MWCNTs have a positive influence the gas separation performance of the membranes;²⁵⁻²⁸ helping to achieve the intrinsic selectivity of Pebax® 1041. Supported membranes with an 8 µm selective layer of Pebax® 1041 with and without MWCNTs can be compared in Fig. 7a.

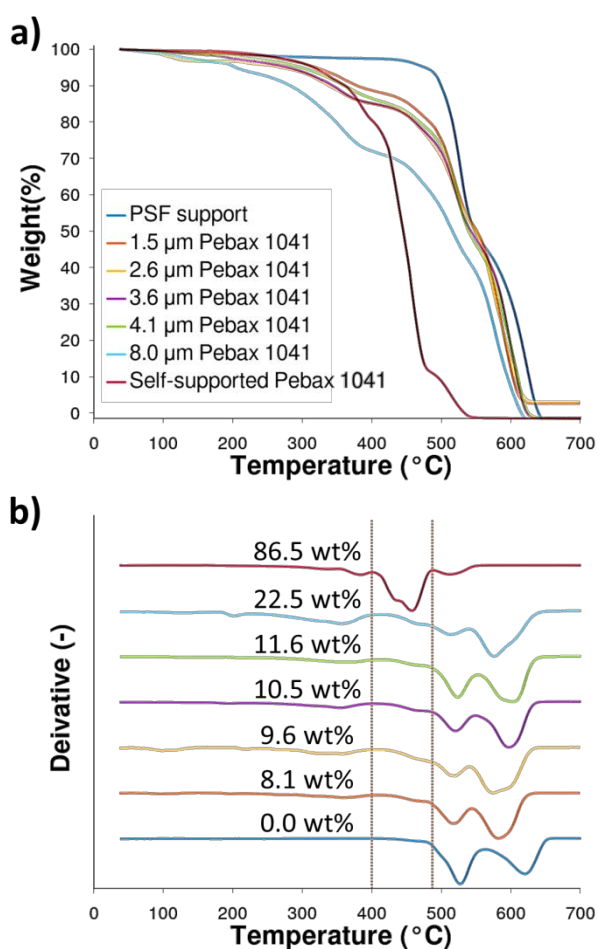


Fig. 5. TGA curves (a) and the corresponding derivatives (b) performed with all the Pebax® 1041 supported membranes, as well as with the PSF supports and Pebax® 1041 self-supported membranes for comparison. The weight loss between 400 and 490 °C is highlighted.

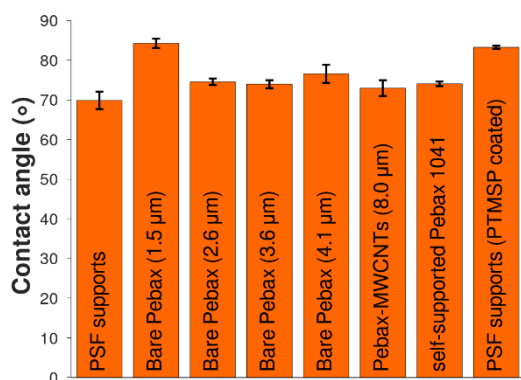


Fig. 6. Contact angle measurements of PSF supports, self-supported Pebax[®] 1041 membranes, PSF supports coated with PTMSP and Pebax[®] 1041 supported membranes prepared with a selective layer of: 1.5 μm , 2.6 μm , 3.6 μm , 4.1 μm and 8 μm containing MWCNTs.

The former showed 2.7 GPU of N_2 and a CO_2/N_2 selectivity of 17.4, while the latter, 3.0 GPU of N_2 and a CO_2/N_2 selectivity of 22.6. Multiplying the CO_2 permeance (3.0 GPU) by the thickness of the Pebax[®] layer (8 μm), a CO_2 permeability of 24 Barrer is obtained, which is consistent with the intrinsic CO_2 permeability of Pebax[®] 1041 displayed in Fig. 3. In terms of CO_2 permeance, supported membranes with an 8 μm layer of Pebax[®] 1041 showed a gas permeance 5-fold higher than that of self-supported membranes (3.0 GPU vs. 0.6 GPU, respectively), justifying all the effort developed in this work to obtain supported membranes with a non-studied in solution Pebax[®] (1041) grade. Finally, Fig. 7b compares all the results obtained in this work with Pebax[®] 1041 supported membranes. It can be seen that the CO_2/N_2 selectivity increased as the thickness of the Pebax[®] selective layer also did, reaching the maximum value when MWCNTs were incorporated.

Table 1. Quantification of the amount of Pebax[®] 1041 in the supported membranes from the 490-500 $^\circ\text{C}$ weight loss in TGA results of Fig. 5

| Membrane | Weight loss (%) | Amount of Pebax [®] 1041 (wt%) |
|-------------------------|-----------------|-----------------------------------------|
| PSF support | 0.0 | 0.0 |
| 1.5 μm | 8.1 | 9.3 |
| 2.6 μm | 9.6 | 11.2 |
| 3.6 μm | 10.5 | 12.2 |
| 4.1 μm | 11.6 | 13.4 |
| 8.0 μm | 22.5 | 26.0 |
| Pebax [®] 1041 | 86.5 | 100 |

However, even with use of the carbon nanotubes the permeance of the membranes is some orders of magnitude below others of the state of the art.⁴

The graph also shows a CO_2/N_2 upper bound. This bound was calculated in GPU from the original values in Barrer of Robeson's work²⁹ (see Table S1 and Fig. S4), following the analogous method that our group has previously applied to obtain the H_2/CO_2 and CO_2/CH_4 upper bounds in terms of permeance and selectivity.^{30, 31} It can be concluded that 8 μm is the minimal thickness necessary to have a fully selective Pebax[®] 1041 membrane prepared by the drop-casting method

implemented in this work. The lack of a continuous polymeric phase in the Pebax[®] emulsion used for the membrane preparation, contrary to what would be obtained with a polymer solution, may have made necessary such a high thickness to build a defect-free selective layer. A comparison with other Pebax[®] based membranes found in the literature is also provided in Table S2.

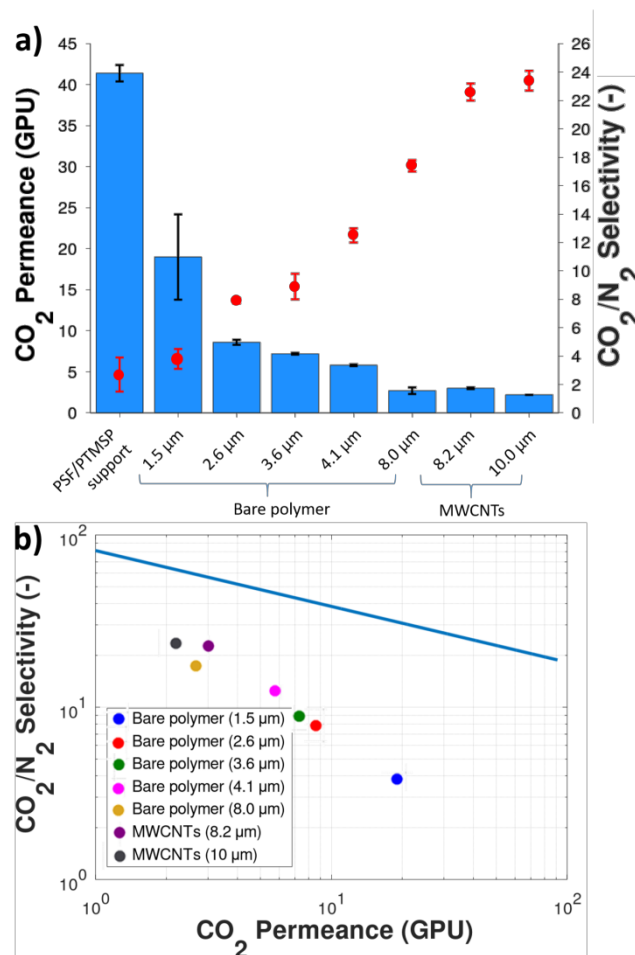


Fig. 7. CO_2/N_2 gas separation performance at 35 $^\circ\text{C}$ and 3 bar feed pressure of the supported Pebax[®] 1041 membranes prepared by drop-casting with several selective layer thicknesses. Bars stands for permeance and scatter for selectivity(a). Upper bound type graph (see Figure S4) comparing the results of all the Pebax[®] 1041 supported membranes (b).

Experimental

Preparation of self-supported dense membranes by solvent evaporation

Pebax[®] 1041 is highly resistant to chemicals and specific information about its solubility is not available. Since in their work Djebbar et. al.¹² were able to dissolve PEBA containing up to 80 wt% of PA12 in *N,N*-dimethylacetamide (DMAc), we thought it could also be a suitable solvent for this Pebax[®] grade. This way, pellets of Pebax[®] 1041 (kindly provided by Arkema) were first dissolved in DMAc ($\geq 99.5\%$, Sigma Aldrich), stirring

under reflux at 120 °C for 1 h to obtain a 5 wt% casting solution. The solution was cast into a leveled Petri dish, which was left uncovered overnight inside an oven at 90 °C to allow the solvent to evaporate. The following day, the membranes were peeled off from the Petri dishes and treated in a vacuum oven at 80 °C and 10 mbar for 24 h for the complete removal of the remaining solvent.

Preparation of self-supported membranes by phase inversion

Pebax® 1041 was dissolved as in the previous section to prepare casting solutions of 2, 5 and 10 wt% in DMAc. The polymer solution was cast hot onto a glass Petri dish to avoid gelation and immersed into a tap water bath at 25 °C after a few seconds, when the resulting film was cold enough, producing the precipitation of the polymer. After that, the membranes were kept in a DI water bath overnight and then rinsed with methanol (MeOH, Scharlau, HPLC grade) and n-hexane (Scharlau, extra pure) to remove the remaining DMAc. As for the membranes prepared by solvent evaporation, the films were dried at 80 °C under vacuum previous to use.

Preparation of polysulfone asymmetric supports

Flat asymmetric supports of polysulfone (PSF) were prepared following the phase inversion technique in a process similar to that previously used in our research group to prepare P84® supports.^{30, 32} The PSF pellets (Udel® P-3500 LCD, *Solvay Advanced Polymers*) were dissolved in N-methyl-2-pyrrolidone (NMP, Panreac, 99% PS) under stirring at room temperature to obtain a 20 wt% casting solution. This polymer solution was cast onto a glass plate using an Elcometer 4340 Automatic Film Applicator and immediately immersed into a tap water bath at 25 °C. After precipitation, the membranes were kept in a DI water bath overnight and then rinsed with MeOH. The films were finally dried at 100 °C for 18 h.

Once dried, the top of the PSF support was coated with a gutter layer of poly [1-(trimethylsilyl)-1-propyne] (PTMSP). For this purpose, the PSF supports were dip coated with a 1 wt% solution of PTMSP (*Gelest Inc.*) in n-hexane. The supports were then allowed to evaporate for 4 h at room temperature and finally dried at 100 °C for 18 h.

Preparation of Pebax® 1041 supported membranes by drop-casting

To prepare this kind of membranes, the first step was to obtain a 5 wt% solution of Pebax® 1041 in DMAc, following the steps previously explained. The solution was poured little by little while hot into stirring tap water, obtaining a suspension of precipitated Pebax® that was washed twice with DI water by centrifugation to remove all traces of DMAc. This suspension was homogeneously dispersed using the IKA T25 ULTRA-TURRAX® emulsifier at 8000 rpm for 2 min, to eventually obtain a stable emulsion. For the membranes containing multi-walled carbon nanotubes (MWCNT), 10 mg of MWCNT (Sigma Aldrich, thin, <5% metal oxide) was dispersed in 0.99 g of the Pebax® 1041 emulsion using the ultrasonic liquid processor Vibra-Cell™ CV33. Only this amount of MWCNTs was dispersed because higher loadings led to agglomeration problems.

Amounts comprehended between 400 and 2400 µL of the Pebax® 1041 emulsion were deposited by drop-casting onto the PSF supports, in the form of a circle of 2 cm diameter, using a micropipette and were left still on a leveled surface at room temperature for 18 h to evaporate the water. Afterwards, the resulting supported membranes were activated under 10 mbar vacuum and 80 °C for 1 day.

Membrane characterization

Thermogravimetric analyses (TGA) were carried out using a Mettler Toledo TGA/STDA 851e. Samples (10 mg) placed in 70 µL alumina pans were heated in 40 cm³(STP) min⁻¹ of air flow from 35 to 900 °C at a heating rate of 10 °C min⁻¹. Scanning electron microscopy (SEM) images were obtained using a FEI Inspect F50 model SEM, operated at 20 kV. Cross-sections of the membranes were prepared by freeze-fracturing after immersion in liquid N₂ and subsequently coated with Pd. The X-ray diffraction (XRD) patterns of the membranes were obtained with the Panalytical Empyrean equipment, using CuK_α radiation (λ = 1.540 Å), taking data from 2θ = 2.5° to 40° at a scan rate of 0.03 ° s⁻¹. Fourier transform infrared spectroscopy (FTIR) was performed with a Bruker Vertex 70 FTIR spectrometer equipped with a DTGS detector and a Golden Gate diamond ATR accessory. The spectra were recorded by averaging 40 scans in the 4000-600 cm⁻¹ wavenumber range at a resolution of 4 cm⁻¹. Differential scanning calorimetry (DSC) analyses were performed on a Mettler Toledo DSC822e. Samples (10 mg) placed in 70 µL aluminum pans were heated in 40 cm³(STP) min⁻¹ of nitrogen flow from 25 to 300 °C at a heating rate of 10 °C min⁻¹. The contact angle of the membranes was measured with a Krüss DSA 10 MK2 by dripping a water microdrop at three different places on each surface examined.

Gas separation analysis

The membranes were placed in a module consisting of two stainless steel pieces and a 316LSS macroporous circular disk support of 2 cm diameter (from Mott Co.) with a 20 µm nominal pore size, and gripped inside with silicon o-rings. The permeation module was placed in a UNE 200 Memmert oven to control the temperature of the experiments (35 °C). Gas separation measurements were carried out by feeding a CO₂/N₂ mixture (15/85 cm³(STP) min⁻¹) at 3 bar to the feed side by means of two mass-flow controllers (Alicat Scientific, MC-100CCM-D), while the permeate side of the membrane was swept with a 2 cm³(STP) min⁻¹ mass-flow controlled stream of He at 1 bar (Alicat Scientific, MC-5CCM-D). Concentrations of CO₂ and N₂ in the outgoing streams were analyzed by an Agilent 3000A online gas microchromatograph equipped with a thermal conductivity detector. Permeances were calculated in GPU (gas permeance unit, 10⁻⁶ cm³(STP) cm⁻² s⁻¹ cmHg⁻¹) and permeabilities in Barrer (10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹) once the steady-state of the membrane module exit stream was reached (after at least 2 h). The separation selectivity was calculated as the ratio of permeances/permeabilities. At least 2-3 membrane samples of each type were fabricated and measured to provide the corresponding error estimations.

Conclusions

Both self-supported and supported Pebax® 1041 membranes have been developed in this work and tested for the separation of CO₂/N₂ mixtures. Self-supported membranes can be prepared by solvent evaporation and phase inversion, where the latter is a greener method, avoiding the formation of toxic vapors of DMAc during membrane preparation. Independently of the methodology followed and the polymer concentration in the casting solution, the prepared membranes resulted in dense films with a thickness around 33 µm. The characterization performed showed the typical FTIR vibration modes and XRD intensities of block copolymers based on PTMO and PA12. Besides, the thermal analysis set the conditions for the right activation of the membranes and agreed with the melting temperature of PA12. The gas separation performance of these membranes exhibited the intrinsic CO₂ permeability and CO₂/N₂ selectivity of Pebax® 1041 (30 Barrer and 21, respectively). Supported Pebax® 1041 membranes can be prepared by drop-casting with an emulsion of polymer. This emulsion was obtained from a Pebax® solution in DMAc that had been previously precipitated in DI water. Amounts from 400 to 2400 µL of bare polymeric emulsion can be drop-cast on polysulfone asymmetric supports, leading to an increasing selective Pebax® layer up to 10 µm thickness. The amount of Pebax® deposited can be quantified by TGA and contact angle measurements assessing the quality of the support covering. The gas separation tests showed how as the thickness of the Pebax® 1041 increased, the CO₂ permeance lowered its value and the CO₂/N₂ selectivity augmented, reaching the intrinsic selectivity of Pebax® 1041 at an 8 µm thickness. In addition, with this membrane thickness, the CO₂ permeance increased by a factor of 5 when compared to that of the self-supported membrane. Dispersing MWCNTs in the polymer emulsion led to the highest selectivity (23.4±0.7) with a selective layer thickness of 10 µm.

Conflicts of interest

There are no conflicts to declare

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