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Vapor Phase Interfacial Polymerization: A Method to Synthesize Thin Film Composite Membranes without Using Organic Solvents†

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Thin film composite membranes (TFC) of polyamide (PA) prepared by interfacial polymerization (IP) between a diamine and an acyl chloride are those applied to industrial nanofiltration and reverse osmosis. Water, to dissolve the diamine, and n-hexane, to dissolve the acyl chloride, solvents are involved in the IP process. Eliminating the use of n-hexane would be crucial to produce a greener TFC membrane synthesis method. This is achieved here by carrying out an interfacial polymerization from the vapor phase. First, the membrane support was impregnated with the aqueous diamine solution. Second, the support with the diamine was contacted with vapor of the acyl chloride to unchain the IP reaction. Besides the absence of n-hexane, the acyl chloride was applied more efficiently avoiding its loss during the cleaning operations carried out in the typical IP process. These membranes were applied to the nanofiltration of simulated micropollutants in water (rose Bengal, sunset yellow and acridine orange), with higher water permeance (up to 3.3 L·m⁻²·h⁻¹·bar⁻¹) than that of conventional TFC membranes and rejections higher than 94 % in all cases.

Introduction

Nanofiltration (NF) is a process that aims at separating water and organic solvents from ionic solutes and organic molecules with molecular weights between 200 to 1000 g·mol⁻¹, by economic and efficient means.¹ Due to the intermediate characteristics of NF between reverse osmosis (RO) and ultrafiltration (UF), NF membranes are the optimum choice for specific separation processes where RO membranes exhibit limitations to the solvent permeation and UF membranes do not separate the solute efficiently.^{1,2}

Among the different approaches to obtain highly permeable and easily synthesizable NF membranes, the fabrication of thin film composite (TFC) and thin film nanocomposite (TFN) membranes through interfacial polymerization (IP) is the most appealing. Since the invention of TFC membranes in the 80s by Cadotte et al.,³ numerous research groups have intensively improved this technology using alternative monomers,^{4,5} diverse additives,^{6,7} optimized substrates,^{8–12} or nanoparticles^{5,13–15} to obtain new and highly permeable TFN membranes. Finally, due to the promising results, in the last two decades some large companies have shown interest in these investigations,¹⁶ investing resources to bring both TFC and TFN membranes to the market.

In spite of the abundant modifications of the IP parameters to synthesize the polyamide (PA) thin film, both immiscible solvents involved in the process remained unchanged in almost every investigation. That is, water to dissolve the diamine and n-hexane to dissolve the acyl chloride. However, it is known that using solvents such as n-hexane in an industrial process can usually be tricky since there can be plenty of incompatibilities with some of the materials used to build the infrastructure (mainly with polymers). Besides, the use of organic solvents can also be expensive, harmful and environmentally unsustainable. Therefore, we propose in this investigation the elimination of the n-hexane that dissolves the acyl chloride carrying out the IP in vapor phase. As this monomer is relatively volatile and has a quite low melting temperature, the synthesis process would not require high temperatures to take place. Among the advantages of this vapor phase method, we highlight the elimination of a toxic, inflammable and volatile residue, as the n-hexane is, and also the rationalization of the use of the acyl chloride monomer whose excess has to be removed during the conventional membrane synthesis. In other words, with this method, the TFC membrane production would be more sustainable, potentially less harmful, more environmentally friendly and more economical (due to monomer saving). As far as we are concerned, there are no publications regarding the elimination of the organic solvent in a TFC or TFN membrane fabrication, thus this is likely a novel idea that will have a high impact in the membrane synthesis research field. Besides, even if the concept can be different to that applied here, the vapor phase polymerization and the chemical vapor deposition of different polymers were previously addressed with the purpose of producing different coatings and thin films on several types of substrates.^{17–19} More specifically, polyphosphoesters were obtained by interfacial polycondensation in a vapor–liquid

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system in which an organic solvent was not required.²⁰ However, none of these approaches pretended to produce the polyamide membranes studied here. In any event, this research is in line with others carried out to reduce the harmful effect of organic solvents and monomers during TFC membrane preparation.^{21–24}

In this work, TFC membranes are fabricated following a novel vapor phase IP (VP-IP) method. As we consider essential to find out which synthesis conditions are the optimum to obtain defect-free membranes, different values of temperature and reaction times have been tried. To validate the new synthesis method, the membranes obtained were used in aqueous NF to separate dyes such as rose Bengal (RB, 1030 Da), sunset yellow (SY, 452 Da) and acridine orange (AO, 265 Da) from water. Furthermore, all membranes were fully characterized using electron microscopy techniques and X-ray photoelectron spectroscopy.

Experimental section

Asymmetric support synthesis

The polyimide (PI) porous supports were home-made, prepared using a 24% (w/w) polymer dope solution of P84® (HP polymer GmbH) in DMF (99.5%, Scharlab) stirred overnight as a casting solution. It was then cast, using the Elcometer 4340 Automatic Film Applicator, on polypropylene non-woven 40 x 30 cm sheet supports and immediately immersed in a deionized water bath for 15 min, where the phase inversion process took place leading to the formation of an asymmetric porous support. The polypropylene sheet reinforces the polyimide support to provide the needed mechanical stability to the polyamide membrane prepared as described below. After the phase inversion, the supports formed were washed in an additional clean deionized water bath for 1 h to remove rests of DMF that may be contained in their porosity. The supports were then

immersed in two successive baths with isopropyl alcohol (IPA – 99.5%, Scharlab) for 1 h each to remove any remain of water. Afterwards, the first chemical treatment took place. This consisted in a bath of 120 g/L of hexanediamine (HDA – 98%, Sigma Aldrich) in IPA for 16 h to produce the cross-linking process, which enhanced the stability of the support in organic solvents.²⁵ Four baths with IPA were then applied to remove polyethylene glycol (PEG – synthesis grade, Scharlab): IPA. This prevents pore collapse during the formation of the ultrathin selective layer on the top of the support.^{26,27} The supports were then wiped with tissue paper. traces of HDA from the supports. Finally, the supports were immersed overnight in a solution with a 3:2 volume ratio of polyethylene glycol (PEG – synthesis grade, Scharlab): IPA. This prevents pore collapse during the formation of the ultrathin selective layer on the top of the support.^{26,27} The supports were then wiped with tissue paper.

TFC membranes synthesis: VP-IP and conventional IP methods

The PA thin film was prepared using *m*-phenylenediamine (MPD, 99%, Sigma Aldrich) as the diamine and 1,3,5-benzene tricarboxyl chloride (TMC, 98%, Sigma Aldrich) as the acyl chloride (Figure 1A).

Firstly, 60 cm² porous polyimide (PI) discs were cut to be used as supports. They were immersed in an aqueous solution with 2% (w/v) MPD for 2 min. After that, the excess solution on the surface was removed using tissue paper. Then, the MPD saturated disc was placed upside down on a Petri dish with a diameter of 6.9 cm that contained 0.500 g of TMC (see Figure S1A and B). On top of it, another Petri dish with a larger diameter was put on the support with weight on it (see Figure S1C and D), so the PI disc was perfectly flat and no TMC vapor would leak during the synthesis. Finally, the recipient that contained the setup (see Figure S1E) was closed and placed in an oven at 40 °C when required (see Figure S1F). Figure 1B shows an scheme of the synthesis process used to obtain TFC membranes by the vapor phase method.

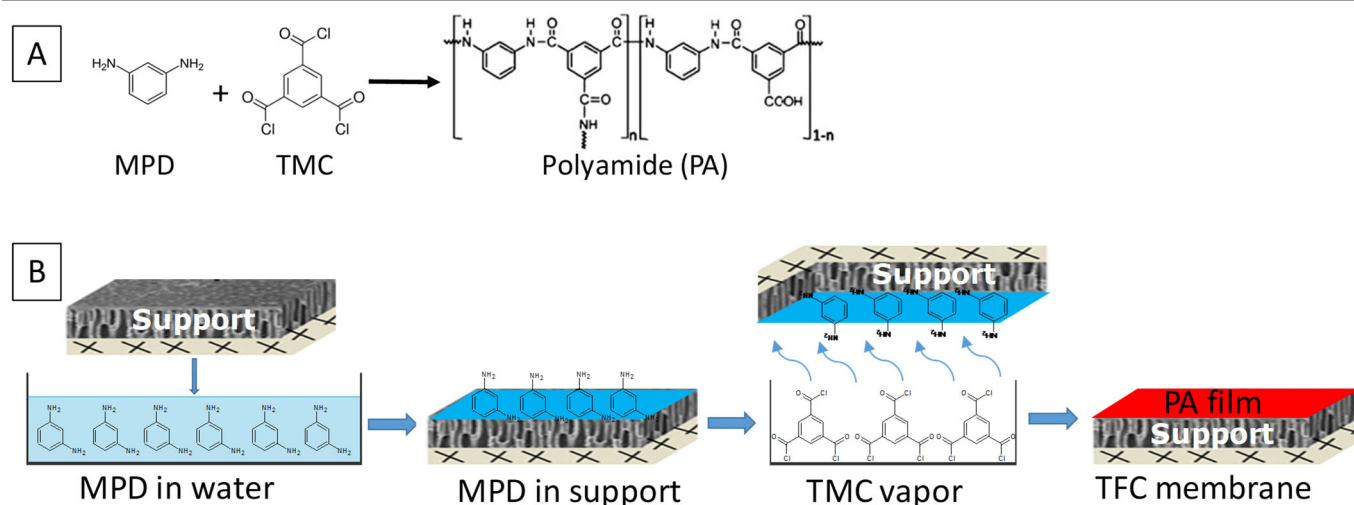


Figure 1: A) Interfacial polymerization reaction. B) Scheme of the synthesis process of TFC membranes by vapor phase interfacial polymerization method.

A temperature above room temperature of 40 °C was chosen as a reference in the VP-IP because it is slightly higher than the TMC melting point (32-38 °C). With respect to room temperature, the higher temperature increased the vapor pressure during the reaction and the reaction rate.

Both synthesis time and temperature are the main variables that influence the formation of the PA film, thus different values of them were studied to find out the conditions to obtain the membrane with the best performance (see The morphology of the surface of all synthesized membrane samples were observed in images taken by scanning electron microscopy (SEM). The equipment used was a FEI-Inspect F20 SEM working at an acceleration voltage between 10 and 20 kV with spots between 2.5 and 3.5 nm.

As the PA layers obtained by the conventional and vapor phase methods were probably chemically different, the C/N and O/N ratios of each layer were measured to estimate the polymer cross-linking. The content of C, O and N atoms was obtained using the X-ray photoelectron spectroscopy (XPS). The samples were fragments of each membrane cut and deposited on different sample supports. XPS characterization was performed with a Kratos Axis Ultra spectrometer using a monochromatic Al K α (1486.6 eV) X-ray source at 10 mA and 15 kV and a power of 150 W.

NF experiments

The NF experiments were carried out in a dead-end membrane module (Sterlitech HP4750), where a feed of 20 mg/L of a dye in water was pushed to permeate through a membrane with constant stirring. The effective membrane area was 12 cm² and the feed volume was 250 mL (the total capacity of the module was 300 mL and the maximum operating pressure 69 bar). All experiments were carried out at a feed pressure of 20 bar and). When the synthesis was finished, the discs were rinsed with deionized water to remove the excess MPD solution absorbed in the support. The membranes obtained by this VP-IP method were compared in terms of NF performance and characterization to TFC membranes obtained by the conventional IP used in previous publications (referred here as c-TFC membranes).^{1,3}

The synthesis steps in this case are: immersion of the support in an aqueous solution of MPD at 2% (w/v) for 2 min, removal of excess solution by means of tissue paper and immersion of the MPD-saturated support in an organic solution of TMC in n-hexane (extra pure, Scharlab) at 0.1% (w/v) for 1 min.

Finally, while in the VP-IP method the TFC membranes obtained are only washed with 10 mL of deionized water to remove excess aqueous solution, in the conventional IP method three washing steps are used, two with 10 mL each one of n-hexane (to remove excess organic solution), and one with 10 mL deionized water. If TMC was hydrolyzed into trimesic acid, this amount of water (10 mL) should be enough for proper washing out of it from the polyamide membrane environment in agreement with the trimesic acid solubility in water: ca. 1.7 and 3.8 mg/mL at 27.9 and 42.1 °C, respectively.²⁸ Three membrane samples were prepared at the same conditions to demonstrate

the reliability of the methodologies applied. All steps at room temperature.

Membrane characterization

Transmission electron microscopy (TEM) was needed to have a closer view of the PA layers and the borderlines with the PI membranes that support them. The samples observed were cross-sections of all membranes synthesized using the VP-IP and the c-TFC membrane embedded in an epoxy resin. The preparation of the TEM specimens, fragments of each membrane were embed in resin. The blocks of resin were then cut in ultra-thin slices using a Leica EM UC7 ultramicrotome, and deposited on copper grids. The microscope was a FEI Tecnai T20 TEM used at an acceleration voltage of 300 kV.

Table 1: The four types of membranes synthesized and the temperature and reaction time values for each case. RT stands for room temperature (20 °C).

| Membrane code | IP method | T (°C) | t (min) | N ^o samples |
|---------------|--------------|--------|---------|------------------------|
| c-TFC | Conventional | RT | 1 | 3 |
| vp-TFC RT/60 | VP-IP | RT | 60 | 3 |
| vp-TFC 40/60 | VP-IP | 40 | 60 | 3 |
| vp-TFC 40/30 | VP-IP | 40 | 30 | 3 |

The morphology of the surface of all synthesized membrane samples were observed in images taken by scanning electron microscopy (SEM). The equipment used was a FEI-Inspect F20 SEM working at an acceleration voltage between 10 and 20 kV with spots between 2.5 and 3.5 nm.

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$$Q = \frac{V}{A \cdot t} = \left[\frac{L}{m^2 \cdot h} \right] \quad (1)$$

$$Permeance = \frac{Q}{\Delta P} = \left[\frac{L}{m^2 \cdot h \cdot bar} \right] \quad (2)$$

$$\text{Rejection (\%)} = \left(1 - \frac{C_{\text{permeate}}}{C_{\text{residue}}}\right) * 100 \quad (3)$$

where V represents the volume (L), A the NF membrane area (m^2), t the time for permeate collection (h), and ΔP the pressure drop through the membrane (bar). Concentrations of permeate (C_{permeate}) and residue (C_{residue}) were both measured using an UV spectrometer (Jasco V-670 spectrophotometer) using water as solvent. For this purpose, the last 3 mL of permeate and 3 mL of residue left in the module were taken as samples for analysis. Absorbance and concentration values for each solute used were related by an equation obtained from the calibration.

The dyes used for this separations were the rose Bengal (RB, 1017 Da, 95%, Sigma Aldrich), sunset yellow (SY, 452 Da, 90%, Sigma Aldrich) and acridine orange (AO, 260 Da, 55%, Across Organics).

RESULTS AND DISCUSSION

Membrane synthesis and characterization

The fabrication of TFC membranes by this vapor phase method provides important assets in reagent saving, health and environmental terms compared to the conventional method. The main novelty of this work lies in the complete elimination of the *n*-hexane and the important reduction of the TMC amount used in the synthesis of TFC membranes by IP. Table 2 shows the reagents and solvents needed to synthesize TFC membranes by the conventional method^{13,29,30} and the needed when the synthesis is carried out by the vapor phase method. The TMC needed in the vapor phase method was estimated taking into account both, the TMC vapor presents in the Petri dish volume applying the equation of Clausius-Clapeyron (see Table S1) and the TMC reacted to form the PA layer from the stoichiometry of the IP reaction. As shown, the vapor phase method achieved a 100% of saving in case of solvent *n*-hexane and a 96.2% in case of reagent TMC. These great savings are important not only in terms of production costs, but also in health and environmental terms due to the toxicity and hazard of both organic compounds.

Song et al.³¹ proved, using AFM and SEM imaging techniques, that the so-called ring-like shapes that characterize the PA thin film are formed by the gas release from the aqueous phase as the exothermic polymerization reaction heats up the surroundings. The gases released, confined in the superficial pores of the substrate that supports the thin film, create bubble-like structures that when dehydrated give rise to the morphology that is usually seen in SEM images for this type of membranes.

In our view, this mechanism can explain the differences in morphology between the TFC membranes synthesized by the VP-IP method and the conventional IP method. All PA layers of the vp-TFC membranes fabricated lack of ring-like shapes (see Figure S2B, C and D) that the c-TFC membranes have (see Figure S2A). The reason for this evident difference is that the gas bubbles have likely abandoned the aqueous phase by the time the PA thin film is formed. This hypothesis is supported by the longer synthesis times used in the VP-IP method compared to

those used in the conventional IP (30 min as minimum, compared to 1 min). In this conditions, the gas bubbles have plenty of time to be released before the superficial porosities were clogged by the PA formed. This supposition becomes even stronger when carrying out the VP-IP at 40 °C, as gas solubility in liquids decreases with temperature. This argument can also be supported by the fact that in the VP-IP method the surface on which the PA is formed was upside-down. Consequently, the gases may be either confined in the pores of the support or, more unlikely, released through the back of the support.

Moreover, it is obvious that this vapor phase method presents a limitation of the reaction polymerization. The TMC monomer, present in the vapor phase at a lower concentration than it is in the *n*-hexane solution when applying the conventional interfacial polymerization method, needs to reach the water surface and then react at the interface $\text{H}_2\text{O(l)}$ -TMC(air) interface. This suggests that the limitation for the reaction is the supply of TMC to the water phase, in agreement with the fact that an increase in the temperature (favoring the diffusion process and increasing the vapor pressure of TMC) increases the membrane thickness. At this stage, a reaction time of 60 min, even it does not imply additional amounts of solvents and reactants than the other shorter times, can be considered as a drawback with potential implications in the energy cost (supplied to maintain the temperature at 40 °C) and volume of reaction system. These concerns would be considered in a future extended work addressing the industrial suitability of the vapor phase procedure.

The TEM images confirmed what was previously observed on the SEM images: the c-TFC thin film has ring-like shapes, seen as knobs from the cross-section perspective (Figure 2A), while the vp-TFC thin films are completely flat (Figure 2B, C and D). In addition, the cross-section views allow to measure the average thickness of each thin film. As shown in Figure 2, the PA layer seems to be thinner as the reaction temperature decreases from 40 °C to RT but time remains unchanged at 60 min (7.3 ± 1.3 nm compared to 12.4 ± 2.9 nm), and thicker as the reaction time increases but the temperature remains at 40 °C (12.4 ± 2.9 nm compared to 8.9 ± 1.2 nm). Interestingly, the c-TFC membrane thin film was in average thicker (15.7 ± 4.2 nm) than the others, even though it was formed in only one minute.

The XPS results (Figure S2) demonstrate that two polymeric films with the same thickness can be chemically and physically different. In other words, the vp-TFC 40/60 and c-TFC membranes have PA thin films with similar thickness, but both of them are differently cross-linked. The first has a lower cross-linking degree than the latter, as it has higher C/N and O/N ratios (more C and O atoms per N atoms, see Figure 3). In statistics terms, the vp-TFC 40/60 membrane seems to be the more homogeneous, while the other two present wider standard deviations suggesting that the lower temperature or shorter synthesis time are not good enough conditions to create a homogeneous PA membrane. All in all, the three different types of VP membranes were likely less cross-linked than the c-TFC membrane, probably due to the working conditions with TMC in much less excess. It is possible to obtain the cross-linking

degree of the PA thin film using the O/N ratios, as other authors previously indicated in the literature.^{32,33}

Table 2: Reagents and solvents needed in the synthesis of TFC membranes by the conventional (c-TFC) and vapor phase (vp-TFC) methods per cm² of membrane area.

| | MPD (g/cm ²) | TMC (g/cm ²) | Solvent | | Saving (%) | | | |
|--------|-----------------------------|-----------------------------|---------------------------------|--------------------------------|------------|------|--------|-------|
| | | | Hexane (mL/cm ²) | Water (mL/cm ²) | MPD | TMC | Hexane | Water |
| c-TFC | 1.32E-2 | 6.61E-4 | 1.10 | 6.61E-1 | - | - | - | - |
| vp-TFC | 1.32E-2 | 2.51E-5 | | 6.61E-1 | 0 | 96.2 | 100 | 0 |

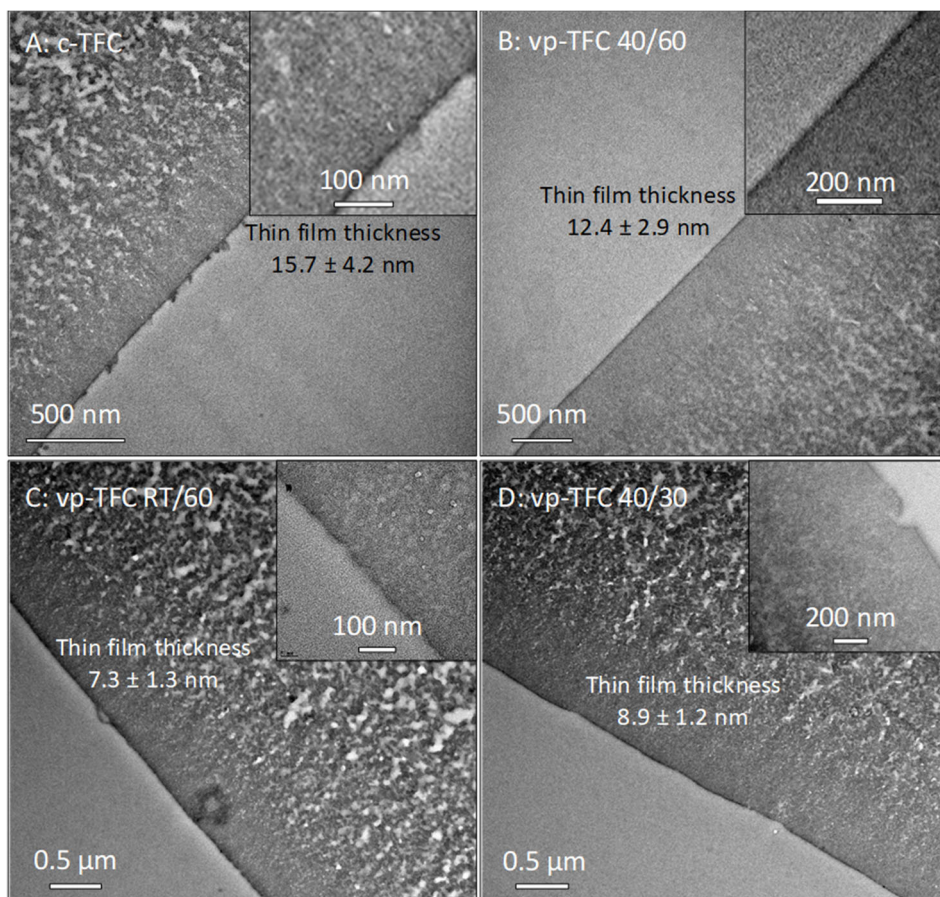


Figure 2: TEM images of microtomes cut from samples of c-TFC (A), vp-TFC 40/60 (B), vp-TFC RT/60 (C) and vp-TFC 40/30 (D) membranes.

This requires knowing the number of O and N atoms present in every cross-linked TMC-MPD pair and in every non-cross-linked TMC-MPD pair, and obtaining from the O/N ratio value the proportion of cross-linked pairs over the total pairs of the polymer chains, as Zhao et al.³² explained in their publication. The cross-linking degree is then represented as a number between 0 (fully linear PA) and 1 (fully cross-linked PA). As Figure 3 depicts, the c-TFC membrane has a cross-linking degree around 0.5 (half cross-linked), while all TFC membranes synthesized following the VP-IP method are less cross-linked (with cross-linking degrees in the 0.3-0.4 range). As expected from the stronger reaction conditions, the vp-TFC 40/60 seems to be more cross-linked than the other two vp-TFC membranes.

Nanofiltration performance

The c-TFC membranes gave rise to very consistent NF performances with average water permeances of 1.2 ± 0.4 and $1.3 \pm 0.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and solute rejections of 97.7 ± 0.1 and

$99.2 \pm 1.0\%$ for RB and SY, respectively (see Figure 4A). In all cases, the TFC membranes synthesized following the VP-IP method showed higher water permeances and slightly lower solute rejections than those corresponding to c-TFC membranes regardless of the reaction conditions (see Figure 4A). This can be ascribed to the lower thicknesses and cross-linking degrees that the vp-TFC membranes exhibited, as seen above. However, considering the compromise between permeance and rejection, the optimum conditions to carry out the IP were a reaction time of 60 min and a temperature of 40 °C (the vp-TFC 40/60 membrane, see Figure 4A). In this case, the water permeances were 2.4 ± 0.7 and $1.8 \pm 0.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ with rejection values of $98.5 \pm 0.3\%$ and $96.9 \pm 1.9\%$ for RB and SY, respectively.

The vp-TFC RT/60 membrane was synthesized at RT for 60 min. Increasing the reaction temperature from RT (vp-TFC RT/60) to 40 °C (vp-TFC 40/60) meant a dramatic water permeance

decrease from 5.9 ± 0.9 and $7.8 \pm 2.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ to 2.4 ± 0.7 and $1.8 \pm 0.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ when filtering RB and SY, respectively (see Figure 4A). According to the results of characterization, this significant decrease is likely related to both a difference in the PA layer thickness (thicker in the TFC membrane synthesized at 40°C than a RT, see Figure 2B and C) and a less cross-linking degree (see Figure 3) since both the RB and SY rejections increased notably as the reaction temperature increased from RT to 40°C (from $98.4 \pm 1.4\%$ of RB and $93.1 \pm 5.2\%$ of SY when using the vp-TFC RT/60, to $98.5 \pm 0.3\%$ of RB

and $96.9 \pm 1.9\%$ of SY with the vp-TFC 40/60 membrane, see Figure 4A).

The reaction time seems to influence the membrane performances too. Keeping the temperature at 40°C , but reducing the reaction time from 60 min to 30 min, means a rejection decrease from $98.5 \pm 0.3\%$ to $98 \pm 2.5\%$ in case of RB and from $96.9 \pm 1.9\%$ to $79.8 \pm 7.2\%$ in case of SY, using the vp-TFC 40/60 and vp-TFC 40/30 membranes, respectively (Figure 4A).

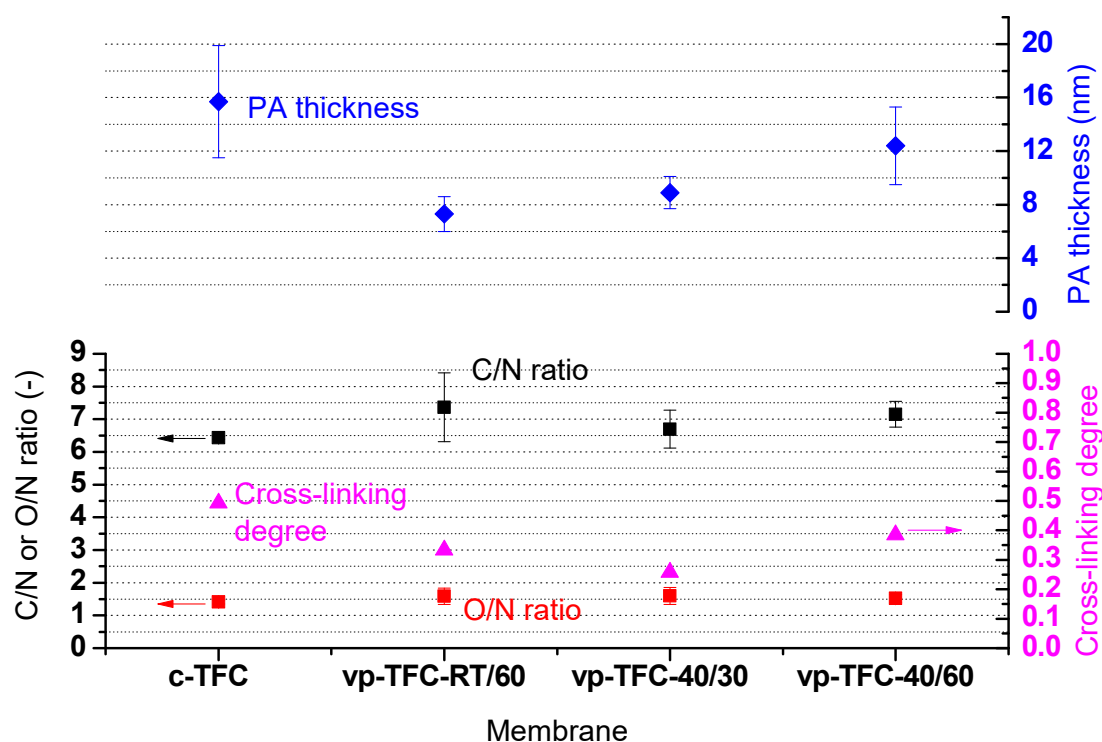


Figure 3: C/N and O/N ratios (in black and red, respectively) of the PA thin film of c-TFC, vp-TFC RT/60, vp-TFC 40/30 and vp-TFC 40/60 membranes. Cross-linking degrees in magenta, calculated following the method published elsewhere,³² and PA thin film thicknesses, measured on the TEM images of Figure 1, in blue. Error bars of C/N and O/N ratios are based on the standard deviations obtained from three different measurements, carried out on three different areas of each membrane type. Error bars of the PA thin film thicknesses are based on the standard deviations obtained from 10 measurements taken with the Image J® software from different TEM images.

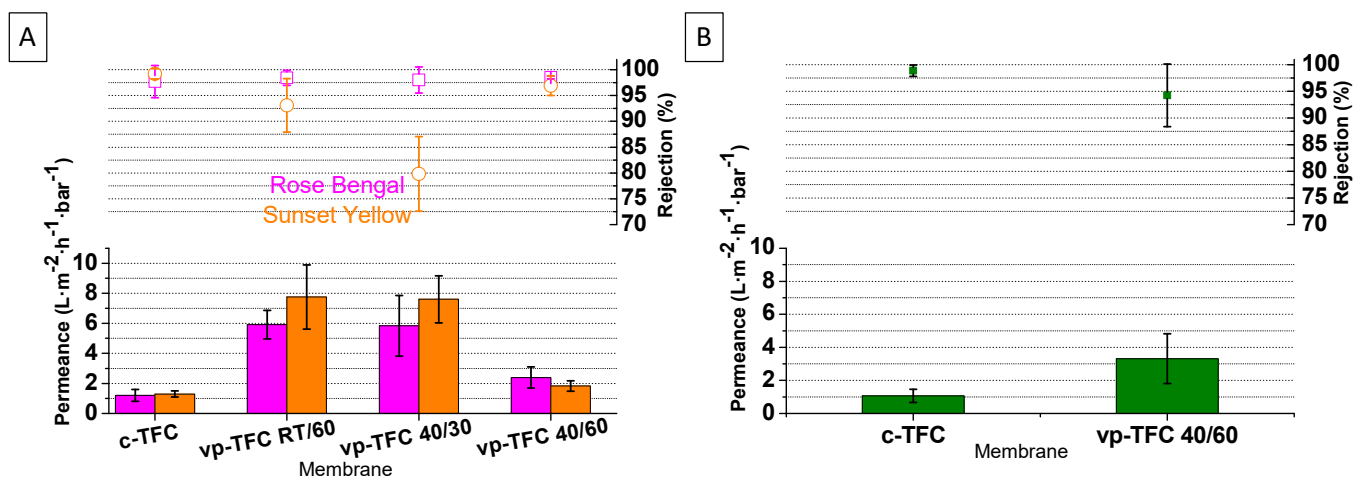


Figure 4: A) Effect of temperature and reaction time in the TFC membranes performance. Comparison of the water permeance and RB, (in purple) and SY (in orange) rejection during NF using a TFC membrane synthesized following the conventional method (c-TFC), a TFC membrane synthesized following the novel VP-IP at room

temperature for 60 min, a TFC membrane synthesized following the VP-IP at 40 °C for 30 min and a TFC membrane synthesized following the VP-IP at 40 °C for 60 min. B) AO (260 Da) and water filtration using the c-TFC and the vp-TFC 40/60 membranes. The values given are an average of three membranes (two in case of vp-TFC 40/60 measured with AO).

These results show that the vp-TFC 40/30 membrane seems to be the most defective membrane, giving rise to the lowest SY rejection of all tested. However, as the reaction time decreased from 60 to 30 min, the permeances increased from 2.4 ± 0.7 and $1.8 \pm 0.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ to 5.8 ± 2.4 and $7.6 \pm 1.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ when filtering RB and SY, respectively (Figure 4A).

As the vp-TFC 40/60 membrane was the most effective membrane in SY and RB separations, it was the selected to be compared to the c-TFC membrane with the smallest solute AO (260 Da) dissolved also in water (Figure 4B). The results were similar to the obtained when filtrating the other two dyes: the c-TFC membrane showed higher AO rejections ($98.9 \pm 1.1\%$) but with much lower water permeances ($1.1 \pm 0.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) compared to the vp-TFC 40/60 membrane ($94.3 \pm 5.9\%$ AO rejection and $3.3 \pm 1.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, see Figure 4B). This experiment allows also to establish a molecular weight cut off (MWCO) of ca. 260 Da for the vapor phase membrane obtained in this work. Thus, the new thin film composite membranes obtained at the best conditions not only were prepared with no organic solvent and reducing drastically the amount of TMC monomer used (as shown in Table 2), but perform much better in terms of water permeance, with similar rejection values to small dyes, than the membranes obtained by the conventional procedure.

All in all, it seems feasible to synthesize a TFC membrane following the VP-IP method that we propose for the first time in this work. As shown in Figure 4A and B, the vp-TFC 40/60 membrane was more permeable than the c-TFC membrane when filtering any of the three dyes and its rejection capacity was almost fully kept. Besides, the fact that the vp-TFC 40/30 was barely effective retaining SY, and therefore its thin film was likely defective, gave an idea of the relatively low reaction rate compared to the c-TFC membrane (synthesized in only one minute).

The literature has already made clear that less roughness (in case of TFC membranes related to the above mentioned ring-like shapes) implies lower permeances, but in our case the opposite was observed. All TFC membranes fabricated following the VP-IP method are more permeable than the c-TFC membrane with relatively high rejection values (particularly for vp-TFC 40/60 membranes) (Figure 4), and all of them are significantly less rough than the c-TFC membrane (see Figure S2A and B). Besides, other membrane parameters such as the thickness of the selective PA layer have to be considered to explain these results. Several studies have shown that the smaller the thickness of the selective PA layer, the greater the permeance obtained.^{34,35} As shown in Figure 2, the thickness of the PA layer is higher in the following order c-TFC > vp-TFC 40/60 > vp-TFC 40/30 > vp-TFC RT/60, whereas in the case of the permeance, the order is the inverse as can be seen in Figure 4.: vp-TFC RT/60 > vp-TFC 40/30 > vp-TFC 40/60 > c-TFC.

Conclusions

The fabrication of TFC membranes has been carried out by a novel vapor phase interfacial polymerization method. This method allows the complete elimination of the n-hexane and an important reduction of TMC used in the conventional synthesis of TFC membranes paving the way for a greener production of this type of membranes. The SEM and TEM microscopies together with XPS characterization showed the absence of the typical ridge-valley surface morphologies, slightly lower cross-linking degrees and thinner membranes fruit of the vapor phase method as compared to the conventional TFC membranes. However, by adjusting the temperature and time synthesis conditions, the vapor phase membrane cross-linking degree approached that of the conventional polyamide membrane.

The aqueous nanofiltration with several dyes revealed that the best results in terms of permeance and rejection were achieved using the membrane obtained at the conditions of 40 °C and 60 min of reaction. This membrane gave rise to water permeances of 2.4, 1.8 and $3.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ when filtering rose Bengal, sunset yellow and acridine orange, respectively, with rejections for all of them above 94%. These results, together with the obtained in the membrane characterization, allow one to conclude that the new vapor phase method applied here to prepare TFC membranes produces similar (in terms of chemical composition and structure) or even better membranes (in terms of much higher nanofiltration permeance with similar rejection values) but with a radical different approach regarding the amounts of reactants and solvents involved in their synthesis. Finally, even if the procedure is susceptible of improvement (e.g. exploring other synthesis conditions which may be more suitable to TFC membranes applied to remove salts or other organic pollutants different from those studied here), we believe this approach to prepare TFC membranes could be implemented with greener monomers than acyl chlorides or to the synthesis of thin film nanocomposite membranes, among others.

Conflicts of interest

There are no conflicts to declare.

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