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Atomistic models of polyamide thin films used for the recycling of water in agrofood industries by reverse osmosis

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Abstract

Distillation of fermented molasses for alcohol and biofuels production uses large volumes of water. Due to environmental concern, the recycling of condensates in the fermentation medium is encouraged subsequently to a purification step. This step could be performed via reverse osmosis (RO) process, in order to remove in the retentate small organic solutes which act as fermentation inhibitors. Currently, no general rule exists to predict the selectivity of RO membranes according to the nature of organic solutes. Similarly, such insights are missing in nanofiltration processes intended to detoxify biomass hydrolysates prior fermentation.

Our objective was to build and validate a molecular model of typical reverse osmosis membranes (exemples: ESPA2 and CPA2 from Hydranautics Membranes, USA), consisting in an active aromatic polyamide layer (APA) with different crosslinking rates. These models will be used in future works to develop general models of transport properties (water swelling, solute partitioning mainly) in RO membranes. The main characteristics of commercial RO membranes were retrieved from isolated APA layers (i.e. separated from the polysulfone-polyester support). Geometrical characteristics such as thickness (about 200 nm), homogeneity and swelling rates were assessed with laser ellipsometry and AFM. The composition and the reticulation rate were inferred from FTIR and XPS measurements. The sorption isotherm of water was sampled with an Intelligent Gravimetric Analyzer. The construction strategy of corresponding atomistic models of dried APA membranes via Molecular Dynamics Simulation (Discover, Accelrys, USA) is presented. The described model gives the theoretical density and neutron scattering spectra of simulated APA. These results could be compared in future works with experimental investigations.

1.Introduction

With the increase in bio-alcohol fuel demand, optimization of the water resource management in the agro-industry plants becomes essential. In beet distilleries, stillage resulting from the distillation step are concentrated by evaporation. Recycling the condensates into the alcoholic fermentation step would represent a good alternative to reduce in the same time the discharge and the consumption of water within the factory as depicted in Figure 1. However, condensates contain volatile solutes such as aromatic compounds, acids, alcohols and aldehydes, which act as fermentation inhibitors. Reverse osmosis (RO) was proved interesting to retain these small organic molecules [1-4]. Commercial RO membranes are organic (cellulose based or aromatic polyamides) and derived from those used for seawater and brackish water desalination [5]. As a result, current RO membranes are not optimized to retain non-electrolyte organic solutes and the selectivity of the membrane for a given organic composition in waste water cannot be known a priori. Current optimization strategy involves optimization from pilot scale up to production plant. Sagne et al. [6] calculated the selectivity of some commercial membranes to target inhibitors and showed that it was controlled by the resistance to diffusion in the bulk and by solute/membrane partitioning. The stoichiometry of monomers during the interfacial polymerization reaction can be used to adjust the density and cohesion of the membrane when it is swollen by water [7]. Our goal is to assess the influence of these parameters on the molecular mechanism of mutual diffusion of water and organic solutes in typical aromatic polyamide membranes. Since the extreme low thickness of the active membrane layer, about 200 nm (Fig. 1b), complicates the direct characterization of transport phenomena, our strategy consists in developing an atomistic model of swollen membrane, where mutual transports could be subsequently investigated.

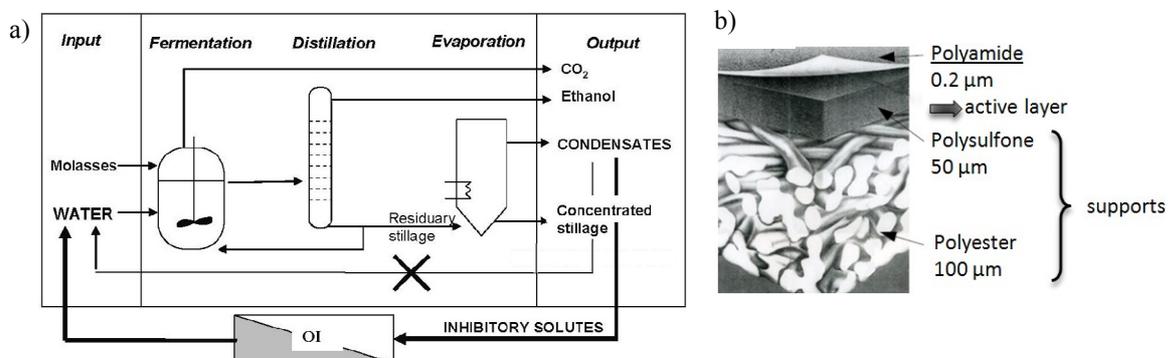


Figure 1: a) Distillery diagram [8], b) Schematic of thin-film-composite reverse osmosis membrane (source: WaterNeed.com).

Only a single atomistic model of aromatic polyamide membrane, known with a commercial reference as FT30 (FilmTech, USA), has been attempted in the literature [9]. As initial assumptions were not completely elucidated, our contribution includes the experimental characterization of two commercial membranes, that could be used in distillery

plants, from macroscopic scale down to atomistic scale. Some properties such as reticulation rates are used to build the model whereas thermodynamics properties are used to validate the construction methodology. A general validation will follow in a next paper by comparing calculated neutron and Xray scattering spectra with experimental ones obtained on dry and swollen membranes.

2. Materials and methods

2.1 Commercial reverse osmosis membranes

Our study was based on two typical RO membranes (references: ESPA2 and CPA2, Hydranautics Membranes, USA), consisting in an active aromatic polyamide layer (APA) with different crosslinking rates. The polymer was obtained by interfacial polymerization directly on the polysulfone support from *m*-phenyl-enediamine (MPD) and trimesoylchloride (TMC) monomers as described in Fig. 2. Variable branching and crosslinking rates are obtained at industrial scale by controlling the stoichiometry of monomers and the polycondensation stage [10]. The detailed mechanism of the step growth polymerization process along the main chains and branching point remains poorly understood [6]. Consequently both the branching and the crosslinking rates were unknown at the beginning of the study.

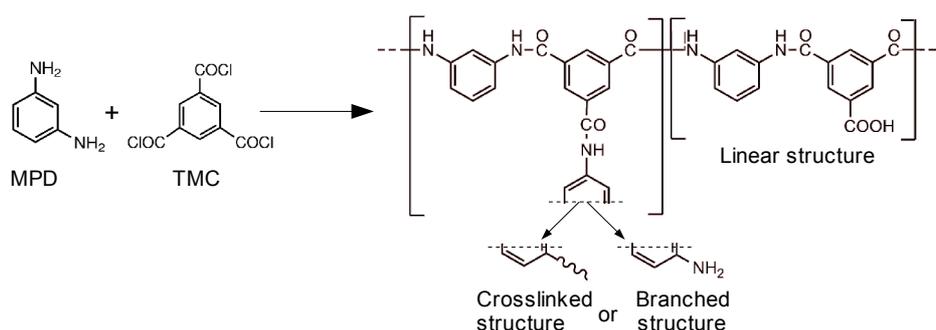


Figure 2: Polymerization of crosslinked polyamide dense layer based on trimesoylchloride (TMC) and *m*-phenyl-enediamine (MPD)

2.2 Active layer isolation

The APA layer was separated from the support ones, by removing iteratively each layer. The first polyester layer was gently mechanically removed. The polysulfone layer was then removed by dissolution with N,N-dimethylformamide (DMF). Two methodologies were used: for detailed analysis of both sides of the APA layer at atomistic scale, it was dissolved in a special container (Fig. 3a). The solvent was renewed several times until complete dissolution of the polysulfone, and by using the buoyancy forces in DMF, the desired side of APA membrane was finally laid down on the surface of a silicon wafer. When large amounts of APA were required, the dissolution was performed on top of a clock glass with DMF flowing down the surface (Fig. 3b). With this technique, 5 milligrams of pellets of dry polyamide was obtained for each membrane. It is worth to notice that the surface state of the material cannot be controlled.

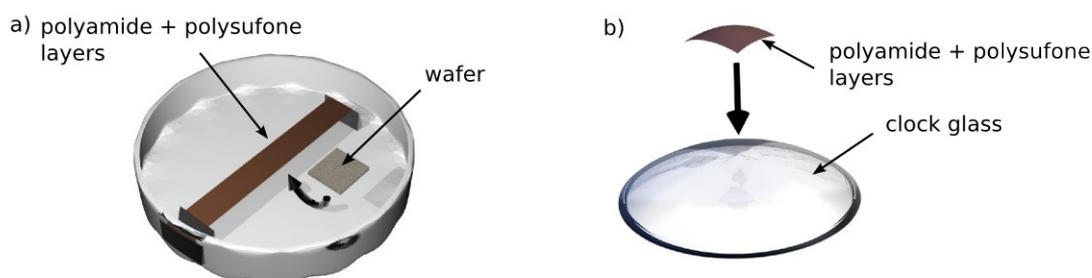


Figure 3: Representation of the sample preparation with DMF solvent a) in a container, b) with clock glass support

2.3 Membrane characterization

Table 1 summarizes the different techniques used to assess thermodynamic and structural properties at different scales. The ellipsometry measures were realized with a Scintech SE400 using a laser wavelength of 632.8 nm. This ellipsometer allows to achieve a vertical resolution of a fraction of nanometer and to obtain a rapid measurement of the thickness of a thin film.

The Hiden IGA-002 Vapour Sorption Analyser (Intelligent Gravimetric Analyser) integrates precise computer-control and measurement of mass change, pressure and temperature to enable determination of gas and vapor sorption-desorption isotherms and isobars in diverse operating conditions.

The AFM instrument used was a Molecular Imaging PicoSPM in contact mode. The polyamide layer from ESPA2 was

laid on silicone wafer. The observations were processed in ambient conditions. The X-ray photoelectron spectroscopy (XPS) was a ESCALAB 250 used on high resolution mode. The infrared spectra were obtained with an AVATAR 320 Fourier transform IR (ATR-FTIR). The measurements were processed with ATR ZnSe crystal in single point mode.

Table 1: Characterization steps of commercial RO membrane

| Interesting physical properties | Thermodynamic properties | | Structural properties | |
|---------------------------------|------------------------------|-------------------------|-----------------------|----------------------------------|
| | - Swelling rate - Density | Water sorption isotherm | Rugosity | Crosslinking and branching rates |
| Typical scale | <300 nm | 1 mm | <10 nm | <1 nm |
| Method | Ellipsometry | IGA | AFM | - XPS - FTIR |

2.4 Simulation details

Twenty entangled chains of APA, consisting in 30 repeating units of blocks A-B or A-C (as depicted Figure 4), were obtained using a compression box technique until reaching the expected density starting from random chain insertions and random reorientations of each block. The blocks B and C were randomly inserted with probabilities of 90% and 10% respectively in order to reproduce a possible crosslinking up to 10%. Indeed, blocks B and C can be crosslinked by eliminating a water molecule. As our objective was to study the feasibility of construction of a dried APA membrane by intermingling chains before crosslinking, final crosslinking was not performed in this work but the final structure was used to assess the probability to create an amide covalent bond between C and an excess of B. During the construction stage, a ramp density between $0.6 \text{ g}\cdot\text{cm}^{-3}$ and a guess density of $1.3 \text{ g}\cdot\text{cm}^{-3}$ was applied. Each compression step was followed by an isovolume and isothermal molecular dynamics simulation at 600 K during 10 ps and a minimization step via conjugate gradient method. Final refinements were obtained by adding Monte-Carlo moves. Two independent assembled systems involving 10400 atoms each were obtained as a periodic cell of $49.02 \times 49.2 \times 49.2 \text{ \AA}^3$. Each system was equilibrated during long-term isobaric and isothermal molecular dynamics simulations at 298 K and 600 K with a time step of 1 fs. Temperature and pressure were kept constant by coupling the simulated cell with an infinite external heat bath (Andersen thermostat) and with an isotropic pressure bath (Berensen barostat). A commercially available forcefield fitted on quantum molecular mechanics results (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies, Accelrys, USA) was used for this study. Van der Waals interactions were calculated with a cutoff of 9.5 Å. Coulombic interactions were calculated using an Ewald summation method with an update width of 1.5 Å. Classical polymer construction and molecular dynamics were performed with Amorphous Cell (Accelrys, USA) and Discover software (Accelrys, USA).

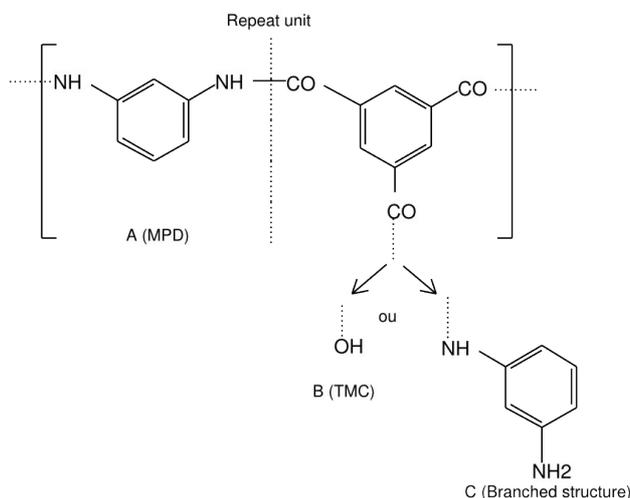


Figure 4: Repeat unit of model chain constituted by A, B and C blocks

3 Results

3.1 Thermodynamic properties

The desorption isotherm obtained from a totally wetted polyamide layer (from ESPA2) is plotted in Figure 5 along with the thickness variation obtained in ellipsometry in similar conditions. The maximum water content (dry base) inside the wet polyamide was estimated about 38%.

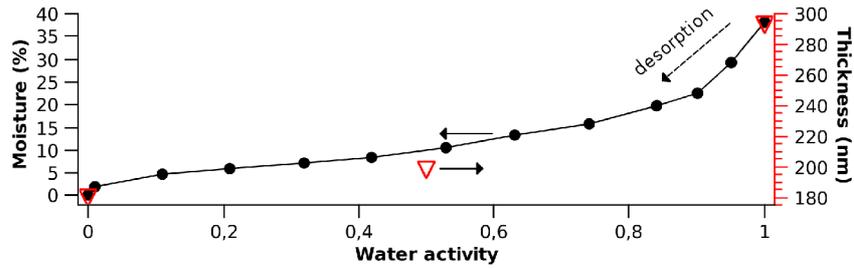


Figure 5: Water desorption isotherm (25°C) and swelling isotherm (cf §3.2)

It was estimated during sample preparation that the surfacing density of polyamide layer from ESPA2 was about $20\mu\text{g}/\text{cm}^2$. The measured thickness of dry polyamide layer was about 180 nm (cf §3.2) thus the density of dry polyamide from ESPA2 was about 1.1.

3.2 Structure properties

The observation of the ESPA2 membrane by AFM shows two roughness levels, one small with an average roughness of 30 nm measured on Figure 6 (0.9 x 0.9 μm zoom) and a waviness average of about 30nm observed on Figure 6 (5 x 5 μm picture). The wavelength used for ellipsometry measures was 632.8 nm. Considering the average roughness to be well lower than laser wavelength, the effect of this roughness on the measurements can be negligible. Thus the APA layer thickness of ESPA2 membrane obtained by ellipsometry in dry condition is $\approx 180\text{nm}$, for ambient condition ≈ 198 nm and for wet condition ≈ 293 nm.

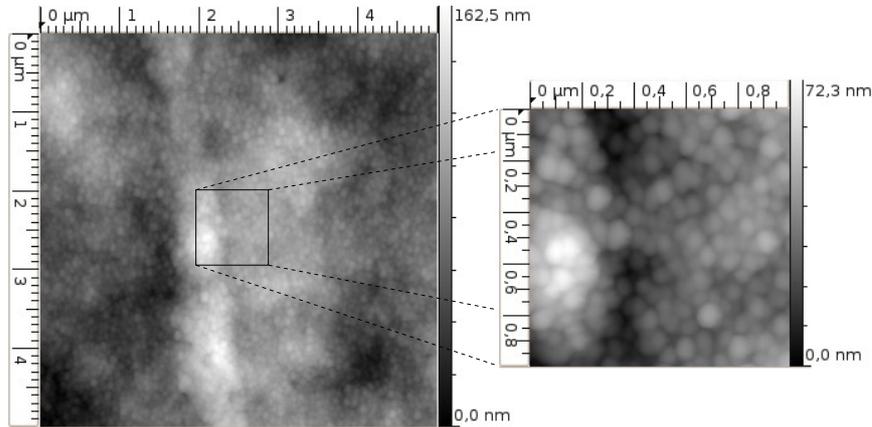


Figure 6: AFM observations of internal side polyamide layer from ESPA2

The results of atomistic composition XPS analysis on polyamide layer from both RO membranes analysed are gathered in Table 2. For each membrane category, three types of samples preparation were made:

- Surface membrane of the entire membrane (Em, Cm)
- External side of the lonely APA layer obtained with DMF treatment (Eext, Cext)
- Internal side of the lonely APA layer obtained with DMF treatment (Eint, Cint)

In fact, it is possible to compare the influence of DMF treatment and to show the difference in composition of the internal and external side of polyamide layer.

Table 2: Atomistic composition measure by XPS for ESPA2 (Em, Eint, Eext) and CPA2 (Cm, Cint, Cext)

| | C (%) | N (%) | O (%) |
|-----------|-------|-------|-------|
| E_m | 75 | 8 | 17 |
| E_{int} | 74 | 9 | 17 |
| E_{ext} | 72 | 9 | 19 |
| C_m | 76 | 7 | 17 |
| C_{int} | 72 | 8 | 20 |
| C_{ext} | 74 | 8 | 18 |

No significant difference was observed between internal and external sides of polyamide layer (between Eint and Eext, and between Cint and Cext), neither between the measures obtained before and after DMF traitement (between Em and

E_{ext}, and between C_m and C_{ext}).

It is noteworthy that no sulphur atoms were detected by XPS, which confirms the total elimination of polysulfone layer during preparation process (cf §2.2).

Polyamide from ESPA2 membrane was analyzed by ATR-FTIR. The spectroscopy results from 1350 to 1750 cm⁻¹ region with deconvolution are shown in Figure 6. The identified peaks are summarized in the table of Figure 6. The spectra obtained show the lack of carboxylic peak at 1720 cm⁻¹ (a) (Amplitude=0), whereas the amide II peaks at 1666 cm⁻¹ (b) are well represented. Moreover, no carboxylic bonds were detected by XPS. To conclude, all the branched groups of APA from ESPA2 membrane are of amide type.

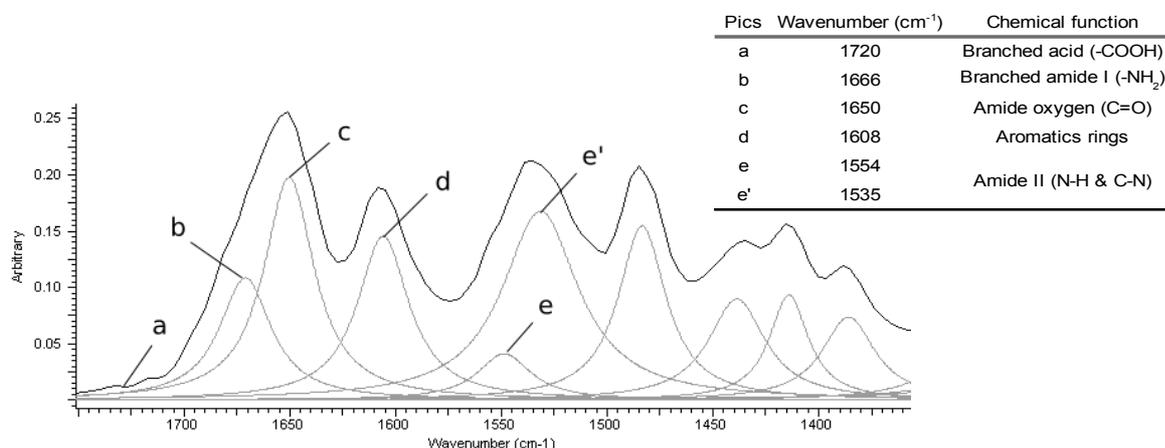


Figure 6: FTIR spectra of aromatic polyamide from ESPA2 with pic deconvolution and associated chemical functions

The APA can be represented by two repeated units named A' and B' showed in figure 7. The crosslinking unit A' and the branched unit B' were repeated m times and n times, respectively. The general chemical formula was derived as follows: $C_{(18m+3n)}H_{(12m+4n)}O_{(3m)}N_{(3m+n)}$, with $m + n = 1$. With the atomistic ratio N/O obtained from XPS measures allow to evaluate the coefficient m which is, in fact, the crosslinking rate: $m = (3 - 3N/O) / (2 - 3N/O)$. The crosslinking rates further obtained for E_m , E_{int} and E_{ext} are presented in table 3.

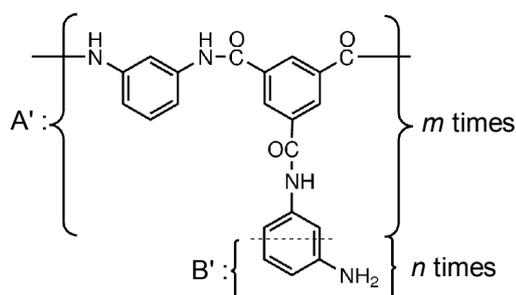


Figure 7: General chemical formula without acid carboxyl group

| Sample | E_m | E_{int} | E_{ext} |
|---------------------------|-------|-----------|-----------|
| crosslinking rate m (%) | 66 | 68 | 60 |

The method accuracy for crosslinking rate determination is not satisfactory ($\approx \pm 10\%$) to state on a significant difference between the internal and external sides, as well as before and after DMF treatment.

The Molecular Dynamical (MD) model permitted to predict the structural factor for different steps of our model building strategy. The Figure 8 shows the theoretical neutron scattering spectra after cell construction and after dynamical simulation, respectively for 600K and 298K. Only in the case of construction cell we observe a little waviness on the scattering profile, that shows a little periodicity in the structure of polymer. The structure was smoothing during the dynamical simulation which represented a system evolution about $5 \cdot 10^{-10}$ s. The increase of the cell structure density was observed for 298K, compared to 600K. The obtained density was 1.28 and 1.34 for the cells at 600K and 298K, respectively, which corresponds to a specific volume of 0.782 and 0.746, respectively. The calculated volumetric thermal expansion coefficient was $157 \cdot 10^{-6} \text{ K}^{-1}$.

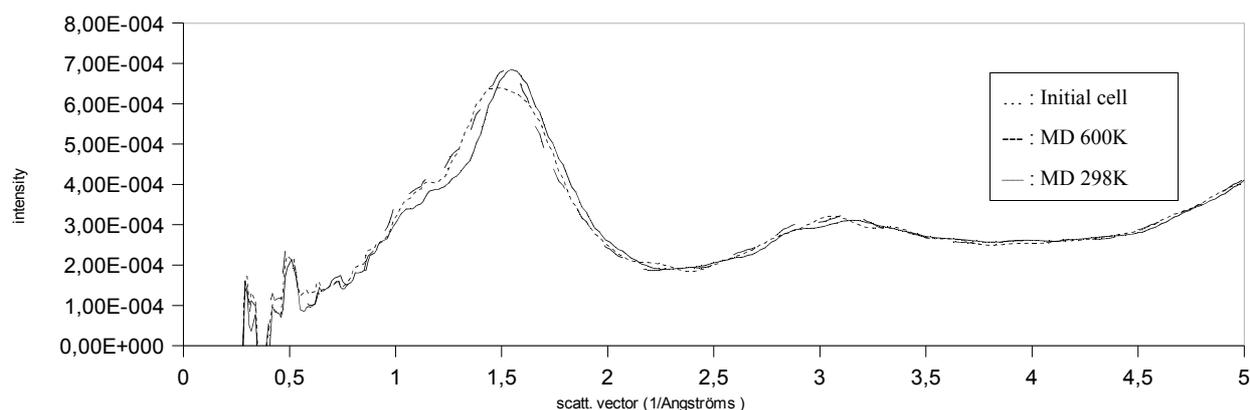


Figure 8: Theoretical neutron scattering spectra: a) for the initial cell at 600K constructed by Amorphous Cell, b) MD simulation at 600K (simulated time: $4 \cdot 10^{-10}$ s) and c) MD simulation at 298K (simulated time: $6 \cdot 10^{-10}$ s).

4. Conclusions

The current study presented the first steps of an ambitious program aiming at developing an atomistic model of crosslinked reverse osmosis membranes swollen with water or not. The first construction assumptions were obtained for two typical commercial membranes from Hydranautics Membranes (USA) (ESPA2 and CPA2). An important contribution relied on the possibility to isolate the active polyamide layer from its support and to submit each membrane side to a specific examination. XPS measurements validated the absence of contamination of the membrane by support constituents. XPS and FTIR measurements demonstrated the absence of acid functions and consequently that APA had a high crosslinking rate of about 65%. Water swelling and water desorption isotherm shapes confirmed that crosslinking rates could contribute only in a small extent to the excess chemical potential of water. A first atomistic construction strategy with no crosslinking structures, consisting in intermingling chains before crosslinking them, was successfully applied to a dried APA layer. Although the atomistic model was not crosslinked at present time, the density, the thermal expansion and the neutron scattering structure factors were close to the expected values for similar polymer.

Future works aims at collecting experimental neutron scattering structure factors at different water swelling rates and to assess unambiguously the crosslinking rates of typical commercial APA layers. After refined validation, the developed atomistic models will be used to investigate the molecular mechanisms of organic solute in reverse osmosis membranes.

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