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High Dehumidification Performance of Amorphous Cellulose Composite Membranes prepared from Trimethylsilyl Cellulose

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Cellulose is widely regarded as an environmentally friendly, natural and low cost material which can significantly contribute the sustainable economic growth. In this study, cellulose composite membranes were prepared via regeneration of trimethylsilyl cellulose (TMSC), an easily synthesized cellulose derivative. The amorphous hydrophilic feature of the regenerated cellulose enabled fast permeation of water vapour. The pore-free cellulose layer thickness was adjustable by the initial TMSC concentration and acted as an efficient gas barrier. As a result, a 5,000 GPU water vapour transmission rate (WVTR) at the highest ideal selectivity of 1.1×10^6 was achieved by the membranes spin coated from a 7% (w/w) TMSC solution. The membranes maintained a 4,000 GPU WVTR with selectivity of 1.1×10^4 in the mixed-gas experiments, surpassing the performances of the previously reported composite membranes. This study provides a simple way to not only produce high performance membranes but also to advance cellulose as a low-cost and sustainable membrane material for dehumidification applications.

Introduction

Dehumidification is necessary for various applications including air conditioning systems^{1,2}, compressed air production³, and flue gas dehydration⁴⁻⁶. Membrane technology stands out among the conventional dehumidification methods such as adsorption, compression, and cooling. It offers compact, continuous, less energy-intensive and highly efficient processes. The partaking of membrane processes in the hybrid air-conditioning systems could lead to significant energy savings⁷. Polymeric membranes usually show a trade-off between permeability and selectivity, i.e. membranes with high permeability exhibit low selectivity and vice versa. However, water vapour selectivity in dehumidification usually increases with water vapour permeability⁸. In dense polymeric membranes, the permeability is controlled by the penetrant solubility and diffusivity, following the solution-diffusion model⁹. Diffusivity is a measure of gas mobility within the membrane structure, while the solubility is controlled by the membrane-penetrant interaction strength. Therefore, key for a successful dehumidification membrane are appropriate membrane

structural features to facilitate selective diffusion and a strong hydrophilic character for high water vapour permeability.

Thin film composite (TFC) membranes have been extensively used in industrial gas and liquid separations. These membranes employ a thin polymer layer to provide selective transport, supported by a mechanically robust mesoporous substrate. Compared to the integrally skinned asymmetric membranes where the selective and support layer are formed simultaneously from the same material, the TFC configuration is advantageous as both the selective layer and the support can be independently tailored to achieve the optimum separation performance. The composite approach also allows the use of expensive polymers as thin coating layer. Hydrophilic TFC membranes thus far developed for dehumidification applications include polyvinyl alcohol (PVA)¹⁰, Pebax®1657¹¹, polyamide¹², cellulose acetate¹³, covalent organic polymer¹⁴, polyacrylamide¹⁵, zeolite¹⁶, and ionic liquid^{17,18}. Despite the substantial progress made in membrane-based dehumidification, it is still a challenge to obtain low-cost membranes with fast and selective transport through simple and scalable fabrication processes.

Cellulose continues to be of vast interest in numerous membrane applications due to its green characteristics, abundant availability, low cost and fascinating physicochemical properties. In particular, cellulose that contains a large amount of hydroxyl groups (see Fig. S1) is capable of attracting water molecules through hydrogen bonding interactions. These interactions favour solubility-enhanced water vapour transport in the polymer matrix. However, the fabrication of pure cellulose membranes is challenging due to cellulose insolubility. Only few organic solvents for cellulose are known;

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Fig. 1 Cellulose silylation and the subsequent regeneration using acid vapour.

and these often possess high reactivity and toxicity¹⁹. Ester derivatives like cellulose acetate and ethyl cellulose are thus preferably used industrially. Moreover, cellulose membranes usually exhibit low selectivity because of their typically porous structure. Therefore, the challenges lie in the convenient cellulose processing, which produces dense membranes with high separation performance.

Previously, we reported the use of trimethylsilyl cellulose (TMSC) as a precursor for the fabrication of cellulose thin film composite membranes for liquid separations^{20–22}. This is a convenient way to prepare dense cellulose membranes and to avoid the cumbersome solvents for cellulose processing. TMSC is a highly soluble material prepared from cellulose by the well-known silylation reaction (Fig. 1). TMSC has excellent film forming properties and can be easily manufactured as very thin pore-free films. The elegance of the method lies in the *in situ* transformation of TMSC back to cellulose, which is reproducible, simple and can be up-scaled for mass production^{21–22}. The membrane sieving performances can be controlled by the initial TMSC concentration and the cellulose regeneration period²².

In this study, a simple strategy of gradually increasing the polymer concentration was applied to achieve the desired film structure suitable for dehumidification. This strategy is expected to restrict air permeation with a minor consequence on the water vapour transmission thereby greatly increasing membrane selectivity. Two types of polyacrylonitrile (PAN) ultrafiltration membranes were used as supports. The performance of the fabricated composite membranes was measured through single and mixed-gas experiments. Wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) were used to determine the membrane crystallinity. The membrane morphology and the phenomenon of polymer intrusion in the supports were investigated using scanning electron microscope (SEM) and spectroscopic ellipsometry (SE).

Experimental

TMSC preparation

TMSC ($M_n = 44,700 \text{ g} \cdot \text{mol}^{-1}$, $M_w = 122,900 \text{ g} \cdot \text{mol}^{-1}$, degree of silylation (D_s) = 2.2, polydispersity index = 2.75) was synthesized from a microcrystalline cellulose (Avicel PH101, Sigma Aldrich) through the silylation reaction as previously described^{21–20}. In brief, the polymer was reacted with hexamethyldisilazane in dimethylacetamide/lithium chloride solvent system at 80°C followed by product precipitation in methanol and vacuum drying.

Membrane preparation

As supports for membrane fabrication, two commercial polyacrylonitrile (PAN) membranes were chosen; GMT PAN from GMT GmbH (Germany) and PAN-350 (denoted as P350) from Sepro Membranes, Inc. (Oceanside, CA). *N*-hexane was supplied from Sigma–Aldrich. The membranes were spun-coated from *n*-hexane solution containing a certain amount of TMSC at 1,000 rpm and 500 rpm^{–1} speed and acceleration. Prior to the spinning step the solution was gently spread over the surface of the support for about 3–4 s for uniform wetting. Cellulose regeneration was then carried out using the vapour phase of 10% hydrochloric acid solution for 15 minutes as illustrated in Fig. S2.

Membrane characterization

SEM imaging was performed using an FEI Quanta 600 to examine the membrane morphologies. Samples were coated with a three nanometer iridium layer to minimize charging effects during imaging. Membrane surface topographies were analyzed by atomic force microscopy (AFM) with an Agilent 5400 SPM microscope (Agilent Technologies) operating in noncontact mode. WAXD using a Bruker D8 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) was carried out to reveal the crystallinity of the raw cellulose (Avicel PH101) from which TMSC was synthesized, the as-prepared TMSC, and the corresponding regenerated cellulose films. Differential scanning calorimetry was performed using TA Instruments, model DSC Q2000. About 2–4 mg samples were weighed in aluminum pans and analyzed with a heating rate of 10 °C/min over the temperature range of 25–200 °C. Water vapour sorption experiments were conducted at 25 °C using a gravimetric sorption balance method on VTI-SA sorption analyzer from TA instruments, USA. The samples were dried inside the sorption analyzer chamber at 100 °C for 2 h prior to the measurements to achieve a constant weight. Sorption measurements were recorded for water activities in the range of 0 to 0.95. Desorption measurements were also recorded over the entire range of activity.

A recently developed method for TFC membranes analysis based on focused beam spectroscopic ellipsometry (RC2, Woollam Co., Inc.) was carried out to determine the skin thicknesses as well as to estimate the pore intrusion within the PAN supports²³. The method uses a change in the polarization state of light reflected from the membrane sample combined with optical modelling to extract meaningful information, such as skin thickness and refractive index of both skin and the support. The optical model used for the ellipsometry analysis consisted of a Cauchy-type dielectric layer representing cellulose thin film deposited on top of a porous PAN substrate. The porous PAN substrate was modelled as an effective medium approximation, which mixed the refractive index of dense PAN ($n = 1.514$), represented by another Cauchy-type layer, and void ($n = 1.000$) that represented the pores. As such, the model could be used to determine the void volume fraction, corresponding to porosity, independently from the properties of a thin film. More information on spectroscopic

ellipsometry modelling and characterization of membranes can be found in the literature²⁴⁻²⁷.

Membrane performance

Single water vapour permeation

Water vapour transmission rates (WVTR) through the composite membranes were investigated by a modified permeability cup method. This method was explained in details in our earlier work^{11, 28}. In summary, a membrane was placed above a modified permeability cup with water inside up to a certain level to avoid contact during handling. Dry nitrogen was used as a sweep gas on the permeate side of the membrane. Finally, the water vapour permeance through the membrane was calculated using Eq. 1.

$$WVTR_m = \frac{dm}{dt} \times \left[A \times P_{sat} \times (R_1 - R_2) \right]^{-1} \quad (1)$$

Where A is the membrane area, P_{sat} is the saturated vapour pressure at the test temperature, R_1 and R_2 are the relative humidity at the source and the vapour sink. Since an air gap existed between the membrane and the water surface, neglecting the effect of air gap would lead to considerable underestimation of the water vapour permeance. As explained in our previous work¹¹, the water vapour permeance was corrected using Eq. 2.

$$WVTR_c = WVTR_m \left[\frac{p_0 - p_2}{p_1 - p_2} \right] \quad (2)$$

where p_0 , p_1 , p_2 are the water vapour partial pressure at the water surface, above and beneath the membrane surface, respectively. About 3-5 different membranes were measured and the permeability was presented in gas permeation unit (GPU), where 1 GPU = $1 \times 10^{-6} \text{ cm}^3 \text{ (STP) (cm}^2 \text{ cmHg s)}^{-1}$.

Single nitrogen permeation

Pure nitrogen (N_2) permeance was obtained using a constant volume/variable pressure test method. Single gas permeance through the membranes was calculated according to the eq. (3). The effective membrane area was 24.98 cm^2 .

$$J = \frac{V \times 22.4}{R \times T \times A \times t} \ln \left[\frac{p_f - p_0}{p_f - p_{(t)}} \right] \quad (3)$$

where V is the permeate volume (m^3), R is the ideal gas constant ($\text{m}^3 \text{ bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the temperature (K), A is the membrane area (m^2) and t is time (s), p_f , p_0 , and $p_{(t)}$ (bar) are the pressures at the feed, permeate side at beginning and permeate side at the end of measurement. An ideal selectivity was used to measure the membrane separation performance and was calculated using Eq. (4) as the ratio of permeance of water vapour over nitrogen.

$$\alpha = \frac{WVTR}{J_{N_2}} \quad (4)$$

Mixed-gas permeation

The experimental set up for conducting mixed water vapour/gas experiment is shown in Fig. S2. Water vapour was produced using a generator, where a demister was used to entrain any liquid droplets. Dry N_2 gas was supplied as a dilution line to modulate humidity in the feed line. The flow rate of both feed gas and dilution gas were controlled by mass flow controllers (MFC, Alicat Scientific Inc., USA). The flow rate of the feed gas was kept constant at 1 L/min and relative humidity was controlled using a dilution line. A back pressure regulator was used on the retentate line to maintain a constant operating pressure in the system. Dry N_2 gas was used as a sweep gas on the permeate side to maintain a constant driving force. The membrane module with an effective membrane area of 11.5 cm^2 was placed in an oven (Binder, FD53) to maintain a constant temperature. Humidity and temperature transmitters (H&T, Probe type 334, Vaisala Oyj, Finland) were used on the feed and permeate side of the membrane to determine humidity and temperature. All the measurements were recorded once the system reached steady state. The water vapour flow rates (Q) (cm^3/s) were calculated using Eq. (5). The mixed gas tests were performed in a way that the humidity in the feed and retentate differed only slightly (very small stage cut).

$$Q = \frac{Q_{N_2} \times \gamma_{H_2O} \times V_m}{M_w} \quad (5)$$

Where Q_{N_2} (cm^3/s) is the reading after the permeate stream passed through the cold trap and was measured by a mass flow meter. γ_{H_2O} is the absolute humidity, V_m (22.4 L) is the molar volume of water vapour (STP) and M_w is the molecular weight of water. The permeance of each component (P_i) in the mixed gas stream was calculated using Eq. 6 and is presented in GPU.

$$J_i = \frac{Q}{\Delta P_i \times A} \quad (6)$$

where A is the membrane area (cm^2) and ΔP_i is the difference in partial pressure between the feed and permeate side of the membrane for component i . The mixed-gas selectivities were calculated as the ratio of each permeance similar to Eq. (4).

Results and Discussion

Support characterization

ATR-IR spectra of both GMT and P350 PAN support membranes are shown in Fig. S4. The spectra revealed that both support membranes were made of a similar polymer with slightly different composition. Fig. 2 depicts the cross-section and surface morphology of both PAN supports at two different magnifications. Both membranes comprised a highly porous sponge-like matrix, while the P350 membrane also had finger-like macro-voids in the sub-layer as shown in the low magnification image. The surface images revealed the mesoporous structure of both membranes. The pore size of

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Fig. 2 Surface and cross-sectional SEM images of the PAN supports.

P350 membrane was higher than for the GMT and also the surface porosity seems to be higher. The AFM images (Fig. S5) showed that the roughness of the P350 membrane was twice the value of GMT PAN. Their calculated mean square roughness were around 3.4 and 7.0 nm for GMT and P350, respectively.

Cellulose intrinsic properties

The experimental sorption data presented in Fig. 3A show the increase in the cellulose weight due to water vapour uptake over the increase in water vapour activity. This sorption capacity strongly depends on the membrane affinity towards water molecules, which is promoted by the three hydrogen bond-forming hydroxyl groups present on the anhydroglucose unit in cellulose (Fig. S1). According to Fig. 3A, the sorption isotherm revealed a typical sigmoid-shaped curve found in natural polymers such as cellulose^{29, 30}, starch³¹ and foodstuffs³². The isotherm evidenced at low relative humidity referred to Langmuir sorption capacity, which is interpreted as a measure of the non-equilibrium free volume, associated with the glassy state of the polymer. This was followed by the rapid uptake with a convex shape to the abscissa starting at about

60% relative humidity, representing the Flory-Huggins isotherm due to swelling. It is well known that at high water vapour content, the cellulose network becomes highly swollen due to the water-induced plasticization arising from strong hydrogen bonding interactions. Therefore, the water-plasticized cellulose may be considered to be close to the rubbery state (lack of sorption – desorption hysteresis). More investigations on cellulose water vapour sorption can be found in the literature³³⁻³⁶.

The WAXD analysis of cellulose (Avicel PH101) from which TMSC was synthesized, the as-prepared TMSC, and the corresponding regenerated cellulose (RC) films revealed entirely different patterns, as shown in Fig. 3B. The diffraction peaks of Avicel PH101 observed at 15.2°, 22.2° and 34.5° corresponded to the reflection planes of cellulose I polymorph, a typical form of native cellulose produced by the living systems. These crystal peaks disappeared in the TMSC diffractogram due to the masking of the most of hydroxyl groups during silylation. The loss of cellulose crystallinity in TMSC explained the high solubility of TMSC in many solvents including hexane, acetone, and tetrahydrofuran. From the broad RC pattern in Fig. 3B, it also seems that our silylation-regeneration procedure significantly eliminated the cellulose crystallinity. Unlike the typical regenerated cellulose that is present in the form of crystalline cellulose II, cellulose regenerated from TMSC using acid vapour was largely in an amorphous state, which is in line with the literature³⁷. Fig. 3C shows the effect of cellulose amorphous property on the water vapour sorption. The DSC curve of the microcrystalline Avicel PH101 exhibited a broad endothermic peak centered at 82°C as a representation of dehydration event. In RC, this peak showed high intensity corresponding to a high heat of dehydration. This demonstrated high water vapour sorption of the sample due to the loss of crystallinity. These results are consistent with the conclusion from WAXD measurements (Fig. 3B). The center of the peak also shifted to about 89°C, which was another indication of the amorphous nature of the film³⁸. These results indicated that the amorphous cellulose prepared in this study interacted much more strongly with water molecules as compared to its crystalline starting polymer.

Fig. 3 A) Water vapour sorption isotherm of regenerated cellulose films at 21°C. B) WAXD pattern of Avicel PH101, the as-prepared TMSC, and the corresponding regenerated cellulose films. C) DSC curve of Avicel PH101 and the regenerated cellulose films.

Fig. 4 AFM images of cellulose regenerated from 1 and 7% TMSC on GMT and P350 support.

Morphology of cellulose composite membranes

Composite membranes were prepared from varying concentrations of TMSC followed by acid-vapour hydrolysis to regenerate the cellulose structure. The TMSC coating solution concentration was varied between 1% to 7% (w/w) and the

corresponding regenerated cellulose membranes were denoted according to their initial TMSC concentrations. According to Fig. 4, the surface of the cellulose films on GMT PAN was smooth with the calculated roughness close to the value of GMT PAN surface (Fig. S5). In contrast, the membrane fabricated from 1% TMSC on P350 appeared rougher than the 1% membrane on GMT PAN. Interestingly, introduction of a higher cellulose concentration on P350 support led to a much rougher topology as compared to the one on GMT PAN. This suggests that the surface structure, in particular the larger pore sizes and the related higher roughness of P350 as compared with GMT, of the support strongly influenced the final morphology of TFC membranes.

The cross sectional SEM images of the composite membranes are depicted in Fig. 5. The red lines are the estimation of the active layer thickness. An apparent increase in cellulose thickness of the composite membranes was observed with increasing polymer concentration. Both the GMT and P350 membranes showed similar thicknesses at the same concentration variations. Further elucidation in membrane thicknesses was carried out using spectroscopic ellipsometry (Fig. 5B). Overall, both measurements were in a relatively good agreement. One advantage of ellipsometry is based on the fact, that it averages the thickness over approximately 0.25 mm² beam footprint in a single spot measurement instead of a few micrometre cross-section images. Ellipsometry was also used to measure the

Fig. 5 A) Cross-section SEM images of composite membranes. Scale bar is 500 nm. Spectroscopic ellipsometry measurement of B) thickness variation and C) refractive index of cellulose layer at different polymer concentrations, and D) thickness mapping of 1% TMSC membrane on a 4 x 4 mm² area.

Fig. 6 A) Surface porosity of the supports with the variation of TMSC concentrations and B) porosity mapping of the P350 substrate upon 1% TMSC coating.

homogeneity of the selective membrane layer on a sub-cm scale using multiple single spot measurements in a mapping mode. The mapping of the 1% membrane on the P350 PAN presented in Fig. 5C demonstrates a variation of cellulose thickness on a 4x4 mm² area. The thickness ranges from 99 to 146 nm, indicating that the membrane possessed a relatively uniform, continuous skin with no apparent voids that could lead to defects.

In ellipsometry analysis the surface porosity of the PAN supports in the presence of deposited thin films can be determined independently. This is because light is able to penetrate the thin film and reflect from the substrate. In such a way, the properties of the substrate in the presence of the film can be probed. This is utilized here to determine the polymer intrusion within the supports in the region immediately below the thin skin to an estimated light penetration depth of several hundreds of nm (comparable to the wavelength of the probing light). According to Fig. 2, both bare supports showed a typical mesoporous structure with some surface porosity possible for polymer intrusion during the coating process. As shown in Fig. 6A, the ellipsometry-derived substrate porosity of the bare P350 substrate (41.5%) was significantly higher than that of the GMT PAN (31.5%) which is consistent with Fig. 2. In both cases, the remaining substrate porosity quickly decreased with the increasing coating solution content in a rather similar fashion for both supports as a result of the coating solution pore intrusion. At the highest concentration of 7% virtually all sub-skin pores in the GMT were filled, while for P350 still approximately 10% porosity remained unoccupied. The ellipsometry results for the coated membranes are in agreement with the cross-sectional SEM images where for the 5% and 7% membranes (Fig. 5A) more diffuse boundaries between the skin and the substrate were observed, indicating significant pore intrusion. We

hypothesise, that the occurrence of pore intrusion is related with the substrate wetting step lasting approximately 3 – 4 s before spinning. The wetting step was critical to obtaining high homogeneity and defect-free skins. During this step capillary action was able to partly suck the coating solution into the pores. The lateral distribution of the pore intrusion, Fig. 6B, indicates that over a larger membrane area, 4 by 4 mm, a rather uniform distribution of sub-surface porosity is achieved upon coating with a 1% TMSC solution. Similar maps for the higher TMSC concentrations showed less uniformity.

Water vapour transmission rate (WVTR)

Prior to examining of the transport properties of the composite membranes, we studied the intrinsic properties of the supports. According to data presented in Table 1, the P350 membrane showed higher WVTR and N₂ permeance than the GMT membrane as a result of its higher porosity. Given that in both cases the PAN layer was hydrophilic with a highly porous structure (Fig. 2), fast transport of water vapour was expected. However, these PAN supports had also a hydrophobic polyester backing, which may act as a considerable resistance for water vapour transport, as reported in the literature³⁹. For our work we took the best commercial support membrane we could get; but for future work it seems worthwhile to design and manufacture a more open support with lower resistance for water vapour.

Table 1 Performance of the bare supports

Support	Thickness (μm)	Porosity ^a (%)	WVTR (GPU)	N ₂ permeance (GPU)	Selectivity
GMT	181	31.5	6,541	39,819	0.16
P350	155	41.5	8,906	57,654	0.15

^a Surface porosity determined using spectroscopy ellipsometry.

Fig. 7 WVTRs of cellulose composite membranes prepared from different TMSC concentrations.

Fig. 7 shows the variation of WVTRs of the composite membranes with different concentration of TMSC solution. The WVTR of the 1% membranes was close to the WVTR of the bare supports presented in Table 1. The presence of cellulose coating decreased the WVTR of bare P350 by 9% and 24% of bare GMT. This reflects that the overall mass transfer resistance was predominantly imposed by the support layer, which is consistent with the literature^{11, 39, 40}.

The WVTRs of P350 supported membranes were dramatically affected by the cellulose thicknesses. Interestingly, we did not observe a similar trend in the case of GMT PAN. There was 20% decrease in water vapour permeance by increasing TMSC concentration from 1% to 7% using the P350 support. On the other hand, the permeances of the membranes with the GMT support were relatively stable at all concentration variations. As would be expected, the decrease in WVTRs of P350 membranes was due to the increase in diffusion path across the increasing skin thicknesses. For the GMT PAN we do not see the decrease of the WVTR with increasing cellulose coating thickness. Apparently the less porous support is the main resistance for the water vapour transport.

Most cellulosic materials are present as semicrystalline polymers in varying conformations depending upon the source and the fabrication history. It is well accepted that gas molecules penetrate only the amorphous region while the crystallites are considered impermeable. The disappearance of the crystallinity in the regenerated cellulose films is favorable as it can increase the fractional permeable area and reduce tortuosity that gives rise to the fast-diffusional transport. Moreover, the amorphous character of the polymer could facilitate higher water vapour sorption in the membrane as explained in the previous section. As a result, high water vapour sorption in combination with fast diffusion accelerated the overall WVTR. The comparison between amorphous and crystalline cellulose in regards to water interaction has recently been reported⁴¹. The crystalline cellulose was found to interact better with water than the amorphous one due to the presence of nanopores. However, this indicated that the water binding ability was not directly correlated with crystallinity as different coating methods applied in the study also led to different film morphology. Similar to our postulation, the influences of polymer crystallinity on WVTR have also been investigated for various polymers; polymers with high crystallinity exhibited lower WVTRs than their corresponding amorphous counterparts^{42, 43}.

Dehumidification performance

The decrease in N_2 permeance with increasing TMSC concentrations along with the calculated ideal selectivity is presented in Fig. 8. The nitrogen permeances were around 1 and 2 GPU using only 1% coating, four orders of magnitude lower than the permeances of the bare supports. These values are indications that the thin layers obtained by coating with a 1% TMSC solution are nearly defect-free.

With the presence of a thin cellulose layer (1% TMSC), the

membranes supported by P350 had already more than 3,400 ideal selectivity as a result of the dramatic fall of the nitrogen permeance (Fig. 8). At the same coating concentration, the gas selectivity of GMT supported membranes was even higher and exceeded 5,000 GPU. This can be explained by the smaller surface pore size and the smoother surface; both factors favour a defect-free coating. The selectivity of the GMT and P350 supported membranes further increased to about 4,000 and 10,000 GPU respectively upon coating with a 3% solution due to the significant decrease of the N_2 permeances. With increasing cellulose thickness the nitrogen permeances decreased much more than the water vapour permeance resulting in higher selectivities. In all cases the selectivity of the membranes with the GMT PAN as support was higher when compared to the P350 supported membranes. The thickest cellulose coating was prepared by coating the P350 and the GMT PAN with a 7% TMSC solution followed by cellulose regeneration. When using the more open P350 PAN support a low nitrogen permeance of 0.13 GPU was observed resulting in a water vapour/nitrogen selectivity of 4.9×10^4 . Remarkably, using the same TMSC concentration led to an even lower nitrogen permeance with the GMT PAN supported membranes, resulting in an about 20-fold greater selectivity of 1.1×10^5 .

In our previous work dealing with organic solvent nanofiltration it was revealed that the increasing cellulose content in the coating solution led to an improvement in the sieving performance, making the membrane more solute impenetrable²². In the present work, it is also apparent that higher TMSC concentrations in the spin coating solution led to decreases in nitrogen permeance, which ultimately resulted in increases in selectivity, as shown in Fig. 8. The selectivity increase is probably a combined effect of the increased skin thickness leading to lower probability of defects and increased pore intrusion leading to drastic decreases of nitrogen permeances. While ellipsometry is sensitive to the porosity in an immediate vicinity of the skin, the technique cannot give an estimated depth of intrusion, which can be potentially much deeper than the light penetration depth. Therefore, the exact quantification of the magnitude of the pore intrusion effect

Fig. 8 Ideal selectivity and nitrogen permeances of the cellulose composite membranes.

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remains challenging.

Cellulose is strongly hydrophilic by nature. In the presence of high water vapour content it absorbs moisture and expands its network easily through hydrogen bonding. This suggests that the mixed-gas performance of cellulose would be very much affected by swelling. Therefore, we measured mixed-gas permeation using humid gas streams using the GMT PAN supported membrane coated with the 7% solution. The results are summarized in Table 2 along with the state-of-the-art composite membranes reported in the literature. The mixed-gas experiment yielded a WVTR of 4,000 GPU. This was lower than the pure-gas WVTR, as expected due to the partial occupancy of the adsorption sites and diffusion path by nitrogen molecules. Nonetheless, compared to the WVTR previously reported by other TFC membranes, this value is among the highest ones. At the same time, the highest mixed-gas selectivity of 11,000 was also achieved by this membrane, even though it was two orders of magnitude lower than the pure-gas selectivity. This demonstrates that our membranes still acted as efficient permanent gas barriers even in the presence of high humidity. While numerous factors affect gas and vapour permeation in polymeric membranes, the amorphous, hydrophilic and rigid nature of the selective layer

prepared in this study have undoubtedly promoted the fast water vapour permeation as well as good selectivity.

Conclusions

Cellulose composite membranes have been prepared through acid vapour regeneration of trimethylsilyl cellulose layers on two different PAN supports, the GMT PAN and the more open P350 PAN. We achieved very high water vapour permeance for these composite membranes due to the hydrophilic character of the selective amorphous cellulose layer. The changes in polymer concentration in the coating solution had hardly any effect on water vapour permeance of the membranes on GMT PAN, whereas the water vapour permeance decreased in the case of the P350 supported membranes. Simultaneously, the increasing initial polymer concentration, which led to the increase of cellulose thickness and the degree of polymer intrusion within the supports considerably decreased the nitrogen permeances in both cases, ultimately resulting in higher selectivities of up to 1.1×10^6 . The cellulose/GMT PAN composite membranes obtained by coating with a 7% TMSC solution showed a WVTR of 4,000 combined with a mixed gas selectivity of 11,000, surpassing

Table 2 Performance of cellulose composite membranes in comparison to previously reported TFC membranes.

Membrane	Support	T (°C)	Single-gas experiment		Mixed-gas experiment	
			WVTR (GPU)	Selectivity	WVTR (GPU)	Selectivity
Tetraethylene glycol ⁴⁴	Polyvinylidene fluoride (Durapel)	15-30	-	-	223	2,000
Ionic liquid ([Emim][Tf2N]) ¹⁸	Polyethersulfone	31	635	3,843	-	-
Pebax 1657 ⁴⁰	Polyether imide (Ultem® 1000)	21	-	-	1,800	1,800
NaA zeolite ¹⁶	Nickel sheet	32	-	-	20,042	178
Cellulose acetate-polyethylene glycol blend ¹³	Polyethersulfone	30	-	-	444	176
Polyamide ⁴⁵	Polyethersulfone (hollow fiber)	30	-	-	3,185	195
Polyamide from 3,5-diaminobenzoic acid ⁴⁶	Polyethersulfone	30	-	-	2,160	34
Polyamide incorporated by TiO ₂ nanoparticles ¹²	Polysulfone (hollow fiber)	30	-	-	1,131	548
PVA incorporated by LiCl ⁴⁷	Stainless steel-mesh scaffold incorporated by TiO ₂	31	-	-	1,667	2,800
PVA incorporated by LiCl ¹⁰	Stainless steel-mesh scaffold incorporated by TiO ₂	-	-	-	1,524	5,781
Polyamide incorporated by silicon nanoparticles ⁴⁸	Polysulfone (hollow fiber)	30	-	-	2,200	501
Covalent organic polymer ¹⁴	Polyethersulfone (hollow fiber)	30	-	-	2,054	119
Pebax 1657 incorporated by graphene oxide ¹¹	Polyacrylonitrile	21	5,000	80,000	-	-
Regenerated cellulose from 7%TMSC (present study)	Polyacrylonitrile	23	4,950	1,080,000	4,000	11,000

the performance of currently reported TFC membranes. Overall, this study has provided a simple and scalable way to obtain amorphous dense cellulose membranes with excellent performance for dehumidification. Moreover, the low-cost and green characteristics of cellulose would boost the replacement of synthetic and expensive materials, leading to more sustainable and economical processes.

Conflicts of interest

There are no conflicts of interest to declare.

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TOC

Composite membranes with a thin cellulose layer with outstanding flux and selectivity for water vapour are achieved via coating with trimethylsilylcellulose.