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2 wt% Nexar

Morphology-Performance

Humidified Stream

Dehumidified Stream

Sweep/Vacuum

9089 GPU

1874 GPU

321 GPU

3 wt%

5 wt%
NEXAR™-coated hollow fibers for air dehumidification

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Abstract

Air conditioning is one of the essential requirements for households as well as work stations. Dehumidification in air conditioning is the highest energy-consuming component, where membranes could play a crucial role. In this work, we propose the coating of NEXAR™, a commercial pentablock copolymer in tetrahydrofuran on polyetherimide hollow fiber support for separation of water vapor from humidified air. The block copolymer in tetrahydrofuran forms a lamellar/parallel cylindrical structure separated by equidistance during the morphological transformation process giving its unique characteristics with higher water vapor transfer efficiency. Both vacuum and sweep gas modes of membrane dehumidification strategies are investigated along with the detailed study of the morphological transformation process under a controlled environment, which is supported by comprehensive scanning electron microscopic and atomic force microscopic imaging. The membrane has shown water vapor permeance up to 9089 GPU with water vapor to nitrogen selectivity up to 3870. The membrane can reduce the relative humidity from 80% to 41% proving one of the competitive materials for membrane dehumidification.

Keywords: membrane, hollow fiber, dehumidification, Nexar, water vapor transport

1. Introduction

The removal of water vapor from humid air is an energy-intensive process. Dehumidification is an essential part of air conditioning systems, especially in tropical and Middle Eastern countries, where temperature goes to 40-45°C with relative humidity (RH) up to 80-85% [1-3]. Cooling and dehumidification are essential to achieve comfortable indoor conditions (25°C and around 45% RH), while preventing mold growth, and enhancing buildings durability [4, 5]. Over 90% of
the current air dehumidification is accomplished by either sorption or vapor compression [4]. The energy utilized in air dehumidification leads to higher costs of electricity and a large carbon footprint [1, 6]. For instance, about 52% of the total energy demand in Saudi Arabia during summer is for air-cooling [6].

Membrane based-air dehumidification offers low energy consumption, simple operation, and a small footprint [1, 4, 7]. It is an isothermal system, which separates water vapor from air without energy-intensive overcooling and reheating steps [5]. Polymeric membranes are preferred for air dehumidification, because they are cheap, defect-free, easy to scale-up, and physically robust [1, 2, 8, 9]. The chosen membranes frequently have hydrophilic moieties, which enhance the water solubility and promote the preferential water permeation [1]. When the purity of the permeating water vapor is not essential, energy saving can be achieved over conventional vapor compression, by using membranes with relatively low water vapor/air selectivity. Yet, for an effective dehumidification of multicomponent systems, the membrane’s water vapor permeability and selectivity need to be improved. In this regard, the nanoscale tuning of the membrane morphology, building channels for preferential water transport, can be a valuable strategy. Block copolymers are known to conveniently combine hydrophobic and hydrophilic segments, leading to a wide variety of morphologies. They have been explored in different ways for membrane preparation [10, 11], targeting gas separation [12], pervaporation [13], ultrafiltration [14, 15] and is a viable option for dehumidification [16].

NEXAR™ is a sulfonated styrenic pentablock copolymer, which has higher separation and permeation capacity for water vapor over the air [17]. The excellent mechanical stability provided by the two tert-butyl styrene (tBS) end blocks, chain flexibility from the two ethylene-copropylene (EP) blocks and formation of water transport channels by the middle sulfonated
styrene (SS) block [18, 19]. Due to the immiscibility of the different NEXAR™ blocks, they self-assemble with microphase segregation. When cast from solution in different solvents, films with various tunable nanostructures and morphologies [17] are obtained. Depending on the polarity of the solvent and copolymers concentration during the self-assembly, alternating lamellar, spherical or mixed morphology with continuous ion-rich pathways can be obtained [20]. These structures can be further tuned with solvent-vapor annealing [21]. All these properties offer great potential to design high-performance NEXAR™ membranes for air dehumidification.

Peinemann and co-workers [22] recently demonstrated the formation of NEXAR™ flat-sheet membranes with a tunable internal nanostructure for air dehumidification. The phase separation starting from solution in different solvents led to different nanoscale morphologies, which eventually played a crucial role in efficient water vapor transport and water vapor/N₂ selectivity.

A highly ordered self-assembly of NEXAR™ in tetrahydrofuran (THF) created ion-rich cylindrical nanochannels. These ordered nanochannels act as highways for the transport of water vapor with 6-fold higher permeability than that of analogous membranes with disordered morphology, and a water vapor/N₂ selectivity an order of magnitude higher. These findings lay the basis for potential practical applications of NEXAR™ in air dehumidification.

In this study, we develop hollow-fiber membranes coated with self-assembled NEXAR™ layers and evaluated their efficiency for dehumidification. Hollow fibers are preferred over the flat-sheet configuration. They have better heat and mass transfer capabilities, with higher surface/volume ratio, primarily due to their high packing densities [3]. The fibers also avoid direct contact between the two sides of the flowing streams, and when liquid desiccants are used, the air contamination with their droplets is prevented [7].
In summary, the objectives of this work are to (1) design novel self-assembled NEXAR™/polyetherimide composite hollow fiber membranes for air dehumidification, (2) investigate the fundamental mechanism of self-assembly, surface morphology and topology of the hollow fiber membranes and (3) correlate the various morphologies with the dehumidification performance.

2. Experimental

2.1. Materials

Polyetherimide, ULTEM® 1000, was purchased from SABIC USA, and NEXAR™ MD9200 films were provided by Kraton Polymers (Houston, TX). Tetrahydrofuran (THF), N-methyl-2-pyrrolidone (NMP), ethylene glycol (EG) and hexamethylene diamine (HMD) were purchased from Sigma Aldrich (UK). Diethylene glycol (DEG) was obtained from Fisher Scientific (UK). Glycerol and methanol were obtained from VWR USA. The solvents were used as received.

2.2. Fabrication of hollow fibers

The polyetherimide hollow fibers were prepared by non-solvent induced phase separation, using a dry-jet wet spinning process [23]. The dope solution was constituted by 20/10/70 wt% ULTEM®/DEG/NMP. The mixture was stirred at 70 °C for two to three days until a clear formation was obtained and degassed overnight before spinning. Table 1 shows the information about spinning condition. The fibers were cross-linked in a 10 wt% HMD in methanol for one day to provide stability in organic solvents, such as THF, later used for coating.
Table 1. Spinning conditions.

<table>
<thead>
<tr>
<th>Spinning Parameter</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dope solution (wt%)</td>
<td>ULTEM®/DEG/NMP (20/10/70)</td>
</tr>
<tr>
<td>Bore fluid (wt%)</td>
<td>EG: Water (95:5)</td>
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<tr>
<td>External coagulant</td>
<td>Water</td>
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<tr>
<td>Bore fluid flow rate (ml/min)</td>
<td>6</td>
</tr>
<tr>
<td>Air gap (cm)</td>
<td>1</td>
</tr>
<tr>
<td>Take-up speed (m/min)</td>
<td>12</td>
</tr>
</tbody>
</table>

2.3. NEXAR™ coating

NEXAR™ (52 mol% degree of sulfonation) was dissolved in THF overnight. The fibers were washed with water several times, and the ends were sealed with epoxy resin to avoid the entry of NEXAR™ solution into the lumen of the fibers. The sealed fibers were dip-coated in the NEXAR™ solution, whose concentration was varied from 2 wt% to 5 wt% for immersion times of 10 to 60 s. Immediately after the dip coating, the fibers were transferred to a closed chamber (40 cm × 30 cm × 20 cm) containing THF vapor. 7 mL of THF were inserted in the chamber and re-filled at regular intervals. The annealing was conducted for one to twenty days. The modules were then fabricated, dried under vacuum overnight before testing in dehumidification experiments.

2.4. Membrane morphology

The morphologies of composite hollow fiber membranes were observed using FEI Nova Nano Scanning Electron Microscopy (SEM). For the cross-section image, the membranes were fractured in liquid nitrogen. The samples are then attached to stubs and sputter-coated with 3 nm of Iridium (two times) before imaging.
The surface morphology, as well as the cross-section, were also imaged by Atomic Force Microscope (AFM) (Bruker Dimension Icon SPM). For the AFM cross-sectional imaging, a sample preparation method commonly used for transmission electron microscopy was adopted. The hollow fibers were first immersed in epoxy resin and cured overnight at 65 °C. Then, 500 nm thick slices were cut on a Ultramicrotome Leica UC7 using a diamond knife. The slices were collected on a silicon wafer and used for AFM characterization.

2.5. Performance of the membranes

A mixed water vapor/gas test method was used to analyze the performance of the composite membranes [24]. A sweep gas/and vacuum has been used to maintain a constant driving force. Detailed information can be found elsewhere [24]. In summary, the humidity and temperature sensors were used to measure the accurate humidity and temperature on the feed as well as the permeate side. The configuration of the setup is shown in Figure 1.

![Figure 1. Schematic representation of dehumidification setup.](image)

The water vapor permeation through the membrane is estimated using equation 1:
\[ Q_{\text{vapor}} = Q_{N_2} \times \gamma_{H_2O} \times \frac{V_m}{M_{w,H_2O}} \]  \hspace{1cm} (1)

Where \( Q_{N_2} \) (cm\(^3\) s\(^{-1}\)) is the nitrogen flow rate at the permeate side, \( \gamma_{H_2O} \) (g m\(^{-3}\)) is the absolute humidity, \( V_m \) (L mol\(^{-1}\)) is the volume of the 1 mol of penetrant at standard temperature and pressure and \( M_{w,H_2O} \) (g mol\(^{-1}\)) is the molecular weight of water.

The water vapor permeance can be estimated using equation 2:

\[ \text{Permeance} = \frac{Q_{\text{vapor}}}{A \times \Delta P} \]  \hspace{1cm} [2]

where \( A \) (cm\(^2\)) is the area of the membrane, and \( \Delta P \) (bar) is the partial pressure difference above and beneath the membrane surface. The permeance is expressed in Gas Permeation Unit (GPU), where 1 GPU = 10\(^{-6}\) cm\(^3\) (STP) cm\(^{-2}\) s\(^{-1}\) cm Hg\(^{-1}\)

The selectivity of membrane for water vapor over nitrogen can be calculated using equation 3:

\[ \text{Selectivity} = \frac{\text{Water vapor permeance}}{\text{Nitrogen permeance}} \]  \hspace{1cm} [3]

3. Results and Discussions

3.1. Polyetherimide hollow fiber fabrication and dehumidification performance

Different coagulants, like NMP, water and EG, have been previously investigated to fabricate porous polyetherimide hollow fibers [23]. The porosity and mean pore size varies with the non-solvent bore fluid viscosity, its thermodynamic interaction with the polymer and the associated precipitation rates. For the current study, EG was used as a bore fluid. The membrane morphology is characterized by two layers of finger-like cavities with double symmetry over the cross-section (Figure S1). During the spinning of fibers, at the shell side, there is a faster movement of water (strong coagulant) into the incipient fibers in exchange with NMP. In the
lumen side, there is a slower movement of EG into the polymer due to its high viscosity, forming an uneven double symmetry. The delayed demixing partially suppresses the finger-like macrovoid [23].

The water vapor permeance and selectivity through the hollow fibers were tested under vacuum. The polyetherimide fibers showed both very high water vapor (up to $13453 \pm 58$ GPU) and negligible selectivity (0.63), due to its higher porosity (72%) and mean pore size (8.6 nm).

3.2. NEXAR™ coating and membrane morphology

Block copolymers are known to self-assemble in different morphologies, such as lamellae, hexagonally packed cylinders, bicontinuous gyroid, spheres, and others, depending on the thermodynamic interactions between blocks, the block sizes, number and relative fractions. The morphology of pentablock copolymers, like NEXAR™, is more complex than classical diblock copolymers. Furthermore, when block copolymer films are prepared from solution in different solvents, as the solvent evaporates, non-equilibrium morphologies might be immobilized, leading to a much larger variety of morphologies. Preferential interactions between the solvent and specific blocks can considerably deviate the morphology of a cast film from the equilibrium one. The morphology also depends on the evaporation rate and the time of exposure to a particular solvent. In pentablock copolymers like NEXAR™, containing sulfonated segments, the nature of the ionic aggregates and the size, shape and orientation orchestrate the final outcome [25]. Nevertheless, other factors, such as the copolymer concentration, also dictate the solution morphology and the mobility of the copolymer during the coating process.

NEXAR™ films and coatings have been investigated by different groups, in significant part using apolar solvents such as hexane, cyclohexane, and toluene [25-29]. Adding polar solvents to the casting solutions, such as n-propanol or methanol [21, 29], preferentially selective for the
sulfonated blocks, or even using ionic compounds such as ionic liquids [30, 31], should affect the morphology and relevant operational properties, such as permeance. The use of less selective solvents, such as THF, could facilitate the preparation of films with a morphology closer to the equilibrium one, exclusively driven by the interaction between blocks, without significant influence of solvents or additives.

Peinemann and co-workers [22] recently fabricated NEXAR™ flat sheet membranes using 2 wt% NEXAR™ solutions in THF and demonstrated a particularly high water vapor permeance. In this work, we explore this observation to develop hollow fibers dehumidification systems. For the optimization, we varied the copolymer concentration, and add solvent vapor annealing steps with different times. A detailed morphological investigation is done to understand the self-assembly and its effect on the water vapor transport.

Figure 2 shows the fibers dip-coated with 2 wt% NEXAR™ solution in THF during different time intervals. The coating duration was varied from 10 s to 60 s to have uniform defect-free layers on the fibers. Since the pristine polyetherimide fibers are not stable in THF, they were cross-linked with 10 wt% HMD solution in methanol for 24 h, before coating. From Figure 2, it is clear that as the time for dip coating increased, the thickness of the coating layer slightly increased (800 nm to 1040 nm). SEM images of the fibers coated with 3 wt% and 5 wt% NEXAR™ solutions are shown in Figure S2 and Figure S3 (supporting information).

When using 3 wt% coating solutions, the fiber has a coating thickness of 1.5 to 2.35 µm, whereas for 5 wt%, the thickness is between 2.2 to 6.2 µm. Zuo et al. [17] fabricated NEXAR™-coated flat-sheet membranes by coating with a 2 wt% copolymer solution in hexane. Even with extended dip coating time (10 min), the thickness of the coating layer did not exceed 280 nm. In the present case, even with the shortest possible dip-coating time (10 s), the thickness of the
coating layer was 800 nm. This difference might arise from a combination of factors, including the solvent quality for each block, the solvent viscosity and evaporation rate, as well as from the solvent vapor annealing time after the dip-coating. The solvent vapor annealing provides more time for the chain relaxation, conformational change and reorientation.

**Figure 2.** SEM cross-section images of cross-linked polyetherimide hollow fibers coated with 2 wt% NEXAR™ during 10 s and 60 s.

Figure 3 shows the AFM images acquired from the surface of the fiber for different NEXAR™ concentrations. Figure 3b indicates the formation of highly ordered lamellas in the form of “highways” as proposed by Akhtar et al. [22] obtained with 2 wt% of NEXAR™. A more detailed observation of the lamellae shows that they are constituted by strings of interconnected nodular domains. When the concentration of NEXAR™ increased from 2 to 3 wt%, the morphology shifted to more evident and randomly distributed nodules (Figure 3b and 3c). These
patterns become more disordered, smaller and diffuse, when the concentration was further increased to 5 wt% (Figure 3d). Therefore, with increased copolymer concentration, the AFM images confirmed a morphological transition from lamellar/cylindrical domains to well-formed spherical nodules and eventually a less ordered irregular nodular network.

Based on Hansen's solubility parameters [32] THF is not as selective for the different blocks as chloroform or cyclohexane, which are preferential solvents for the hydrophobic blocks or methanol, which is preferential for the highly polar sulfonated blocks, Mineart et al. [21] reported mixed cylinder/lamellae morphology for pentablock copolymers with high sulfonation degree, indicating that annealing with THF could be a facile way to achieve the expected equilibrium morphology, which in their study was lamellae. To enhance the chain mobility, help the reorientation of block copolymer nanostructures in the thin films, and induce morphology transitions that could promote faster water transport, the membranes were subjected to solvent vapor annealing. After the first day of annealing, a spherical nodular morphology was imaged (Figure 4, day 1 solvent vapor annealing). In the second day, a hierarchical lamellar structure could be seen with a differentiated nanophase segregation inside the lamellae. After longer annealing times, a simpler lamellae morphology without any visible internal segregation was established.
Figure 3. (a) SEM and (b-d) AFM images of hollow fiber surface coated with (b) 2 wt%, (c) 3 wt%, (d) 5 wt% NEXAR™ solutions in THF.

Because of their non-equilibrium nature, the copolymer concentration, the annealing time in the closed chamber, as well the presence/absence of THF vapor in the sealed chamber plays a pivotal role in the formation of lamella on the surface and their uniformity on the fibers. Initially, the fibers were placed in a closed chamber for slow evaporation without any THF vapor. The AFM analysis revealed the lamellar structure was not uniformly formed, as well as some parts of the fibers were just smooth, without any particular form of architecture. When stacks of coated fibers were placed in a closed chamber without previous saturation with THF, some of the fibers didn’t have the characteristic structure observed in Figure 3b. Therefore, a pre-saturation with vapor was added to the process. We investigated the effect of THF vapor and the exposure time. Figure 4 shows the AFM images of the membrane surfaces, coated with 2 wt% block copolymer solution, exposed and annealed for different time intervals, varying from one to twenty days. After 24 h of annealing, an ordered nodular morphology is observed. After 48 h, a morphological transformation process takes place and a mixture of spherical domains, and lamellas/parallel cylinders are visible. As the time of solvent annealing increases, the spherical cores merge to
form interconnected sequential ionic microdomains. When the annealing time completes five days, a well-organized lamellar structure with few spheres can be seen. After seven days, well-organized lamellases/parallel cylinders, separated by equidistance, were observed throughout the surface of the fibers, which are further organized when 24 hours more were added to the annealing time. The self-assembly process kinetics is slow, nevertheless with controlled solvent vapor annealing, well-defined lamellar morphologies were achieved.

The images in Figure 3b-d and Figure 4 reflect the surface of the coating. The morphology of the coating bulk is not necessarily the same. To obtain information on the internal morphology of the NEXAR™ layer, slices of the fiber were obtained by microtomy, analogously to the procedure applied to the sample preparation for transmission electron microscopy. The microtomed slices were then imaged by AFM. The images after 1 day and 8 day of annealing in THF are shown in Figure 5. Different image modes (Z sensor, and amplitude) are provided. Strings of nodules can be observed, similar to that observed on the surface after the same annealing time. The image corresponding to 1 day of annealing reflects a more random distribution of nodules. In the middle of the image for 8 days there is a pronounced line, which probably results from the microtome cutting process, due to an uneven spot of around 200 nm in the diamond knife. Any other line resulting from cutting would appear with the same orientation. Orthogonally to this line, we see parallel strings of nodule, which are therefore not a cutting artefact, but can be assigned to the self-assembled lamellae imaged also on the coating surface in Figure 4. The morphology and orientation of the block copolymer along the cross-section can be influenced by both the rate of evaporation and solvent block selectivity. The solvent evaporation rate regulates the extent of relaxation of a system. A significant solvent evaporation rate implies insufficient relaxation; hence the morphology or orientation formed in the early stage of solvent evaporation
might remain, if the polymer mobility quickly decreases below the glass transition temperature of at least part of the other blocks. A low rate of evaporation provides adequate relaxation so that the polymer chains can rearrange and eventually overcome the energy barrier needed to reach a more stable morphology [33, 34]. The morphologies in Figure 4 (1 day) and Figure 5 result from a rapid solvent evaporation rate.

**Figure 4.** AFM images of the morphological transformation process observed on fibers coated with 2 wt% NEXAR™ solutions in THF and annealed from one to eight days with THF vapor.
Figure 5. AFM images of microtomed slices of a hollow fiber, coated with 2 wt% NEXAR™ solutions in THF: (a) optical, (b) Z sensor and (c) amplitude images of hollow fiber sections after (top) 1 and (bottom) 8 days of annealing.

When the fiber coated with a 2 wt% NEXAR™ solution for 60 s was tested for dehumidification under vacuum at 200 mbar, the water vapor permeance was clearly dependent on the annealing time after coating, as shown in Figure 6. The fibers annealed for one day in THF vapor had a permeance of 1,321 GPU, which increased to 4,855 GPU, when the annealing time reached ten days. The water vapor permeance rose till day eight and reached then a plateau. This could be related to the morphological transformation process discussed earlier (Figure 4).
Figure 6. Interdependency of water vapor permeance and annealing time for hollow fibers coated with 2 wt% NEXAR™ solutions in THF (coating time: 60 s).

The solvent annealing and polymer concentration are known to control the final structure of the self-assembly. Here we combine different strategies, annealing time control and copolymer concentration variation, to drive the self-assembled structure, and correlate it with the water vapor transport, and therefore with the dehumidification performance of the membrane. The investigation of the morphological transformation process under THF vapor annealing has also been extended to 3 wt% and 5 wt% NEXAR™ coatings. By increasing the concentration from 2 to 3 and 5 wt%, the coating thicknesses increased from 1.04 to 2.35 to 6.19 µm for 60 s dip-coating, justifying a permeance reduction. Figure 7 shows the block copolymer self-assembly process for 3 wt% coating promoted by the annealing in THF. The experiment was conducted for ten days. There is a clear formation of spherical domains starting already from day one, and becoming well defined as the annealing time proceeds. The dehumidification performance revealed that the permeance decreased from 1,651 GPU to 1,492 GPU, when the annealing time
varied from one to five days. This value further reduced to 1,236 GPU when the annealing reached ten days, which indicates that the domains interconnectivity decreased and the hydrophilic pathway for water vapor during the transformation process was partially disturbed. For 5 wt%, there were no significant changes from one to ten days annealing, and the permeance remained similar for the whole period of time (187 GPU- after 24 h, 179 GPU- after 5th day and 175 GPU- after 10th day). These results clearly corroborate our findings about the membrane morphology and their correlation with the water vapor permeance.

Geise at al. [35] measured the liquid water permeability through pentablock copolymer films with different sulfonation fractions of the middle block repeat unit and therefore different ion exchange capacities. Their films were prepared from 10 wt% copolymer solution in heptane/cyclohexane solution. The permeability was highly dependent on the sulfonation degree. Choi at al. [25] investigated the water vapor permeance of pentablock copolymer films with different ion exchange capacities (IEC up to 2.0 meq/g), also cast from heptane/ cyclohexane. The measurement was done by the inverted cup method, showing that by changing the IEC value from 0.4 to 2.0 meq/g, the water transport rate increased 10-fold, from less than 2,500 to 25,000 g/(day m²). The copolymer investigated in our work also has an ion exchange capacity of 2.0 meq/g, which is the highest reported in the above previous investigations, chosen to reach maximum permeance. Keeping the IEC constant, we varied the morphology, the interconnectivity and tortuosity of the sulfonated block phase, by changing the copolymer concentration, the associated viscosity and chain mobility in different steps of solvent evaporation and annealing. We chose THF as solvent, because of the promising preliminary results [22] obtained with flat-sheet membranes and the expectation that THF annealing would guide the formation of effective paths for the water transport.
Figure 7. AFM images of hollow fibers coated with 3 wt % NEXAR™ (coating time 60 s) solution in THF and annealed in THF vapor from one to 10 days.

3.3. Membrane dehumidification performance with vacuum pressure as driving force

The water vapor transport efficiency through coated hollow fibers was investigated by applying vacuum at the lumen side, which creates the necessary partial pressure difference for the transport of water vapor. Figure 8 shows the water vapor permeance and water vapor/N₂ selectivity of membranes at 200 mbar vacuum pressure. The membranes prepared with 2 wt% NEXAR™ coating had very high water vapor permeance (5,230 ± 239 GPU) compared to those coated with 3-5 wt% NEXAR™. The membranes prepared with 2 wt% NEXAR™ in THF yielded well-ordered lamellae or cylindrical hydrophilic channels which enhanced the water vapor transport. When the NEXAR™ concentration was increased, the water vapor transport decreased to 1874 ± 34 GPU for 3 wt% and 321 ± 45 GPU for 5 wt% coating. All the above values correspond to coating time of 10 s. When the concentration increases, the thickness of the
top layer significantly increases. Furthermore, from AFM images, we observed that the lamellar “highways” changed into a nodular morphology, with less effective interconnectivity, when the block copolymer concentration was increased from 2 to 3 wt%. This is in line with the earlier findings by Akhtar et al. [22] where they could achieve an ordered morphology only with 2 wt% concentration and 3 wt% concentration showed undesirable macrophase separation during the drying process.

Figure 8. Comparison of (a) water vapor permeance and (b) water vapor/nitrogen selectivity between NEXAR™ coatings prepared with different copolymer concentrations and coating times (humidified air at the shell side and 200 mbar vacuum at the lumen side).

The membranes have shown excellent selectivity for water vapor over nitrogen gas. For 2 wt%, the selectivity was $2,293 \pm 114$, which then decreased to $944 \pm 151$ when the copolymer concentration increased to 5 wt%. When the coating time increased from 10 to 60 s, there was a slight increase in selectivity ($2,293 \pm 114$ to $2,404 \pm 67$ for coatings prepared with 2 wt% copolymers). The membranes prepared with 5 wt% copolymer solutions (60 s coating time) have
lower permeance but still a high selectivity (2,077 ± 78). This could be useful in applications requiring the separation of a smaller amount of water vapor from other components.

Figure 9 depicts the influence of total permeate side pressure on the membrane selective parameters. The water vapor permeances were calculated using values of the partial water pressure in the feed/retentate and permeate sides. They were estimated from the continuously measured humidity levels measured by sensors placed in both membrane sides, during the whole experiment. The values reported in Figure 9 were taken after the system reached a steady state, when no major variation of permeance could be detected. The nitrogen permeances (and the water vapor/N₂ selectivity) were derived, by considering the total pressure values in both sides of the membrane measured at the final stage of the experiment and the humidity values measured at the same stage. As the total permeate pressure increases from 200 to 600 mbar, the water vapor permeance increases from 5,230 ± 239 GPU to 9,089 ± 22 GPU (for 10 s coating time). This ultimately increases the corresponding selectivity from 2,293 ± 114 to 2,560 ± 19. Ideally, since the permeance value is the permeant flux normalized by pressure, it should be pressure-independent. This would be valid, if no alteration in the membrane or the permeant-membrane interaction would take place under different pressures. We cannot discard that during the experiment, the extent of compaction of the copolymer layer could change under different pressure conditions. This is not unusual in soft homopolymer systems. The case of NEXAR™ is even more complex, since it is a pentablock copolymer with self-assembled hydrophilic and hydrophobic domains. Pressure and exposure to water for several hours could in principle disturb its morphology. As seen in Figures 3-5, 7, a nodular morphology is observed under different preparation conditions. At least in part of the investigated coating layers, a rather hierarchical morphology could be observed, where lamellae actually consist of nodular strings. The
interconnectivity between these strings is fundamental for an effective water transport. The pressure to which the copolymer layer is exposed might favor more or less the connectivity and therefore the permeance. However, if any morphological change takes place, it is minor, reversible or not detectable on the surface. After the completion of water vapor permeation, the surface of the membranes was imaged by AFM (Figure S3 in the supporting information) and no significant morphological changes could be seen with that resolution.

The transport does not show a typical tradeoff [36, 37] between permeability and selectivity. Instead, the increase of water permeance, observed as the pressure in the permeate side increased, was aligned with an increase of water vapor/N\textsubscript{2} selectivity. Besides the reasons we speculated above, differences in pressure could slightly alter the balance of solubility and diffusivity contributions to the permeance, governed by the solution-diffusion model. Diffusivity is inversely proportional to the size of the permeant. The kinetic diameters of water vapor and N\textsubscript{2} are 2.5 and 3.64 Å. In the system investigated in this work, solubility plays a major role. The water transport is promoted by its strong solubility in the hydrophilic sulfonated domains of the copolymer and this might be slightly affected by pressure.
When the feed flow rate was reduced from 1 L/min to 0.5 L/min, keeping the feed RH constant, the retentate RH significantly decreased. For 80% RH, with a feed flow rate of 1 L/min, the moisture at the retentate side decreased from 80 to 41% (at 600 mbar of vacuum pressure). In contrast, when the flow rate of feed decreased to 0.5 L/min, the retentate humidity reached 33%. Since the feed flowrate is high, the rate-limiting step here is the solution-diffusion. The longer residence time, imparted at low feed flowrate thus allows more water vapor permeation, hence significantly reduced retentate RH. In addition, as the feed flow rate reduces, the stage cut (ratio of permeate flow rate to feed flow rate) increased from 0.51 to 0.72. As a result, the concentration of \( N_2 \) increases in the feed side while the permeate stream is significantly enriched with water vapor, thus resulting in a more dehumidified air.

**Figure 9.** Influence of the total pressure at the permeate side (vacuum pressure) on the (a) water vapor permeance and (b) selectivity of membranes coated with 2 wt% NEXAR\textsuperscript{TM}. 

(a) Water Vapor Permeance (GPU) vs Vacuum Pressure (mbar) with feed flow rate 1 L/min and RH 80%

(b) Water Vapor/N \( N_2 \) Selectivity vs Vacuum Pressure (mbar) with feed flow rate 1 L/min and RH 80%
3.4. Membrane dehumidification performance with sweep gas as the driving force

The application of vacuum pressure always provides a higher driving force but requires higher energy input, which increases the overall operational cost of the dehumidification process. Using sweep gas at the lumen side may be an energy-efficient alternative. Hence, instead of vacuum, sweep gas at a different flow rate, and RH was used as the driving force for dehumidification. The water vapor partial pressure difference was created by keeping the RH at the lumen side lower compared to the shell side (Lumen side: pure dry air to 35% RH).

Figure 10 shows the effect of sweep gas flow rate on the water vapor permeance and selectivity for membranes prepared with 2 wt% NEXAR™ coating. The water vapor permeance increased from 4,271 ± 131 GPU to 6,232 ± 149 GPU (for 10 s coating time) as the sweep gas flow rate increased from 0.25 L/min to 0.75 L/min.

As the sweep gas flow rate increases, the vapor permeance also increases, which may be due to the active and quicker dilution of water vapor at the permeate side. One could expect constant water vapor permeance for all sweep gas flow rates since the pressure difference across the membrane is already considered. Figure S4 shows the specific behavior for membrane coated with 2 wt% NEXAR™ for 60 s. As the sweep gas flow rate increased from 0.1 L/min, the permeance increased and reached quasi-steady state after the flow rate changed to 0.85 L/min.

The dilution effect from the sweep gas may increase the permeance but becomes negligible after crossing a certain level of flow rate, which was also observed in the work of Liang et al. [38] and Merkel et al. [39] Another important factor affecting the vapor permeance is the permeate boundary layer resistance for water vapor and nitrogen, whose thickness can be reduced by increasing the sweep gas flow rate up to a critical value.
In contrast to the water vapor permeance, the nitrogen permeance remained almost constant as the sweep gas flow rate increased. This may indicate that the thickness of the permeate boundary layer resistance is more crucial to the water vapor transport. This boundary layer shrinks due to the shearing effect of the sweep gas until a critical thickness, after which the boundary layer becomes resistant to the imposed shear force.

The membrane showed excellent selectivity of water vapor over nitrogen under varying sweep gas conditions. The selectivity increased from 2,828 ± 32 to 3,870 ± 9, parallel to the increased water vapor permeance. The change of selectivity was small compared to the change of permeance. The water vapor permeability under sweep gas as the driving force was smaller than under vacuum; nevertheless, it exhibited excellent selectivity.

Figure 10. Comparison of (a) water vapor permeance and (b) water vapor/nitrogen selectivity for membranes prepared with 2 wt% NEXAR™ (for different sweep gas flow rates at 0% RH).
The usage of dry sweep gas is not economically feasible for the household air-conditioning system. So, we increased the humidity of sweep gas and investigated its effect on vapor removal (Table 2). The sweep gas humidity was varied from 0% to 35% and tested under different sweep gas flow rate. For the 0.75 L/min flow rate, vapor permeance decreased from $6,232 \pm 149$ GPU to $1,876 \pm 176$ GPU when sweep gas humidity increased from 0% to 35%. The value further dropped to $1011 \pm 90$ GPU when the flow rate fell to 0.25 L/min. Nonetheless, even the lower permeance recorded with Nexar™ as the coating layer is still in the better range compared to values observed in literature for various types of membranes (Table 3).

**Table 2.** Effect of sweep gas RH and flow rate on the water vapor permeance.

<table>
<thead>
<tr>
<th>Sweep gas RH (%)</th>
<th>Water vapor permeance (GPU)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.25 L/min</td>
</tr>
<tr>
<td>0</td>
<td>4271 ± 131</td>
</tr>
<tr>
<td>5</td>
<td>4118 ± 16</td>
</tr>
<tr>
<td>15</td>
<td>3786 ± 78</td>
</tr>
<tr>
<td>25</td>
<td>2123 ± 101</td>
</tr>
<tr>
<td>35</td>
<td>1011 ± 90</td>
</tr>
</tbody>
</table>

The water vapor permeance and selectivity of the NEXAR™-coated hollow fibers were compared with composite hollow fiber membranes reported in the literature. Our results show superior performance, compared to the reported values, mainly when sweep gas was used as the driving force.
Table 3. Correlation of vapor permeance and selectivity for hollow fibers in this work and others reported in the literature (V-Vacuum mode, S-Sweep gas mode).

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Operation mode</th>
<th>T (°C)</th>
<th>Water vapor permeance (GPU)</th>
<th>Selectivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEEK-PES(^1)</td>
<td>S</td>
<td>50</td>
<td>28,700</td>
<td>95,666</td>
<td>[40]</td>
</tr>
<tr>
<td>CA+PEG 2000</td>
<td>V</td>
<td>30</td>
<td>444</td>
<td>175</td>
<td>[41]</td>
</tr>
<tr>
<td>Coated PES(^2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDA coated PES(^3)</td>
<td>V</td>
<td>30</td>
<td>3,185</td>
<td>195</td>
<td>[42]</td>
</tr>
<tr>
<td>PDMS-PAN(^4)</td>
<td>V</td>
<td>25</td>
<td>11,126</td>
<td>102</td>
<td>[9]</td>
</tr>
<tr>
<td>Carboxylated TiO(_2)</td>
<td>V</td>
<td>30</td>
<td>1,340</td>
<td>486</td>
<td>[43]</td>
</tr>
<tr>
<td>BDT Incorporated TFC PES(^5)</td>
<td>V</td>
<td>30</td>
<td>2,054</td>
<td>119</td>
<td>[44]</td>
</tr>
<tr>
<td>PAI(^6)</td>
<td>V</td>
<td>30</td>
<td>653</td>
<td>18</td>
<td>[45]</td>
</tr>
<tr>
<td>PEOT/PBT-ZIF71-PAN(^7)</td>
<td>V</td>
<td>25</td>
<td>9,300</td>
<td>3700</td>
<td>[46]</td>
</tr>
<tr>
<td>Nafion-IL-SiO(_2) on PSf(^8)</td>
<td>V</td>
<td>30</td>
<td>2,131</td>
<td>130</td>
<td>[47]</td>
</tr>
<tr>
<td>MOF-MPD-PSf(^9)</td>
<td>V</td>
<td>30</td>
<td>2,244</td>
<td>542</td>
<td>[48]</td>
</tr>
<tr>
<td>PDMS/PAN(^{10})</td>
<td>S</td>
<td>30</td>
<td>3,700</td>
<td>-</td>
<td>[38]</td>
</tr>
<tr>
<td>PDA-PVA on PVDF(^{11})</td>
<td>V</td>
<td>25</td>
<td>2,898</td>
<td>2.02</td>
<td>[49]</td>
</tr>
<tr>
<td>NEXARTM™, ULTEM®</td>
<td>V</td>
<td>25</td>
<td>9,089</td>
<td>1,997</td>
<td>Current study</td>
</tr>
<tr>
<td>NEXARTM™, ULTEM®</td>
<td>S</td>
<td>25</td>
<td>6,232</td>
<td>3,870</td>
<td>Current study</td>
</tr>
</tbody>
</table>

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\(^1\) Sulfonated polyetheretherketone (SPEEEK)- Polyethersulfone (PES) HF
\(^2\) Cellulose acetate (CA)- Polyethylene glycol 2000(PEG) blended solution on Polyethersulfone (PES) HF
\(^3\) Polydopamine (PDA) coated Polyethersulfone (PES) HF
\(^4\) Polydimethylsiloxane (PDMS) coated polyacrylonitrile (PAN) HF
\(^5\) Carboxylated Titanium oxide coated thin film composite (TFC- 3,5-Diamino benzoic acid+ Trimesoyl chloride) on polysulfone (PSf) HF
\(^6\) 1,3-Benzenedithiol (BDT) Incorporated thin film composite (TFC-Trimesoyl chloride) on Polyethersulfone (PES)
\(^7\) Polyamideimide (PAI) HF
\(^8\) Poly (ethylene oxide) terephthalate and poly (butylene terephthalate) (PEOT/PBT)- zeolitic imidazolate framework, ZIF-71 Polyacrylonitrile (PAN) HF
\(^9\) Nafion-Ionic liquid solution with Silicon dioxide nanoparticles on polysulfone (PSf) HF
\(^10\) Metal Organic Framework (MOF) incorporated thin-film composite (TFC- m-phenylene diamine+ Trimesoyl chloride) on polysulfone (PSf) HF
\(^11\) Polydimethylsiloxane (PDMS) coated polyacrylonitrile (PAN) HF
\(^12\) Surface-modified poly (vinyl alcohol)/poly (vinylidene difluoride) (PVA/PVDF) hollow fiber composite membranes with poly(dopamine) (PDA)

Finally, a consideration on the membrane stability should be mentioned after a series of experiments. Two of the membrane sets (2 wt% coating for 10 sec and 60 sec) were prepared and more intensively tested. Tests with continuous operation for 3-4 days, intermittent operations with different sweep flow rates, and sweep gas humidity were carried out. The observed variation in permeance were within an experimental error range (±4%). The
intermittent testing was carried out for more than 90 days with similar performance making the material promising for air dehydration.

**Conclusions**

Cross-linked polyetherimide hollow fibers were prepared and coated with different concentrations of NEXAR™ solutions in THF. The coatings performed with 2 wt% block copolymers followed by annealing in THF led to highly ordered parallel cylinders/lamella acting as a path for the water vapor transfer. The block copolymer self-assembly depends upon the annealing time, which determines the structure as well as the final water vapor transport rate of the material. Both vacuum and sweep gas mode resulted in higher water vapor permeance (up to 9,000 GPU) with excellent selectivity for water vapor over nitrogen (up to 3,900). The developed ultrathin composite membranes demonstrate a strong potential for energy-efficient alternative in the modern air conditioning units requiring lower energies compared to the traditionally available dehumidification solutions.

**Conflicts of Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Acknowledgments**

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References


Supporting Information

NEXAR™-coated hollow fibers for air dehumidification

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**Figure S1.** SEM images of polyetherimide hollow fibers coated with 3 wt% NEXAR™ solution in THF for 10 and 60 s.

**Figure S2.** SEM images of polyetherimide hollow fibers coated with 5 wt% NEXAR™ solution in THF for 10 and 60 s.
Figure S3. AFM images of the fiber surface after the water permeation experiment.

Figure S4. Influence of sweep gas flow rate on the water vapor permeance for a membrane coated with 2 wt% NEXAR™ solution in THF for 60 s.
Highlights

NEXAR™-coated hollow fibers for air dehumidification

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- Membranes with water vapor permeance up to 9000 GPU
- Selectivity for water vapor over nitrogen up to 3900
- Relative humidity reduction from 80\% to 41\% in one step
- Pentablock copolymer coating with optimized morphology
Conflict of Interest

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