

# Silylated CNC/PDMS Composite Membranes with Improved Selectivity for H<sub>2</sub>O/Air Separation at Elevated Temperatures

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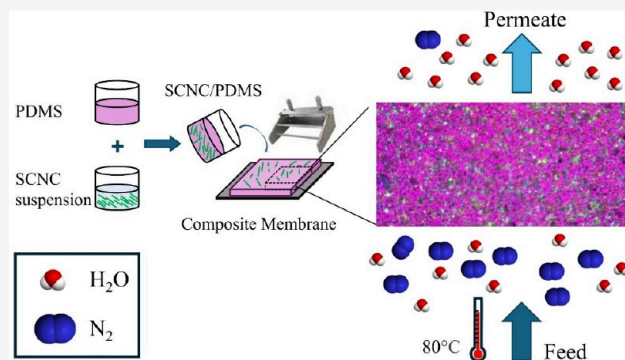


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**ABSTRACT:** Cellulose nanocrystals (CNCs) are purported as potential nanoreinforcements in polymer composites; however, the hydrophilic surface nature of CNCs limits their usage in composites if the polymers are hydrophobic, which results in poor compatibility. In this research, renewable biobased CNCs were modified using silylation, which is based on introducing a siloxane group to increase the compatibility between CNCs and the polydimethylsiloxane (PDMS) polymer. A silylated CNC/PDMS composite membrane was manufactured, which has applications in air dehydration. For this purpose, spray-dried CNC powder was used and modified. The surface modification of CNCs was carried out through the reaction between hydroxyl groups of the CNCs and the silylation agent. Finally, the silylated CNCs (SCNCs) were added to the PDMS solution to make SCNC/PDMS membrane samples with an SCNC weight concentration of 2%. Characterization analyses of FTIR and XRD of SCNCs confirmed the effectiveness of the silylation. SEM, AFM, and polarized light microscopy analyses indicated the improved dispersion of SCNCs in the polymer matrix compared to the not-modified CNC. The SCNC/PDMS membrane exhibited a 23% increase in water vapor permeability and a 79.6% increase in selectivity for water vapor over nitrogen gas at 25 °C compared to the pure PDMS membrane. Furthermore, the thermo-mechanical analysis (TMA) technique provided evidence that the addition of both CNC and SCNC resulted in a decrease in the coefficient of thermal expansion (CTE) of the PDMS membrane. These findings contribute to the development of cellulose-based materials with improved performance for their potential applications in various fields.



## 1. INTRODUCTION

Water vapor is commonly present in various gas streams, including air, flue gas, and natural gas. To meet different industrial demands, it is crucial to remove water vapor from these gas streams.<sup>1</sup> Membrane separation is a promising technology for water vapor removal from the air or gas attributed to its advantages over traditional methods (such as, absorption, adsorption, condensation, etc.), such as simplified operation, energy efficiency, and low capital investment.<sup>2,3</sup> The target application in this study focuses on water vapor/air separation. This technology involves the separation of water vapor from air via a dense membrane without any accompanying phase or temperature changes. As a result, this process is also referred to as isothermal membrane-based air dehumidification (IMAD).<sup>4</sup> IMAD has been successfully implemented in numerous industries that require moisture control during manufacturing processes, including but not limited to food, chemical, and pharmaceutical industries.

The efficiency of water vapor/air separation technology largely depends on membrane materials used. Polymeric membranes, including glassy and rubbery polymers, are favored because of their excellent permeability and processability. Glassy polymers, such as polysulfone and polyimide,

usually have exceptional permeability but are limited by expensive raw materials, harsh synthetic conditions, and low chemical stability.<sup>2</sup> Among rubbery polymers, polydimethylsiloxane (PDMS) is recognized as one of the most permeable rubbery polymers because of its flexible siloxane linkages and a satisfactory H<sub>2</sub>O/N<sub>2</sub> selectivity (around 140, for instance).<sup>1,2,5,6</sup>

Polymer membranes, despite being a promising technology for various separation processes, often encounter a trade-off between permeability and selectivity, referred to as Robeson's upper bound.<sup>7</sup> The demand for novel membrane materials has become essential for improving the efficiency of separation technologies.<sup>7</sup> The focus of current membrane separation research is on developing materials that exhibit high permeability, selectivity, and tunable interactions with target

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penetrants, while also being robust against thermal and mechanical stresses.<sup>8</sup> Mixed matrix membranes (MMMs) have emerged as an effective approach for enhancing the performance of polymeric membranes by combining the polymer with nanofillers.<sup>8</sup> Performance improvement of MMMs for separation applications depends on several key factors, including the intrinsic properties of the dispersed phase (such as size, shape, and porosity) and the interface compatibility between the polymer and nanofiller.<sup>9</sup> There have been many nanoparticles such as TiO<sub>2</sub>,<sup>10</sup> ZnO,<sup>11</sup> SiO<sub>2</sub>,<sup>12</sup> Zeolite<sup>13</sup> and more for reinforcing PDMS. However, the majority of these nanoparticles are considered unsustainable and, in certain instances, are derived from petroleum-based sources.

Cellulose nanocrystals (CNCs) are derived from renewable biomass resources, such as wood pulp, exhibiting a high aspect ratio, large surface area, unique surface chemistry, and easy chemical modification. These characteristics make CNCs appealing as nanofillers to enhance the mechanical and physical properties of various materials, including polymers.<sup>14,15</sup> In addition, CNCs offer exceptional benefits such as remarkable mechanical properties, low coefficient of thermal expansion and hydrophilic nature. These exceptional properties besides being biodegradable, nontoxic, and biocompatible, provide an eco-friendly alternative to conventional nanofillers associated with environmental and health risks.<sup>16</sup>

Therefore, in light of the growing concerns regarding environmental sustainability, the development of polymeric materials reinforced with CNCs has been studied for decades.<sup>15,16</sup> Visakh et al. demonstrated that incorporating 2.5 and 5 w.t.% concentrations of CNCs extracted from bamboo pulp enhances the thermal and mechanical stability of natural rubber.<sup>17</sup> In another study, Siqueira et al. found that after the addition of CNC suspension to natural rubber, dynamic mechanical analysis showed improved stiffness for the resulting nanocomposites.<sup>18</sup> However, these studies primarily focused on the mechanical and thermal properties of composites, lacking investigations into the gas permeability of the CNC/polymer composite films. Consequently, there exists a research gap in exploring the potential of CNCs as nanofillers in PDMS to enhance water vapor/air separation, an aspect that remains unexplored by other researchers.

Therefore, the incorporation of CNC in the PDMS was studied by our research group, and it was revealed that the addition of 2 wt % CNC to PDMS increased the water vapor permeability of the PDMS by 24.8% at room temperature, decreased the coefficient of thermal expansion by 9% and the selectivity was retained.<sup>19</sup> However, it noted that CNC suspension in water was used, and the agglomeration of CNCs in PDMS occurred due to water evaporation during drying and the hydrophilic nature of CNCs, which limits proper dispersion within hydrophobic polymers.<sup>16</sup>

The hydrophilic properties of CNCs, characterized by the abundance of hydroxyl groups, result in inadequate compatibility with hydrophobic polymer matrices.<sup>15,16</sup>

After this challenge was found in our last study, this motivated our research group to solve this challenge by using CNC powder and chemical modification. Therefore, spray-dried CNC particles were used, a cost-effective drying method that offers scalability, easy dispersion as particle reinforcement, and consistent particle sizes.<sup>20</sup> Among several techniques of surface modification for enhancing the hydrophobicity of nanocellulose materials, including graft polymerization with

hydrophobic polymers, low molecular weight esters, and silane coupling agents,<sup>16</sup> the silylation technique (i.e., silane coupling agents) has been widely used due to its simplicity and effectiveness.<sup>15,16</sup>

As for PDMS, some studies tried to modify CNCs to increase the compatibility with PDMS. In one study, Yang et al. reported an experiment of adding modified CNCs to silicone rubber and observed an increase in the tensile strength as the concentration of modified CNCs increased from 0 to 3 w.t.%.<sup>15</sup> In another study, with the addition of 4 wt % silylated CNC to PDMS, the storage modulus was improved.<sup>21</sup> However, these studies did not study the effect of modified CNCs as a nanofiller in PDMS to improve water vapor/air separation, and there is a knowledge gap.

The goal of this study is to employ the silylation technique to modify the surface of spray-dried CNCs (SCNCs) and effectively disperse the SCNCs in a PDMS matrix, resulting in SCNC/PDMS nanocomposites. In addition, the other objectives were to characterize the prepared SCNC/PDMS and study the dispersion of the SCNCs within the PDMS with different characterization methods. Then, the water vapor permeability, nitrogen permeability and selectivity of the prepared membranes as well as the mechanical and thermal stability were studied.

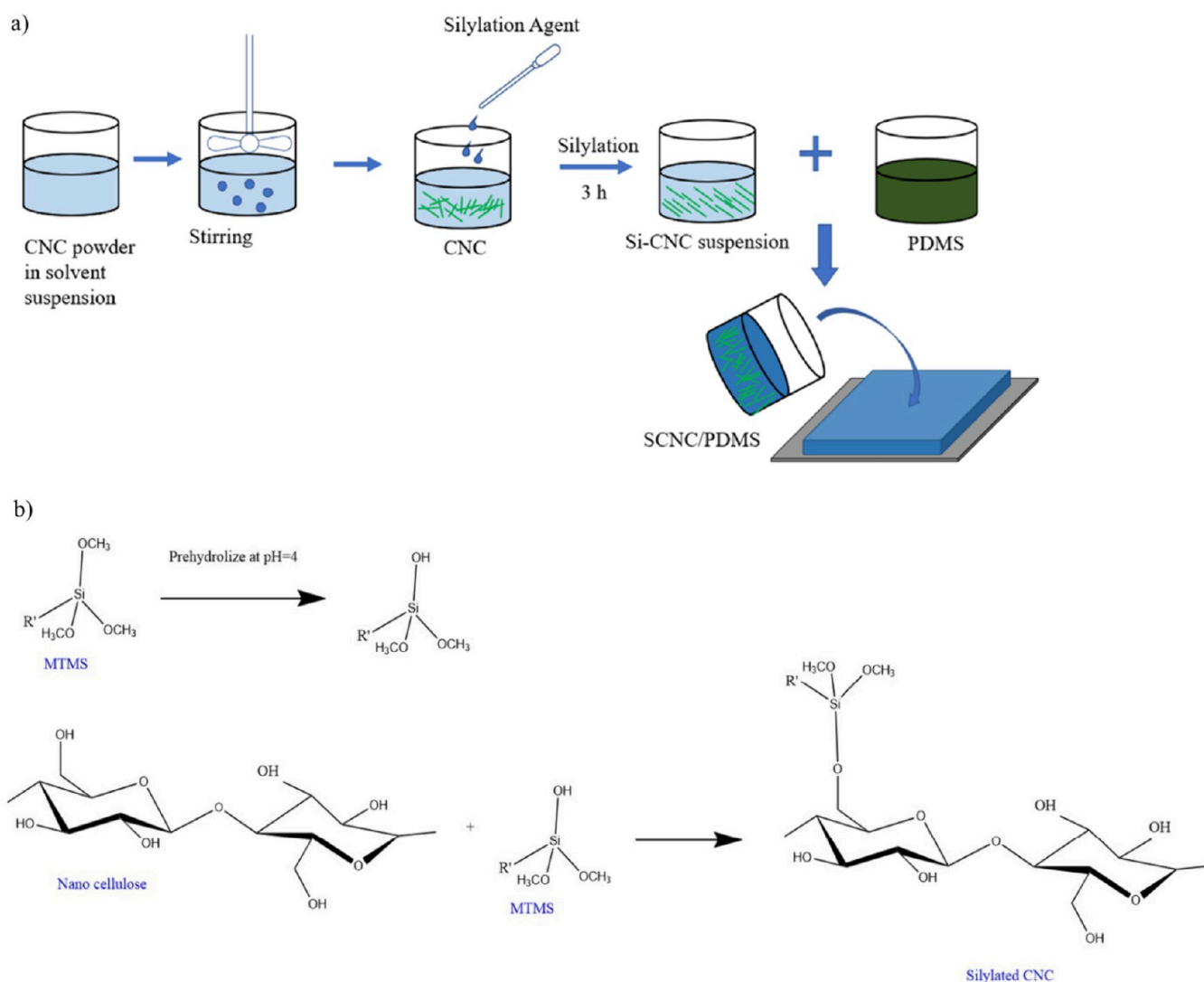
## 2. MATERIALS AND METHODS

**2.1. Materials.** A CNC suspension at 11.8 wt % solids was purchased from the USDA Forest Products Laboratory and distributed by the Process Development Center of the University of Maine (ME, USA), which was used to fabricate CNC/PDMS composite membrane as a control. Spray-dried CNC powder was obtained from the Advanced Structures and Composites Center (ASCC) of the University of Maine (Orono, Maine, U.S.). The spray-dried CNC material's manufacturing process and the morphology characterization was well described by Huang et al.<sup>22,23</sup>

PDMS prepolymer and curing agent kits (Dow SYLGARDTM 184 Silicone Elastomer kit) were purchased from Dow Inc. (MI, USA). Trimethoxymethylsilane (MTMS), the silylating agent, was obtained from [sigma-aldrich.com](http://sigma-aldrich.com), U.S. *n*-Hexane was obtained from Thermo Fisher Scientific Chemicals (Ward Hill, Massachusetts, U.S.). Acetic acid was purchased from Fisher Scientific (New Jersey, U.S.).

**2.2. Methods.** **2.2.1. Silylation of CNC.** The obtained CNC powder was further dried in an oven at 60 °C overnight to eliminate residual water. First 0.4 g of the dried CNC powder was dispersed in 20 mL of *n*-hexane and was mechanically mixed for 1 h. The pH of the suspension was adjusted to 4.0 using glacial acetic acid. Then 10 mL of MTMS (silylation agent) was added to the suspension. And then continued mechanical mixing for 3 h to complete the silylation reaction between hydroxyl groups of the CNCs and the silylation agent and the SCNC suspension was prepared.<sup>15,16</sup>

**2.2.2. Preparation of SCNC/PDMS Membranes.** To prepare the SCNC/PDMS membranes, a mixture of PDMS prepolymer and curing agent in a weight ratio of 10:1 was mechanically mixed for 5 min. Subsequently, an appropriate amount of the SCNC suspension was added to the PDMS/curing agent mixture to achieve a concentration of 2 wt % (w.t. %) of SCNCs in PDMS. The mixture was mechanically stirred for 1 h and was then degassed for 45 s to eliminate any air bubbles using a centrifugal bubble-free mixer (THINKY ARE-310, Tokyo, Japan). The degassed mixture was then cast onto



**Figure 1.** (a) Diagram of the fabrication method of the SCNC/PDMS membrane and (b) chemical formulas of silylated CNCs and the SCNC/PDMS membrane.

Petri dishes. A schematic of this preparation method and the corresponding chemical reactions are illustrated in Figure 1a and b. In the next step, to ensure the removal of any remaining air bubbles in the wet membranes, they were initially placed in a vacuum desiccator with a vacuum pressure of 88 kPa for 1 h at room temperature.<sup>24</sup> Following this, the membranes were dried for 24 h at room temperature and were carefully removed from the Petri dishes, resulting in the SCNC/PDMS membranes.

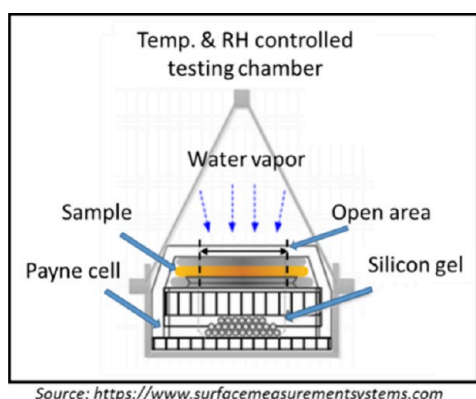
**2.2.3. Preparation of CNC/PDMS and PDMS Membranes.** In order to synthesize CNC/PDMS membranes, 10 gr of PDMS base with 1 g of the curing agent were subjected to mechanical mixing for 5 min at ambient temperature. To achieve a CNC solid concentration of 2%, an appropriate quantity of cellulose nanocrystal (CNC) in water suspension was introduced into the solution. Subsequently, the mixture underwent mechanical agitation for 1 h, resulting in the formation of a finely homogenized mixture. The mixture was then subjected to a 45 s degassing process before being cast onto a Teflon plate.<sup>21,24</sup>

For the synthesis of pure PDMS membranes, the same procedure was followed, except that the addition of CNC

suspension was omitted. To eliminate any remaining air bubbles within the wet membranes, the wet membranes were initially dried at ambient temperature in a vacuum desiccator maintained at a vacuum pressure of 88 kPa for a duration of 1 h. Subsequently, the partially cured membranes were transferred to an oven and subjected to a curing process at a temperature of 50 °C for a period of 24 h.<sup>24</sup>

The thicknesses of the dry film samples were accurately measured using a digital micrometer (Mitutoyo, IL, USA) with a precision of 0.001 mm. Multiple measurements were conducted to ascertain the average thickness of the film samples, which was used for the calculation of permeability of water vapor and nitrogen, respectively. The sample thickness is provided in Table S.1.

**2.2.4. Water vapor Permeability Measurement.** In order to measure the water vapor permeability of the membranes, a dynamic vapor sorption (DVS) instrument was used, specifically the DVS Advance model by Surface Measurement Systems, London, UK, as illustrated in Figure 2. Before testing, the samples were conditioned in an environmental chamber at room temperature and 55% RH until reaching an equilibrium status. To conduct the measurements, the specimen was sealed



**Figure 2.** Experimental setup for WVTR testing on a dynamic vapor sorption instrument (dry cup) with the test sample sealed at the Payne cell.

within a Payne cell. Within the cell, silicone gel beads were placed to adsorb any incoming water vapor, maintaining a constant relative humidity (RH) of 0% inside the cell. The environmental conditions surrounding the Payne cell were meticulously controlled by the DVS instrument to achieve the desired testing parameters.

For each type of sample, nine (9) replicates were taken from three identical membranes and subjected to testing. The thickness of each sample was precisely determined using a digital micrometer. The sample thickness is provided in Table S.1. Testing was performed at three different temperatures: 25 °C, 50 °C, and 80 °C, while maintaining a constant RH of 60%. Simultaneously, the increase in mass of the Payne cell assembly with time was continuously recorded. These tests were conducted in accordance with the ASTM E96 Standard test method for water vapor transmission of materials (ASTM 2016).

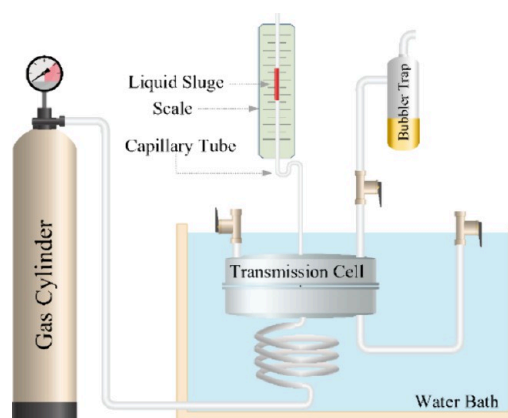
The water vapor permeability ( $P_{H_2O}$ ) was computed using eq 1:

$$P_{H_2O} = \frac{WVTR \times T_{mem}}{\Delta p_{Vapor}} = \frac{(\Delta m / \Delta t) \times T_m}{A \times \Delta p \times 18} \left( \frac{\text{mol}}{\text{m} \cdot \text{s} \cdot \text{Pa}} \right) \quad (1)$$

Within the provided equation,  $\Delta m / \Delta t$  represents the slope of a linear section in the mass versus time relationship, measured in grams per second (g/s).  $T_m$  signifies the thickness of the sample membrane, expressed in meters (m). While  $A$  denotes the open area of the Payne cell, which is equal to  $1.18 \times 10^{-4}$  square meters ( $\text{m}^2$ ).  $\Delta p$  corresponds to the partial pressure difference of water vapor and is calculated as  $\Delta p = \frac{\Delta RR}{100} \times \text{Saturated water pressure at } 25^\circ\text{C, } 50^\circ\text{C, and } 80^\circ\text{C}$ , in pascals (Pa) [Saturated water vapor pressure at 25 °C = 3171 Pa, 50 °C = 12351 Pa, 80 °C = 47415 Pa]. Additionally, the molecular weight of  $\text{H}_2\text{O}$  is 18 g/mol.

**2.2.5. Nitrogen Gas Permeability Measurement.** The pure nitrogen gas transmission rate (NGTR) was determined using a single gas transmission cell provided by Custom Scientific Instruments Inc., PA, USA, as depicted in Figure 3. This investigation adhered to the ASTM D1423–82(2015) Standard test procedure for evaluating the gas permeability characteristics of plastic film and sheeting, as stipulated in ASTM 2015.

Sample specimens that were conditioned at room temperature and 55% RH prior to testing were cut into circular shapes



**Figure 3.** Schematic of a single gas transmission cell.

with a diameter of 0.12 m, and their thickness was also documented. One such sample was affixed within the cell to create a barrier between the upper and lower chambers. Compressed nitrogen gas was introduced into the lower chamber, diffused through the sample, and entered the upper chamber. The volumetric expansion of the upper chamber was monitored by tracking the displacement of a colored liquid slug within a capillary tube. For each type of sample, nine (9) replicates were subjected to testing.

The gas transmission cell was situated within a temperature-controlled water bath to maintain the desired temperatures of 25 °C, 50 °C, and 80 °C. The pressure differential between the lower and upper chambers was gauged with a pressure measurement device. The  $\text{N}_2$  gas permeability was subsequently computed employing eq 2.

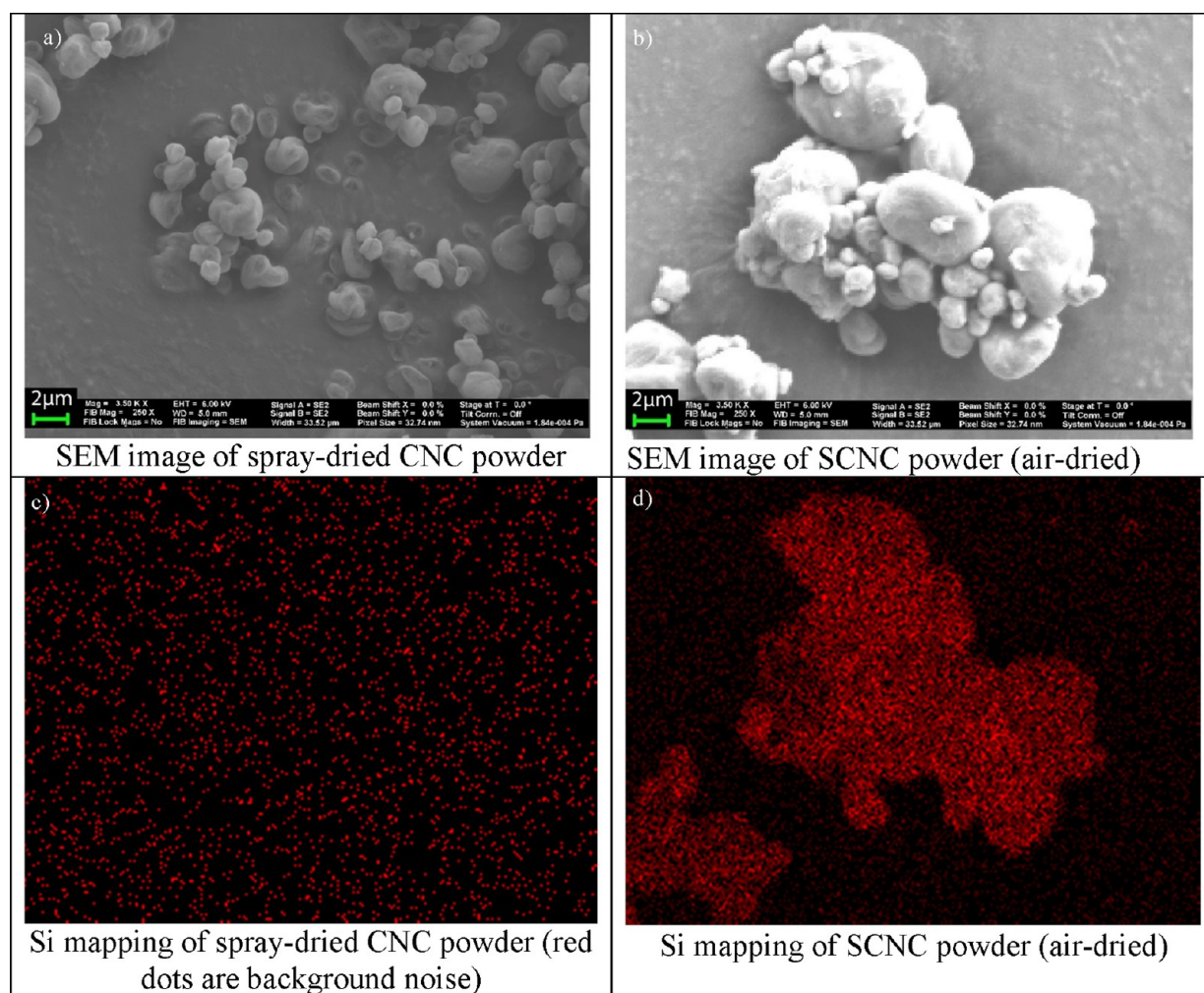
$$P_{N_2} = \frac{NGTR \times T_m}{\Delta p} = \frac{P_0 \times S \times \pi D^2 \times T_m}{\Delta p \times 4ART} \left( \frac{\text{mol}}{\text{m} \cdot \text{s} \cdot \text{Pa}} \right) \quad (2)$$

In the given equation,  $P_0$  represents the standard atmospheric pressure, which is 101325 Pa (Pa).  $S$  stands for the rate of rising of the capillary slug, measured in meters per second (m/s).  $D$  is the inner diameter of the capillary tube, which equals  $0.4957 \times 10^{-3}$  meters (m).  $A$  denotes the open area of the cell, measuring  $0.6655 \times 10^{-2}$  square meters ( $\text{m}^2$ ).  $T_m$  signifies the thickness of the sample membrane, expressed in meters (m). The sample thickness is provided in Table S.1.  $\Delta p$  represents the pressure difference between the lower and upper chambers, specifically gauge pressure, measured in pascals (Pa).  $T$  denotes the gas temperature, recorded in Kelvin (K).  $R$  stands for the gas constant and is quantified as  $8.3143 \text{ (m}^3 \cdot \text{Pa) / (mol} \cdot \text{K)}$ .

**2.2.6. Calculation of Selectivity of Water Vapor and Nitrogen.** The selectivity ( $\alpha$ ) was determined as the ratio of water ( $\text{H}_2\text{O}$ ) permeability to nitrogen ( $\text{N}_2$ ) permeability, as expressed by Equation 3.

$$\alpha = \frac{P_{H_2O}}{P_{N_2}} \quad (3)$$

**2.2.7. Coefficient of Thermal Expansion (CTE).** The in-plane coefficients of thermal expansion (CTE) for the membrane samples were assessed using a thermomechanical apparatus, specifically the Q400 TMA from TA Instrument. Each sample, measuring 5 mm  $\times$  5 mm, was individually interposed between two crystal wafers to ensure uniform force



**Figure 4.** SEM images of CNC powder and SCNC powder and Si mapping images.

distribution. An expansion probe, subjected to a 0.02 N preload, was brought into contact with the sample's surface. The temperature was systematically increased from 25 to 100 °C at a controlled heating rate of 5 °C/min. Throughout this process, alterations in the sample's thickness were continuously recorded, facilitating the subsequent derivation of CTE via the linear slope of the expansion-temperature relationship, as stipulated by Equation 4.<sup>25</sup>

$$\text{CTE} = \frac{\Delta L}{L_0 \times \Delta t} \quad (4)$$

Here,  $L_0$  represents the initial length of the sample ( $\mu\text{m}$ );  $\Delta t$  denotes the temperature change (°C), and  $\Delta L$  signifies the thermal expansion or contraction of the sample following the temperature variation. For each concentration, a total of 3 samples were prepared and subsequently subjected to triplicate testing. As a result, the mean CTE value for each sample type was determined based on the analysis of nine (9) replicates.

**2.2.8. Scanning Electron Microscopy (SEM) Analysis.** The morphology of the membrane samples was examined through scanning electron microscopy (SEM) employing an NVision 40 instrument by Zeiss, Germany. The samples were securely affixed to a specimen mount using carbon tape and subsequently coated with conductive silver. Regions of particular interest in the samples were further sputter-coated with a 23-nanometer-thick layer of gold, a process accom-

plished using the Cressington 108 auto sputter coater provided by Ted Pella Inc., Redding, CA, USA. Image capture was conducted under an accelerating voltage of 3 (kV).

**2.2.9. Force Microscopy (AFM) Analysis.** The membrane samples were prepared as 5 mm × 5 mm sections for examination using an Atomic Force Microscope (AFM), specifically the MFP-3D model by Oxford Instruments Oxon, UK. Imaging was carried out with AC200TS-R3 probes featuring spring constants of  $9 \pm 6$  (nN/nm). The imaging process was performed in alternating current mode, maintaining a set point of 0.4 V and a constant free air amplitude of 1 V.

**2.2.10. X-ray Diffraction (XRD).** The XRD patterns of powder CNCs and SCNCs in the scattering angle ( $2\theta$ ) range from 10° to 50° were analyzed using a Siemens D500 diffractometer at the Frontier Institute for Research in Sensor Technologies (FIRST) of the University of Maine, at a scanning speed of 1°  $2\theta$ /min. For each sample type, three replicates were conducted.

**2.2.11. Dynamic Mechanical Analysis (DMA).** Dynamic mechanical analysis (DMA) was conducted using a Q850 dynamic mechanical analyzer (TA Instruments) in tension mode. The experiments were performed at a fixed frequency of 1.0 Hz an initial force of 0.02 N, and a strain of 0.05%. The temperature varied from −80 to 100 °C at a heating rate of 5 °C/min, and a strain of 0.05% was applied. The experiments

were done in the air. For each sample type, three replicates were conducted.

**2.2.12. Polarized Light Microscopy (PLM).** Imaging was performed using an AmScope polarized light microscope (Model ME520TA, Irvine, CA, USA). The microscope was equipped with an AmScope MU900 digital camera featuring a pixel size of  $1.67\ \mu\text{m}$  by  $1.67\ \mu\text{m}$  and a 12-bit parallel analog-to-digital converter, which converts the 8-bit RGB data to a digital format for computer analysis. During the observations, samples were placed between the crossed polarizers and a lambda retardation filter.<sup>26</sup> A halogen bulb was utilized as the light source. A total of three replicates were performed for each type of sample.

**2.2.13. Statistical Analysis.** Two-way analysis of variance (ANOVA) was performed for two independent variables (Type of membrane and temperature) to understand the main effects and interaction effects of them on the water vapor and nitrogen gas permeability, and selectivity of the membrane samples. One-way ANOVA was conducted for the effect of the independent variable (Type of membrane) on CTE, followed by Tukey's multiple comparisons test. Significance was set at  $P < 0.05$ . All statistical analyses were run in OriginPro software version 2022b<sup>27</sup>

### 3. RESULTS AND DISCUSSION

**3.1. Morphology of CNCs and SCNCs.** The morphology of the CNCs, and CNCs after silylation with MTMS were analyzed with SEM. As shown in Figure 4a the unmodified spray-dried CNCs have spherical shape. Individual CNC is not seen. Figure 4b shows that the CNCs after silylation maintain the round shape and the morphology of the CNCs after silylation (i.e., SCNCs) does not change significantly. Because the SCNCs were dried into film to be presented in the SEM, they look to be agglomerated. However, in the process of making composite SCNC/PDMS membranes, there is no step of drying of SCNCs and therefore this agglomeration does not happen. The SEM-EDS results (Figure 4c and 4d) show that the silicon (Si) element is uniformly detected all over the SCNCs, but this Si element was not detected in the CNCs. This confirms successful and uniform silylation of CNC.

**3.2. ATR - FTIR Analysis.** FT-IR (Figure 5) was used to verify the silylation of CNCs. The SCNC spectrum revealed multiple additional absorption peaks. The new bands

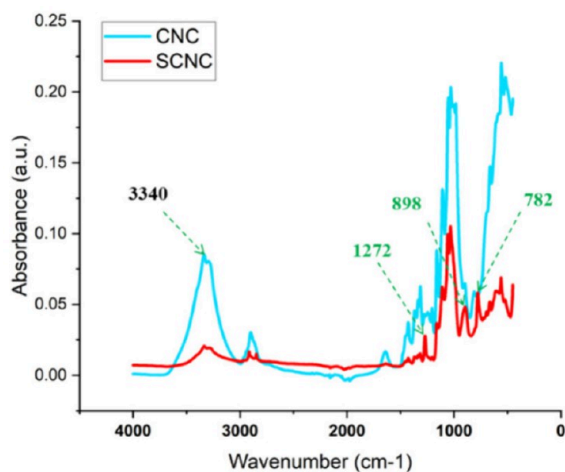


Figure 5. FT-IR spectra of CNC powder and SCNC powder.

appearing at 1272, 898, and  $782\ \text{cm}^{-1}$  represent the bending of the C-H bonds in the methyl group, the stretching of the Si-OH bond, and the Si-C or Si-O bonds, respectively. The existence of these peaks proves the successful silylation of CNCs. In addition, a reduction of the O-H absorption peak intensity at  $3340\ \text{cm}^{-1}$  was observed, which shows most of the O-H groups on the surface of CNCs had been replaced with new functional groups.<sup>21,28</sup>

**3.3. X-ray Diffraction (XRD).** Figure 6 shows the XRD diffraction patterns for the spray-dried CNCs and the air-dried

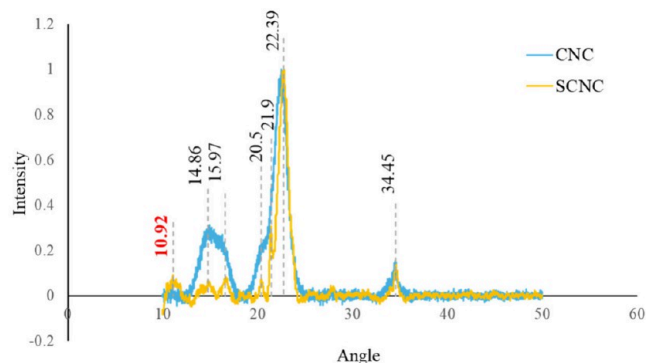


Figure 6. XRD patterns of CNC powder and SCNC powder.

SCNCs. Both samples show peaks at  $2\theta$  of  $14.86^\circ$ ,  $15.97^\circ$ ,  $20.5^\circ$ ,  $22.39^\circ$ , and  $34.45^\circ$  which are characteristic peaks of cellulose I.<sup>15,28,29</sup> It can be seen that after the silylation the locations of the peaks are not changed, indicating that the cellulose crystalline structure I type was maintained after the silylation, however, the intensities for the planes  $\bar{1}10$  ( $14.86^\circ$ ),  $110$  ( $15.97^\circ$ ), and  $102$  ( $20.5^\circ$ ) were substantially decreased, indicating a decreased crystallinity. The intensities at  $21.9^\circ$ ,  $22.39^\circ$ , and  $34.45^\circ$  did not change substantially.<sup>21,30</sup> A new peak was observed in  $2\theta$  of  $10.92^\circ$  corresponding to the silylation agent (MTMS).<sup>31</sup>

#### 3.4. Appearance of SCNC/PDMS Membrane Samples.

The appearance of PDMS, CNC/PDMS, and SCNC/PDMS films is depicted in Figure 7. Pure PDMS exhibits transparency, while the CNC/PDMS film displays translucence which could be attributed to nanocrystal agglomeration. Conversely, the SCNC/PDMS film exhibits improved clarity compared to the CNC/PDMS film due to the superior dispersion of silylated CNCs within the PDMS matrix. Although membrane clarity is not a critical issue, it is an indicator of the quality of nanocrystal dispersion within the PDMS matrix.

#### 3.5. Morphological Analysis and Polarized Light Spectroscopy.

Figure 8 shows the morphology of CNC/PDMS and SCNC/PDMS membranes as observed with FE-SEM. Figure 8a shows the SEM image of pure PDMS with no particles on the surface. Figure 8b is the SEM image from the surface of the CNC/PDMS membrane. Particles appearing on the surface of the CNC/PDMS membrane are mostly larger than  $1\ \mu\text{m}$ , indicating an agglomeration of the CNCs. Figure 8c is an image of SCNC/PDMS membrane. In contrast, after introducing SCNCs into the PDMS, submicron sized particles are observed, reflecting a better dispersion of particles in the PDMS matrix than those seen in the unmodified CNCs in PDMS. Moreover, examination of the SEM images revealed that both the PDMS, CNC/PDMS, SCNC/PDMS membranes exhibit a dense structure, devoid of any observable pores or defects at the current magnification level.

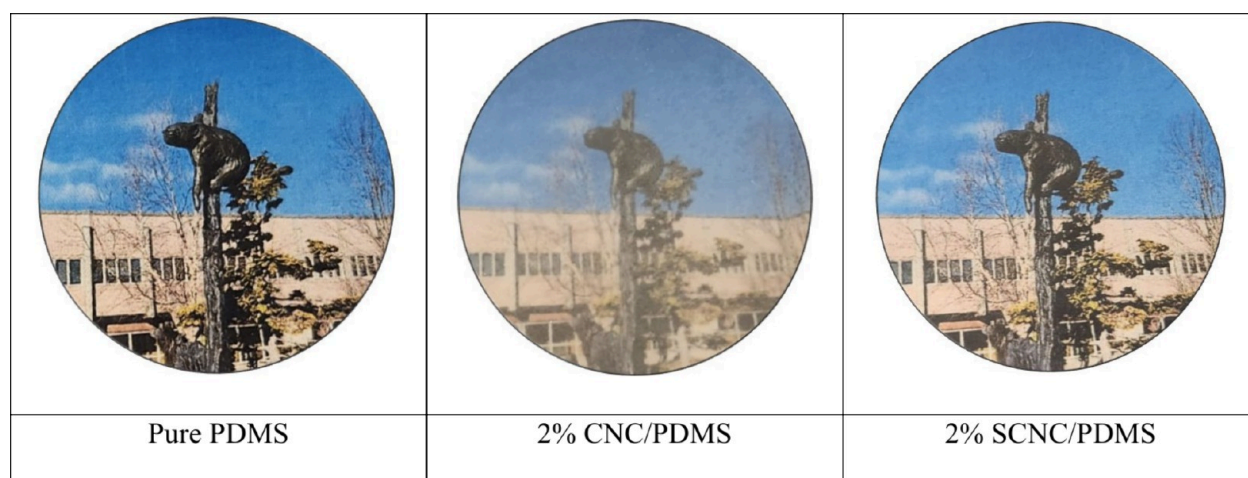


Figure 7. Appearance of the membrane samples.

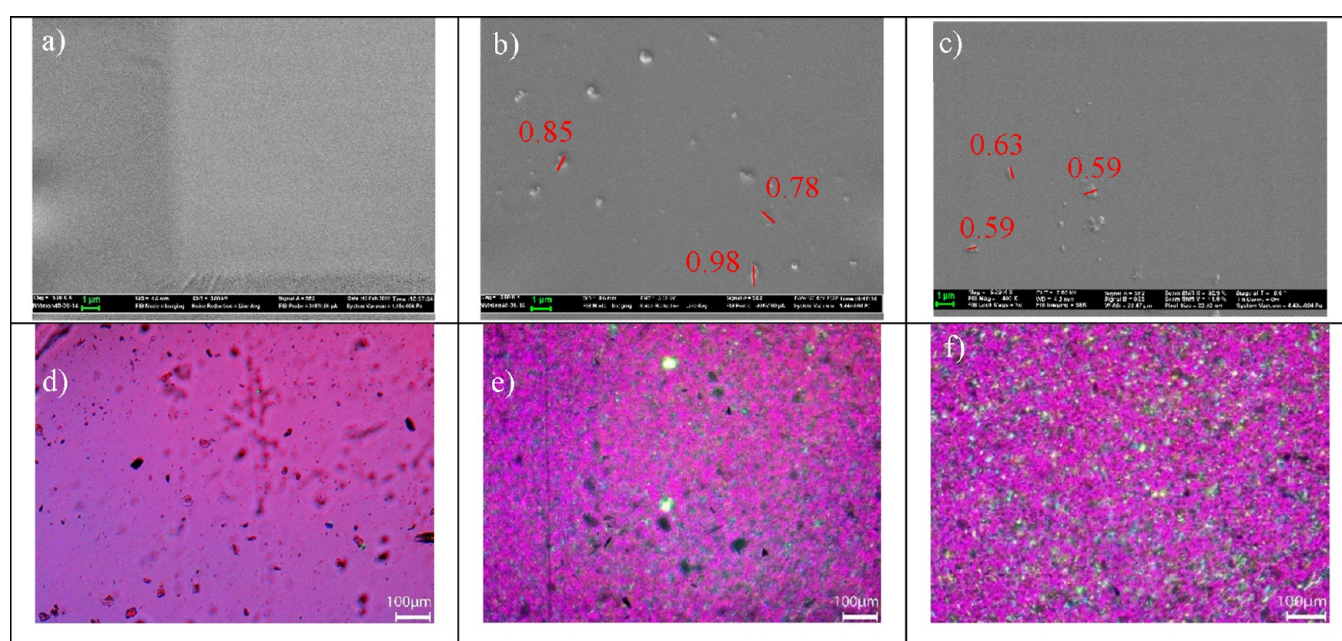


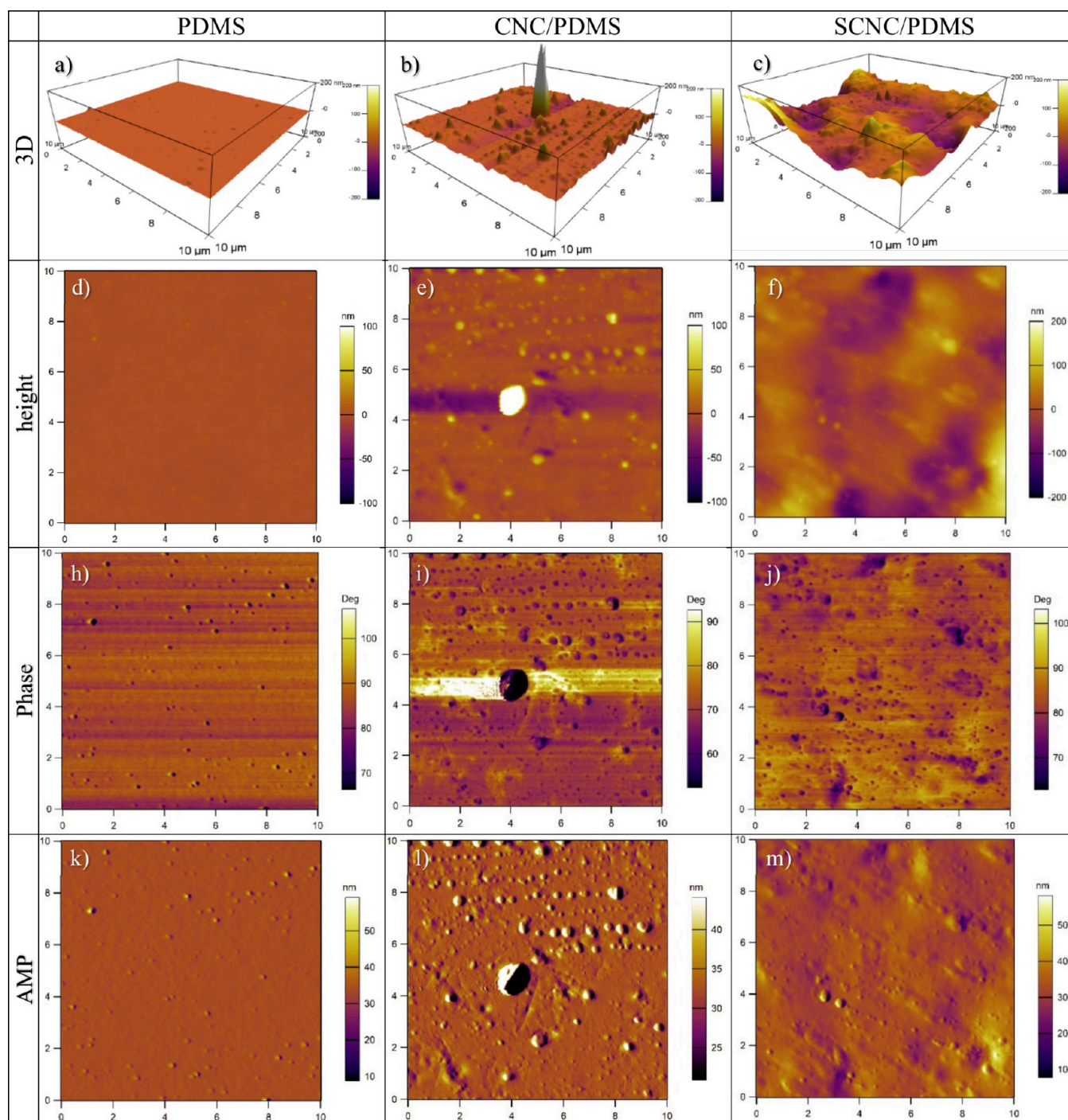
Figure 8. SEM images of composite membrane materials of CNC/PDMS: (a) pure PDMS, (b) 2% CNC/PDMS, and (c) 2% SCNC/PDMS. Polarized light results of composite membrane materials of CNC/PDMS: (d) pure PDMS, (e) 2% CNC/PDMS, and (f) 2% SCNC/PDMS

In addition, polarized light spectroscopy was further used to analyze the dispersion of nanoparticles within the membranes. CNCs exhibit birefringence. When looking at a film under the polarized light microscope, the light passing through the film can reveal the size and distribution of CNC particles inside the film as well as on the surface. The red, blue, and green spots in the images as shown in Figure 8e and 8f represent CNCs or SCNCs particles distributed in the polymer. Different colors are seen depending on the different orientations of CNCs inside the polymer. The magenta color represents the transparent area of the PDMS phase, as displayed in Figure 8d except for some contaminants on the surface. Figure 8e and 8f display colorful spots overlapping on the magenta background, but the spots in Figure 8f are smaller and denser, indicating the SCNCs had a better dispersion inside the PDMS than the unmodified CNCs. This is because there is better compatibility between the PDMS and silylated CNCs.

The SCNC loses some of the OH functional groups as proved by the FTIR results; therefore, it has less tendency to

bond with itself and is less likely to agglomerate. In comparison, the SEM images only show the dispersion of the nano particles on the surface of the membranes, while the polarized light spectroscopy shows the nano particles on the surface as well as inside the membrane.

**3.6. Atomic Force Microscopy (AFM).** The study utilized AFM images, presented in Figure 9, to assess the dispersion and dimensions of CNC and SCNC nanoparticles in PDMS. The 3D images (Figure 9. a, b, and c), and height (Figure 9. d, e, f) are provided to look at the height of the particles. Figure 9e, which is for CNC/PDMS, shows that the agglomerated nanocrystals are smaller than 2  $\mu\text{m}$  and Figure 9b shows that these CNC particles have the highest peak of larger than 200 nm, suggesting that the CNC nanoparticles are relatively large and not well dispersed in the PDMS matrix. In contrast, Figure 9f demonstrates that SCNCs are distributed in smaller sizes and in a more random manner throughout the polymer matrix compared to the CNCs. The highest peak of the SCNCs as shown in Figure 9c are significantly smaller than that of the



**Figure 9.** The unit of all of the figures is micrometer. AFM results of the top surface of the composite membrane material: pure PDMS, 2% CNC/PDMS, and 2% SCNC/PDMS. (a–c) 3D images, (d–f) height images, (h–j) phase, and (k–m) amplitude results.

CNC nanoparticles in Figure 9b. The decrease in the highest peak is attributed to the improved compatibility between the SCNCs and PDMS matrix after the silylation process. The AFM images reveal that the SCNC/PDMS sample has a smoother surface compared to the CNC/PDMS sample, indicating better nanoparticle dispersion in the polymer matrix.

In addition, phase and amplitude results are provided in Figure 9 to better study the dispersion of the particles within PDMS. These results also demonstrated better distribution of SCNCs within PDMS compared to PDMS. As a baseline, pure PDMS was also examined and shown in Figure 9a, and no

nanoparticles were observed. The highest peak on the AFM image of pure PDMS is significantly smaller than the highest peaks observed in the AFM images of the CNC and SCNC nanoparticles in PDMS. This confirms that the observed peaks in the AFM images of the CNC/PDMS and SCNC/PDMS samples were indeed attributed to the presence of the nanoparticles and not artifacts of the AFM imaging process.

Additionally, valuable insights into surface roughness were obtained through AFM analysis. The surface of pure PDMS displayed the lowest roughness, while the SCNC/PDMS membrane exhibited a smoother surface than the CNC/PDMS

membrane. The improved distribution of SCNCs within the PDMS matrix may be the reason for this observation. The greater compatibility of SCNCs with PDMS and the uniform distribution of nanoparticles decrease the chain mobility of PDMS and therefore reduces the variation in the density. Consequently, the incorporation of SCNCs in PDMS results in a smoother surface in comparison to CNC/PDMS. In a separate study, Gwon et al. reported a smoother surface in modified CNC-reinforced poly(lactic acid) (PLA) polymer, likely because of the improved compatibility between the modified CNC and PLA and reduced density differences.<sup>14</sup>

### 3.7. Permeability and Selectivity of Membranes.

Figure 10 shows the water vapor permeability of pure

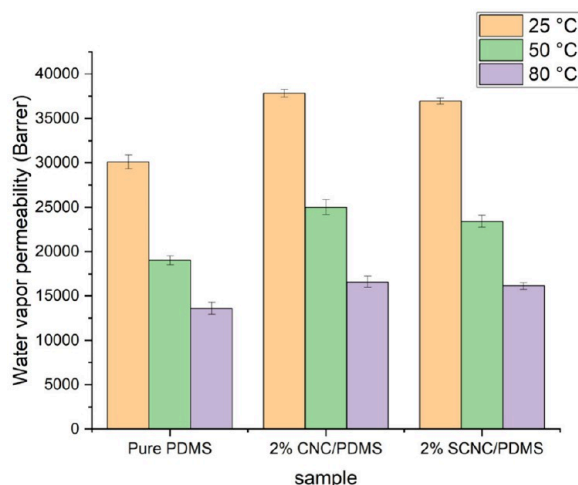


Figure 10. Water vapor permeability of the membrane samples.

PDMS, 2 w.t.% CNC/PDMS, and 2 w.t.% SCNC/PDMS membrane samples. The addition of both the SCNCs and CNCs increased the water vapor permeability at all three temperatures. The water vapor permeability values of SCNC/PDMS were comparable to those of the CNC/PDMS, both of which were higher than those of the pure PDMS. The values for the SCNC/PDMS membrane were smaller than the ones for the CNC/PDMS. The lower values could be attributed to the modification of the CNC which makes it more compatible with PDMS and reduction of free volume compared to the CNC/PDMS. The same phenomena were observed in a different study in which they used two kinds of surface-modified SiO<sub>2</sub> nanoparticles. The nanoparticles that had better compatibility and a higher degree of interaction with PDMS, resulted in lower free volume formation and consequently, reduced the gas permeability compared to the nanoparticles that had lower compatibility with PDMS.<sup>12</sup>

Two-way ANOVA results reveal that the effect of the type of membrane, temperature, and their interaction on water permeability were statistically significant (Table S.2). Furthermore, the comparison between membranes (Table S.3), shows that the PDMS, 2% CNC/PDMS, and 2% SCNC/PDMS are significantly different from each other.

Furthermore, the effect of the temperatures on the water vapor permeability of the membranes was studied. The results showed that by increasing the temperature from 25 to 80 °C, the water vapor permeability is decreased. The reason is that with increasing temperature, the diffusivity of water vapor increases, and the solubility decreases, but the effect of

solubility is dominant. Therefore the permeability decreases with increasing temperature.<sup>32</sup>

Figure 11 shows the nitrogen gas permeability of the membranes. The values for the pure PDMS are in agreement

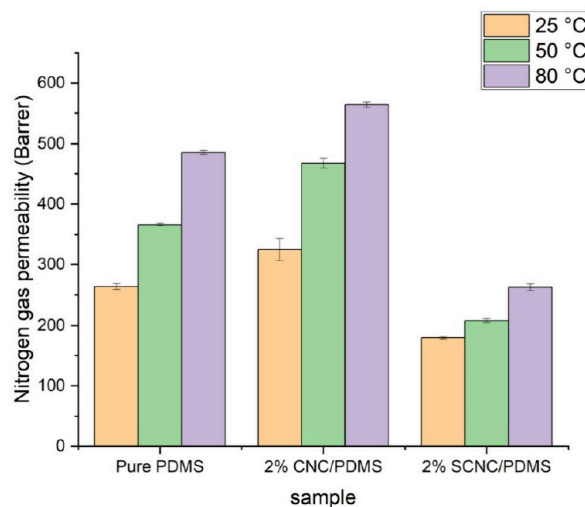
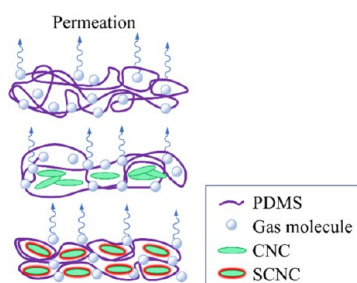


Figure 11. Nitrogen gas permeability of the membrane samples

with a previous study.<sup>33</sup> The addition of the CNC to the PDMS has increased the nitrogen gas permeability by 23.2% at 25 °C. While the addition of SCNC to the PDMS has decreased this value by 31.5% compared to the pure PDMS at the same temperature. The reason could be because, after silylation of the CNCs, The SCNCs become more compatible with the PDMS polymer, and a more uniform and improved dispersion of the SCNCs within the PDMS matrix takes place as observed in the PLM, AFM, and SEM results. The improved dispersion of the nano fillers within a polymer matrix results in the reduction of polymer chain mobility<sup>14</sup> and this results in the reduction of film permeability. This effect is more significant for low-sorbing gases such as N<sub>2</sub> and O<sub>2</sub>. So, this could be the reason for the reduction of N<sub>2</sub> permeability through the SCNC/PDMS membrane.<sup>12</sup> In addition, the transportation of the water vapor molecules might be able assisted by absorbing through CNC particles because of the hydrophilic nature and also by passing between the polymeric chains, however, for other gas species (N<sub>2</sub> and O<sub>2</sub>) the only pass might be passing through between the polymeric chains.

The transportation of water vapor molecules could potentially be facilitated through absorption by cellulose nanocrystal (CNC) particles owing to their hydrophilic properties, as well as by permeation through the gaps within the polymeric chains. However, in the case of other gaseous species (N<sub>2</sub>, O<sub>2</sub>), their primary route of passage appears to be limited to traversing the spaces between the polymeric chains.

As illustrated in Figure 12, the pure PDMS membrane has a polymer structure. After adding the CNCs into the PDMS, because of the low compatibility between the CNCs and PDMS, agglomeration of the CNCs within the PDMS structure is observed, and attributed to this agglomeration, the surface has higher roughness and, in some areas, more nanoparticles agglomerate and, in some sections, fewer particles exist. This results in a difference in the density of the membrane in different sections and this causes increased free volume.<sup>12</sup> However, after adding the SCNCs, attributed to the improved compatibility between the SCNC and PDMS,



**Figure 12.** Schematic illustration of pure PDMS and PDMS nanocomposite films.

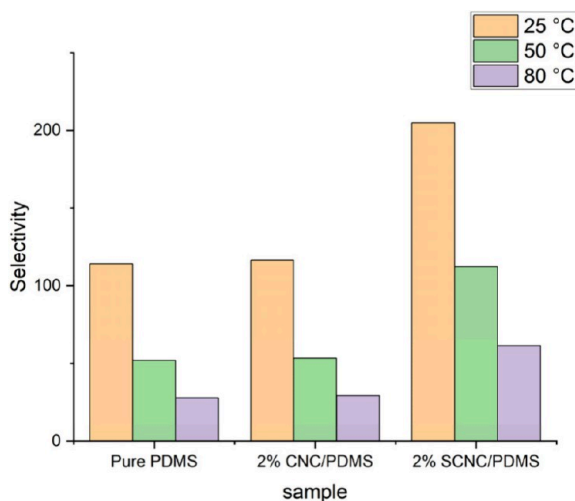
there is a better dispersion and more uniform structure, which causes a reduction of the polymer chain mobility. Thus, the gas permeability decreases. However, this effect is more pronounced for low-sorbing gases like  $N_2$  and  $O_2$  rather than water vapor, which is condensable and non-low-sorbing gas.

The effect of temperature on the nitrogen gas permeability of the membranes is also studied. As the temperature increased from 25 to 85  $^{\circ}C$ , the  $N_2$  permeability increased. This is because both the diffusivity and solubility of  $N_2$  increase with increasing of temperature.<sup>32</sup>

In addition, two-way ANOVA results show the effect of type of membrane, temperature and their interaction on nitrogen permeability were significant (Table S.4). Furthermore, the comparison between different membranes (Table S.5), reveals that PDMS, 2% CNC/PDMS and 2% SCNC/PDMS membranes are significantly different.

The nitrogen gas permeability values of SCNC/PDMS were much lower than the CNC/PDMS and pure PDMS. The nitrogen gas permeability decreased by about 31.6% at 25  $^{\circ}C$ , 43.1% at 50  $^{\circ}C$ , and 45.9% at 80  $^{\circ}C$  compared with the pure PDMS, and by about 44.5 at 25  $^{\circ}C$ , 55.5% at 50  $^{\circ}C$ , and 53.4% at 80  $^{\circ}C$  in comparison to the CNC/PDMS.

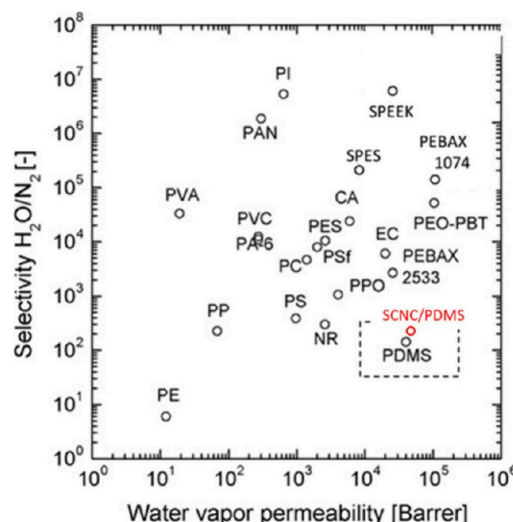
Because of this reduction in the  $N_2$  permeability of the SCNC/PDMS membrane, there was an increase in the selectivity of the membrane for water vapor/ $N_2$  as observed in Figure 13. The selectivity of  $H_2O/N_2$  of the SCNC/PDMS was higher than that of the pure PDMS and the CNC/PDMS: about 79.6% and 75.9% at 25  $^{\circ}C$ , 116.1% and 110.2% at 50  $^{\circ}C$ , and 119.0% and 108.1% at 80  $^{\circ}C$ , respectively.



**Figure 13.** Selectivity of the membrane samples.

Two-way ANOVA results (Table S.6) show that the effect of the type of membrane, temperature, and their interaction is significant on selectivity. In addition, the comparison between different membranes (Table S.7), reveals that 2% SCNC/PDMS membrane is significantly different from other samples, while PDMS and 2% CNC/PDMS are not significantly different.

### 3.8. SCNC Nanofillers in PDMS: Effectiveness and Comparison with Other Nanofillers. Figure 14 presents a



**Figure 14.** Water vapor permeability and  $H_2O/N_2$  selectivity of various polymer-based membranes. Adapted with permission from ref 34. Copyright 2008 Elsevier.

summary of the selectivity and permeability of water vapor for PDMS and other common membranes, reflecting insights from prior studies.<sup>10</sup> The enhancement of water vapor permeability and water vapor/ $N_2$  selectivity upon incorporating SCNC into PDMS is depicted in Figure 14.

This study utilizes a chemically modified biobased material, Silylated CNC, as a nanofiller within the PDMS matrix to enhance the performance of PDMS membranes for air dehydration. The hydrophobic properties of CNC, along with its renewable and sustainable characteristics, position it as a viable alternative to nonrenewable nanofillers such as zeolites (ZIF), silicon dioxide ( $SiO_2$ ), and titanate nanotubes (TNTs), which have been used in previous studies.<sup>8,12,13,35</sup>

Our research demonstrated that the water vapor permeability and nitrogen permeability of the PDMS membrane at room temperature were 3,684 Barrer and 264 Barrer, respectively, which aligns with the findings from prior studies.<sup>33,36</sup>

In the current study, after adding the optimal concentration of 2% Silylated CNC, the water vapor permeability at room temperature increased by 20.4% and nitrogen gas permeability at room temperature decreased by 31.6%.

The improvement in water vapor permeability may be attributed to the presence of hydroxyl groups on silylated CNCs<sup>37</sup> which could play a crucial role in improving the solubility of water vapor, thereby enhancing its permeability.

However, the reduction in nitrogen gas permeability may be attributed to the decreased movement of polymer chains in the PDMS. When nonporous and chemically compatible nanofillers are incorporated into rubbery membranes like PDMS, their chemical compatibility allows PDMS's flexible chains to

**Table 1. Nanofiller/PDMS Mixed Matrix Membranes**

| membrane                          | water vapor permeability (barrer)  | nitrogen permeability (barrer)   | conditions                       | amount of nanofiller | reference  |
|-----------------------------------|------------------------------------|----------------------------------|----------------------------------|----------------------|------------|
| SCNC/PDMS                         | PDMS = 30683<br>SCNC/PDMS = 36950  | PDM = 263<br>SCNC/PDMS = 180     | $T = 25\text{ }^{\circ}\text{C}$ | 2 wt %               | this study |
| ZIF-L/PDMS                        | PDMS = 25000<br>ZIF-L/PDMS = 27000 |                                  | $T = 40\text{ }^{\circ}\text{C}$ | 30 wt %              | 8          |
| organosilane-modified silica/PDMS |                                    | PDMS = 310<br>Si-DMPS/PDMS = 240 | $T = 35\text{ }^{\circ}\text{C}$ | 10 wt %              | 12         |
| ZIF-L/PDMS                        |                                    | PDMS = 266<br>ZIF-L/PDMS = 140   | $T = 35\text{ }^{\circ}\text{C}$ | 20 wt %              | 13         |
| PDMS                              |                                    | PDMS = 270                       | $T = 20\text{ }^{\circ}\text{C}$ |                      | 33         |
| PDMS                              | PDMS = 30000                       |                                  | $T = 25\text{ }^{\circ}\text{C}$ |                      | 36         |

easily accommodate these fillers. As a result, no significant increase in free volume occurs, leading to a decrease in diffusion (D) values. This reduction in D is generally linked to an extended diffusion path. Consequently, the restricted movement of polymer chains lowers membrane permeability, with this effect being more pronounced for low sorbing gases (such as  $\text{N}_2$  and  $\text{O}_2$ ).<sup>9,12,38</sup> This explains the observed decrease in nitrogen gas permeability following the addition of SCNCs to rubbery PDMS.

One study reported that the addition of modified nanoparticles into the PDMS structure, when the nanoparticles were compatible with PDMS, led to a reduction in the movement of PDMS polymer chains. Since PDMS is a rubbery polymer, this reduction in chain mobility consequently resulted in a decrease in the membrane's nitrogen ( $\text{N}_2$ ) permeability.<sup>12</sup>

Another study reported that incorporating ZIF-L particles into PDMS reduced  $\text{N}_2$  permeability. This effect is likely due to the intrinsic properties of ZIF particles, which enhance the rigidity of the PDMS polymer chains, and the addition of ZIF-L may also create a more tortuous path for  $\text{N}_2$  gas diffusion.<sup>13</sup>

However, CNCs offer several advantages over ZIF nanoparticles. For example, they require a much lower weight ratio to achieve comparable improvements in water vapor and nitrogen gas permeability. Additionally, CNCs are sustainable and renewable materials. A detailed comparison between this study and other nano-PDMS mixed matrix membranes is provided in Table 1.

**3.9. Coefficient of Thermal Expansion (CTE) of Membranes.** Figure 15 illustrates the coefficient of thermal expansion (CTE) of the membranes, which reflects their dimensional stability with temperature variations. The average

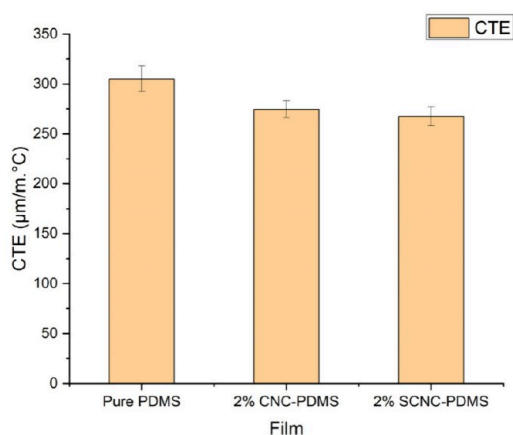
value  $\pm$  standard deviation (SD) of CTE for pure PDMS, ranging from room temperature to  $100\text{ }^{\circ}\text{C}$ , was measured as  $301.1 \pm 12.6\text{ }\mu\text{m/m}\cdot^{\circ}\text{C}$ . This measured value aligns well with the published CTE value for PDMS, which is  $309\text{ ppm}/^{\circ}\text{C}$ .<sup>14</sup> Upon incorporating 2% CNC, the mean  $\pm$  SD of CTE decreased to  $274.4 \pm 8.5\text{ }\mu\text{m/m}\cdot^{\circ}\text{C}$ , representing a reduction of approximately 11% compared to pure PDMS. This decline in CTE was expected since CNC exhibits an exceptionally low CTE of  $9\text{ }\mu\text{m/m}\cdot^{\circ}\text{C}$  and aids in limiting PDMS expansion at elevated temperatures when dispersed within the PDMS matrix.<sup>39</sup> However, the mean  $\pm$  SD of CTE of SCNC/PDMS was  $267.2 \pm 9.5\text{ }\mu\text{m/m}\cdot^{\circ}\text{C}$ , which is 14% lower than pure PDMS and it shows improvement in the dimensional stability of the membrane.

One-way ANOVA results (Table S.8) show that the effect of the type of membrane is significant. In addition, the comparison among different membranes (Table S.9) shows that PDMS is different from 2% CNC/PDMS and 2% SCNC/PDMS. However, there is no statistical significance observed between the 2% CNC/PDMS and 2% SCNC/PDMS membranes. These results show that both the CNC and SCNC were able to reduce the CTE of PDMS by some levels.

**3.10. Dynamic Mechanical Analysis (DMA).** Figures 16 a and b illustrate the impact of the CNCs and SCNCs on the storage modulus ( $E'$ ) and loss factor ( $\tan\delta$ ) of the membranes, respectively. The  $\tan\delta$  results indicated that the introduction of the CNCs and SCNCs has a weak effect on the glass transition temperature ( $T_g$ ) of the membranes. Typically, the glass transition temperature of PDMS membranes ranges from  $-45\text{ }^{\circ}\text{C}$  to  $-50\text{ }^{\circ}\text{C}$ , which is a characteristic of the PDMS component.<sup>21</sup>

Despite the low loading level of the SCNCs, the storage modulus ( $E'$ ) of the SCNC/PDMS composite exhibited improvement at low ( $-50\text{ }^{\circ}\text{C}$ ), room ( $30\text{ }^{\circ}\text{C}$ ), and elevated ( $80\text{ }^{\circ}\text{C}$ ) temperatures compared to the neat PDMS and CNC/PDMS composite membranes. This enhancement in the storage modulus demonstrates the significant impact of SCNCs on the mechanical properties of PDMS.

It is worth noting that cellulose nanocrystals possess high mechanical modulus, ranging from 100 to 200 GPa depending on their sources, in contrast to the low modulus of 2–3 MPa exhibited by the soft PDMS matrix at room temperature.<sup>21</sup> Specifically, in this study, the addition of only 2 w.t.% of SCNC to the PDMS resulted in an increased storage modulus ( $E'$ ) of 2.28 MPa at  $25\text{ }^{\circ}\text{C}$ , whereas the values for CNC/PDMS and PDMS membranes were 1.91 and 1.74 MPa, respectively. This result highlights the beneficial effect of incorporating SCNC into the PDMS matrix.

**Figure 15.** CTE values for different samples.

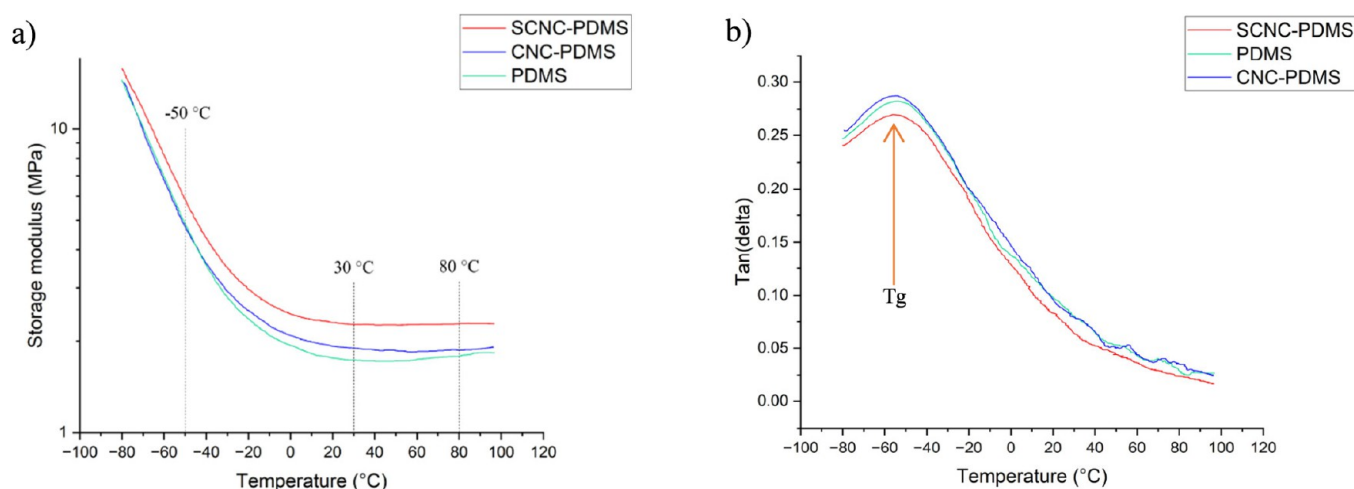


Figure 16. DMA results of membranes.

In the case of CNC/PDMS, the improvement in the storage modulus is not significant, possibly due to low compatibility between CNC and the hydrophobic PDMS matrix. However, after silylation of the CNC surface, the increase in storage modulus can be attributed to improved adhesion at the filler/matrix interface, resulting from enhanced compatibility between SCNC and PDMS.<sup>24</sup>

#### 4. CONCLUSIONS

This study developed a cellulose nanocrystal (CNC)-reinforced polydimethylsiloxane (PDMS) membrane with improved properties for air dehydration applications. To enhance compatibility between the hydrophilic CNCs and the hydrophobic PDMS, CNCs were modified via silylation, resulting in silylated CNCs (SCNCs). Characterization analyses, including FTIR, XRD, and SEM, confirmed successful surface modification and improved dispersion of SCNCs within the PDMS matrix.

The 2% SCNC/PDMS membrane exhibited a 23% increase in water vapor permeability and a 79.6% improvement in selectivity for water vapor over nitrogen at 25 °C, compared to pure PDMS. Additionally, Thermo-mechanical Analysis (TMA) showed a decrease in the coefficient of thermal expansion (CTE) with the addition of both CNCs and SCNCs. These results demonstrate the potential of SCNC/PDMS membranes for applications in air dehydration and similar fields, offering a renewable, high-performance alternative for polymer composite materials. The future work can focus on the influence of the competition of two gas components in a mixed gas stream on the permeability and selectivity of the SCNC/PDMS membrane.

#### ■ ASSOCIATED CONTENT

##### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.4c03658>.

Information on membrane properties and detailed ANOVA results from the research conducted (PDF)

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##### Author Contributions

Nasim Alikhani: methodology, visualization, writing—original draft. Ling Li: resources, writing—review and editing, and funding acquisition. Jinwu Wang: resources, writing—review and editing, and funding acquisition.

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##### Notes

The authors declare no competing financial interest.

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University of Maine, and the thesis is accessible online at <https://digitalcommons.library.umaine.edu/etd/3871>.

## REFERENCES

- (1) Liang, C. Z.; Chung, T. S. Robust Thin Film Composite PDMS/PAN Hollow Fiber Membranes for Water Vapor Removal from Humid Air and Gases. *Sep Purif Technol.* **2018**, *202*, 345–356.
- (2) Fang, M.; Wu, C.; Yang, Z.; Wang, T.; Xia, Y.; Li, J. ZIF-8/PDMS Mixed Matrix Membranes for Propane/Nitrogen Mixture Separation: Experimental Result and Permeation Model Validation. *J. Membrane Sci.* **2015**, *474*, 103.
- (3) Netusil, M.; Dittl, P. Comparison of Three Methods for Natural Gas Dehydration. *Journal of Natural Gas Chemistry* **2011**, *20*, 471–476.
- (4) Qu, M.; Abdelaziz, O.; Gao, Z.; Yin, H. Isothermal Membrane-Based Air Dehumidification: A Comprehensive Review. *Renew. Sustain. Energy Rev.* **2018**, *82* (3), 4060–4069.
- (5) Metz, S. J. *Water Vapor and Gas Transport through Polymeric Membranes*. Ph.D. Thesis, University of Twente, 2003. <https://research.utwente.nl/en/publications/water-vapor-and-gas-transport-through-polymeric-membranes> (accessed 05-02-2021).
- (6) Perry, J.; Nagai, K.; Koros, W. Polymer Membranes for Hydrogen Separations. *MRS Bull.* **2006**, *31*, 745.
- (7) Rezakazemi, M.; Shahidi, K.; Mohammadi, T. Hydrogen Separation and Purification Using Crosslinkable PDMS/Zelite A Nanoparticles Mixed Matrix Membranes. *Int. J. Hydrogen Energy* **2012**, *37*, 14576.
- (8) Mao, H.; Zhen, H. G.; Ahmad, A.; Li, S. H.; Liang, Y.; Ding, J. F.; Wu, Y.; Li, L. Z.; Zhao, Z. P. Highly Selective and Robust PDMS Mixed Matrix Membranes by Embedding Two-Dimensional ZIF-L for Alcohol Permselective Pervaporation. *J. Membr. Sci.* **2019**, *582*, 307–321.
- (9) Chung, T.-S.; Jiang, L. Y.; Li, Y.; Kulprathipanja, S. Mixed Matrix Membranes (MMMs) Comprising Organic Polymers with Dispersed Inorganic Fillers for Gas Separation. *Prog. Polym. Sci.* **2007**, *32* (4), 483–507.
- (10) Vaimakis-Tsogkas, D. T.; Bekas, D. G.; Giannakopoulou, T.; Todorova, N.; Paipetis, A. S.; Barkoula, N. M. Effect of TiO<sub>2</sub> Addition/Coating on the Performance of Polydimethylsiloxane-Based Silicone Elastomers for Outdoor Applications. *Mater. Chem. Phys.* **2019**, *223*, 366–373.
- (11) Ammar, S.; Ramesh, K.; Vengadaesvaran, B.; Ramesh, S.; Arof, A. K. Amelioration of Anticorrosion and Hydrophobic Properties of Epoxy/PDMS Composite Coatings Containing Nano ZnO Particles. *Prog. Org. Coat.* **2016**, *92*, 54–65.
- (12) Beltran, A. B.; Nisola, G. M.; Cho, E.; Lee, E. E. D.; Chung, W.-J. Organosilane Modified Silica/Polydimethylsiloxane Mixed Matrix Membranes for Enhanced Propylene/Nitrogen Separation. *Appl. Surf. Sci.* **2011**, *258*, 337.
- (13) Şahin, F.; Topuz, B.; Kalıpçılar, H. ZIF Filled PDMS Mixed Matrix Membranes for Separation of Solvent Vapors from Nitrogen. *J. Membr. Sci.* **2020**, *598*, 117792.
- (14) Gwon, J. G.; Cho, H. J.; Chun, S. J.; Lee, S.; Wu, Q.; Lee, S. Y. Physiochemical, Optical and Mechanical Properties of Poly(Lactic Acid) Nanocomposites Filled with Toluene Diisocyanate Grafted Cellulose Nanocrystals. *RSC Adv.* **2016**, *6* (12), 9438–9445.
- (15) Yang, X.; Li, Z.; Jiang, Z.; Wang, S.; Liu, H.; Xu, X.; Wang, D.; Miao, Y.; Shang, S.; Song, Z. Mechanical Reinforcement of Room-Temperature-Vulcanized Silicone Rubber Using Modified Cellulose Nanocrystals as Cross-Linker and Nanofiller. *Carbohydr. Polym.* **2020**, *229*, 115509.
- (16) Yu, H. Y.; Chen, R.; Chen, G. Y.; Liu, L.; Yang, X. G.; Yao, J. M. Silylation of Cellulose Nanocrystals and Their Reinforcement of Commercial Silicone Rubber. *J. Nanopart. Res.* **2015**, *17*, 361.
- (17) Visakh, P. M.; Thomas, S.; Oksman, K.; Mathew, A. P. Crosslinked Natural Rubber Nanocomposites Reinforced with Cellulose Whiskers Isolated from Bamboo Waste: Processing and Mechanical/Thermal Properties. *Compos Part A Appl. Sci. Manuf* **2012**, *43* (4), 735–741.
- (18) Siqueira, G.; Tapin-Lingua, S.; Bras, J.; da Silva Perez, D.; Dufresne, A. Mechanical Properties of Natural Rubber Nanocomposites Reinforced with Cellulosic Nanoparticles Obtained from Combined Mechanical Shearing, and Enzymatic and Acid Hydrolysis of Sisal Fibers. *Cellulose* **2011**, *18*, 57–65.
- (19) Alikhani, N. *Cellulose Nanocrystals/Polydimethylsiloxane Composite Membranes for Air Dehydration With the Aim of Energy-Use Reduction in Wood Kiln Drying*. Ph.D. Thesis, University of Maine, 2023.
- (20) Sanders, J. E.; Wang, L.; Brinkley, G.; Gardner, D. J. Production of Nano-Scale Cellulose Nanocrystal Powder via Electrospray Drying (ESD) for Sustainable Composites. *Cellulose* **2023**, *30*, 6303.
- (21) Xia, T.; Yuwen, H.; Lin, N. Self-Bonding Sandwiched Membranes from PDMS and Cellulose Nanocrystals by Engineering Strategy of Layer-by-Layer Curing. *Compos. Sci. Technol.* **2018**, *161*, 8–15.
- (22) Hwang, S.; Han, Y.; Gardner, D. J. Morphological Characteristics of Spray Dried Cellulose Nanofibers Produced Using Various Wood Pulp Feedstocks and Their Effects on Polypropylene Composite Properties. *Compos B Eng.* **2024**, *268*, 111093.
- (23) Hwang, S.; Walker, C. C.; Ozcan, S.; Tekinalp, H.; Han, Y.; Gardner, D. J. Characterization of Spray Dried Cellulose Nanofibrils Produced by a Disk Refining Process at Different Fineness Levels. *Cellulose* **2024**, *31*, 263–277.
- (24) Planes, M.; Brand, J.; Lewandowski, S.; Remaury, S.; Solé, S.; Le Coz, C.; Carlotti, S.; Sèbe, G. Improvement of the Thermal and Optical Performances of Protective Polydimethylsiloxane Space Coatings with Cellulose Nanocrystal Additives. *Appl. Mater. int.* **2016**, *8* (41), 28030–28039.
- (25) Saba, N.; Jawaid, M. A Review on Thermomechanical Properties of Polymers and Fibers Reinforced Polymer Composites. *Journal of Industrial and Engineering Chemistry* **2018**, *67*, 1–11.
- (26) Ghasemi, S.; Rahimzadeh-Bajgiran, P.; Tajvidi, M.; Shaler, S. M. Birefringence-Based Orientation Mapping of Cellulose Nanofibrils in Thin Films. *Cellulose* **2020**, *27* (2), 677–692.
- (27) OriginPro; OriginLab Corporation: Northampton, MA, 2022.
- (28) Rosli, N. A.; Khairudin, F. A.; Kargarzadeh, H.; Othaman, R.; Ahmad, I. Hydrophobic-Oleophilic Gamma-Irradiated Modified Cellulose Nanocrystal/Gelatin Aerogel for Oil Absorption. *Int. J. Biol. Macromol.* **2022**, *219*, 213–223.
- (29) Peng, Y.; Gardner, D. J.; Han, Y.; Kiziltas, A.; Cai, Z.; Tshabalala, M. A. Influence of Drying Method on the Material Properties of Nanocellulose I: Thermostability and Crystallinity. *Cellulose* **2013**, *20* (5), 2379–2392.
- (30) SriBala, G.; Chennuru, R.; Mahapatra, S.; Vinu, R. Effect of Alkaline Ultrasonic Pretreatment on Crystalline Morphology and Enzymatic Hydrolysis of Cellulose. *Cellulose* **2016**, *23*, 1725–1740.
- (31) Lana, S. L. B.; Seddon, A. B. X-Ray Diffraction Studies of Sol-Gel Derived ORMOSILs Based on Combinations of Tetramethoxysilane and Trimethoxysilane. *J. Solgel Sci. Technol.* **1998**, *13* (1–3), 461–466.
- (32) Spatafora Salazar, A. S.; Sáenz Cavazos, P. A.; Mújica Paz, H.; Valdez Fragoso, A. External Factors and Nanoparticles Effect on Water Vapor Permeability of Pectin-Based Films. *J. Food Eng.* **2019**, *245*, 73–79.
- (33) Leemann, M.; Eigenberger, G.; Strathmann, H. Vapour Permeation for the Recovery of Organic Solvents from Waste Air Streams: Separation Capacities and Process Optimization. *J. Membr. Sci.* **1996**, *113* (2), 313–322.
- (34) Sijbesma, H.; Nymeyer, K.; van Marwijk, R.; Heijboer, R.; Potreck, J.; Wessling, M. Flue Gas Dehydration Using Polymer Membranes. *J. Membr. Sci.* **2008**, *313* (1–2), 263–276.
- (35) Li, B.; Xu, D.; Zhang, X.; Jiang, Z.; Wang, Y.; Ma, J.; Dong, X.; Wu, H. Rubbery Polymer-Inorganic Nanocomposite Membranes: Free Volume Characteristics on Separation Property. *Ind. Eng. Chem. Res.* **2010**, *49* (24), 12444–12451.
- (36) Koester, S.; Roghman, F.; Wessling, M. Water Vapor Permeance: The Interplay of Feed and Permeate Activity. *J. Membr. Sci.* **2015**, *485*, 69–78.

(37) Yuan, B.; Li, L.; Murugadoss, V.; Vupputuri, S.; Wang, J.; Alikhani, N.; Guo, Z. Nanocellulose-Based Composite Materials for Wastewater Treatment and Waste-Oil Remediation. *espublisher.com* **2020**, *1*, 41–52.

(38) Merkel, T. C.; Freeman, B. D.; Spontak, R. J.; He, Z.; Pinnau, I.; Meakin, P.; Hill, A. J. Sorption, Transport, and Structural Evidence for Enhanced Free Volume in Poly (4-Methyl-2-Pentyne)/Fumed Silica Nanocomposite Membranes. *Chem. Mater.* **2003**, *15* (1), 109–123.

(39) Müller, A.; Wapler, M. C.; Wallrabe, U. A Quick and Accurate Method to Determine the Poisson's Ratio and the Coefficient of Thermal Expansion of PDMS. *Soft Matter* **2019**, *15* (4), 779–784.