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Nanocellulose-Incorporated Composite Membranes of PEO-Based Rubbery Polymers for Carbon Dioxide Capture

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To achieve sustainable and energy-efficient CO_2 capture processes, it is imperative to develop membranes that possess both high CO_2 permeability and selectivity. One promising approach involves integrating high-aspect-ratio nanoscale fillers into polymer matrices. The high-aspect-ratio fillers increase surface area and improve interactions between polymer chains and gas molecules passing through the membrane. This study focuses on the integration of cellulose nanocrystals (CNCs) with an impressive aspect ratio of around 12 into rubbery polymers containing polyethylene oxide (PEO), namely PEBAX MH 1657 (poly[ether-block-amide] [PEBA]) and polyurethane (PU), to fabricate mixed-matrix membranes (MMMs). By exploiting the interfacial interactions between the polymer matrix and CNC nanofillers, combined with the surface functionalities of CNC nanofillers, the rapid and selective CO_2 transport is facilitated, even at low filler concentrations. This unique feature enables the development of thin-film composites (TFCs) with a selective layer around 1 µm. Notably, even at a filling ratio as low as 1 weight percent, the resulting membranes exhibit remarkable CO_2 permeability (>90 Barrer) and CO_2/N_2 selectivity (>70). These findings highlight the potential of integrating CNCs into rubbery polymers as a promising strategy for the design and fabrication of highly efficient CO_2 capture membranes.

Keywords: cellulose nanocrystals; mixed-matrix membranes; phase separation; polyether block amide; polyurethane

1. Introduction

Anthropogenic climate change is undoubtedly one of the most pressing environmental concerns ever, requiring dramatic worldwide action to reduce carbon dioxide (CO_2) emissions [1]. As a result, there is high demand for the rapid development of easily deployable carbon capture and storage (CCS) technologies for both industrial processes and power generation [2]. Therefore, thanks to their smaller equipment sizes, low operating costs, and high energy efficiencies, membranebased gas separation technology garnered huge attention as a core CCS technology [3]. However, the widespread application of membrane-based CO_2 capture is currently hampered by the lack of affordable yet effective membrane materials. Various materials for developing CO_2 capture membranes have been investigated, including (organic) polymers [4] and inorganics [5] to polymer-inorganic hybrids [6]. Polymeric membranes offer favorable mechanical properties and high processability, but the inherent tradeoff between their permeability and selectivity performances poses a challenge [7]. Inorganic membrane materials with defined pore structures (such as carbon molecular sieves and zeolites), on the other hand, can surpass the tradeoff relation of organic polymers [8, 9]. Yet, cost and processability issues often limit their prospects for industrial-scale applications.

As a practical approach, the combination of organic polymers and inorganic materials, yielding mixed-matrix membranes (MMMs), also offers a path to exceed the permeability–selectivity tradeoff of polymeric membranes [10]. Based on various inorganic fillers, such as silicon dioxide, active carbon, and zeolites, the MMM approach has enabled high-performance CO_2 separations [11]. Nonetheless, the low compatibility of organic polymers and inorganic fillers typically causes nonselective voids at the matrix-filler interfaces, making the inorganicparticle-filled MMMs hard to optimize [12].

While the optimization of fabrication methods [13] or particle functionalizations [14] may enhance the compatibility of inorganic fillers with polymer matrices, adding an additional complexity is undesirable from a manufacturing point of view. To address this challenge, organic–inorganic hybrid fillers, such as metal–organic frameworks (MOFs), [15] have attracted extensive attention. But interestingly, the potential of organic particles as MMM fillers is still largely untapped, except for rather advanced systems, such as supramolecular nanoparticles [16].

Cellulose nanocrystals (CNCs) are renewable nanomaterials mainly obtained through the acid hydrolysis of celluloserich materials [17, 18]. Owing to their several appealing material properties, affordability, and environmental friendliness, CNCs also attracted attention for developing MMMs [19, 20]. Although the CNC-incorporated MMMs are in the early stages of development, encouraging performance results have already been reported. Moreover, with their needly shape (high aspect ratio) and high mechanical strength, CNCs can act as mechanical reinforcing agents in MMMs. Torstensen et al. [21], for instance, reported promising outcomes in their study of polysulfone-supported poly(vinyl alcohol) (PVA)/ CNC membranes designed for CO₂/N₂ separation, achieving a notable CO₂/N₂ selectivity of 39. In another study, the membranes were fabricated by dip coating of PVA solution comprising 0.5-4 wt% CNC on polysulfone membranes. The CO₂/CH₄ selectivity of PVA with 1.5 wt% CNC increased from 6 to 39 as the humidity rose from 30% to 100% with a CO_2 permeance of 0.27 m³(standard temperature and pressure $[STP])/(m^2 \cdot bar \cdot h)$. The enhancement was attributed to the nanocellulose surface charge, which facilitated the permeation of CO₂ [22]. Venturi et al. [23] developed self-standing composite membranes by blending a commercial polyvinylamine solution with up to 70 wt.% nanofibrillated cellulose (NFC), with NFC fillers facilitating the transport of CO₂ molecules within the polymer matrix. The membrane permeability consistently increased with higher humidity levels. Notably, at 70 wt% NFC content, the membrane demonstrated an ideal selectivity of 135 for CO_2/CH_4 and 218 for CO_2/N_2 at 60% relative humidity (RH), reaching a maximum permeability of 187 Barrer at 80% RH [23]. However, the matrix's high swelling and dilation at increased water content caused a significant boost in methane and nitrogen permeability, resulting in reduced CO_2/N_2 and CO_2/CH_4 selectivity under high humidity.

Here, we report on the incorporation of CNC nanofillers into two types of CO_2 -philic rubbery copolymers containing polyethylene oxide (PEO), that is, poly(ether-block-amide) (PEBA) and polyurethane (PU), for developing CO_2 capture MMMs. At a filling ratio as low as 0.5–1 wt.%, we observed both permeability and selectivity enhancement in both PEBA and PU cases for CO_2/N_2 separation. Notably, although we employed CNC fillers without functionalization, interfacial adhesion of CNCs and polymer matrices was good enough to maintain structural integrity. As a result, we achieved improved mechanical and thermal stability in CNC-incorporated MMMs concurrently.

2. Experimental

2.1. Materials. PEBAX MH 1657 (PEBA) was purchased from Arkema in pellet form. Reagent-grade ethanol, o-Tolidine, and Pluronic F-68 (in short, Pluronic) were obtained from Sigma-Aldrich. H₂SO₄ (98%), polyethylene glycol (PEG, $M_w = 20,000 \text{ g/mol}$), isophorone diisocyanate (IPDI), and dibutyltin dilaurate (DBTDL) were supplied by Wako Pure Chemical Industries. All chemicals were used as received without further purification. α -Alumina disks (ceramic supports) with a surface porosity of 100 nm (25 mm diameter) were purchased from Fraunhofer IKTS, Germany. Poly(1-trimethylsilyl-1propyne) (PTMSP) with a purity of 95% and an average molecular weight of 400,000 g/mol was procured from BOC Science, USA.

2.2. Synthesis of CNCs. We prepared CNC suspensions from Whatman No.1 filter paper (98% cotton fiber) as described in a previous report [24]. Briefly, the filter paper was first cut and shredded. Then, the shredded cellulose paper was hydrolyzed with 65% H₂SO₄ at 70°C for 15 min. The obtained slurry was centrifuged and washed repeatedly with distilled water to remove residual acid. After several cycles, the sample is placed in a dialysis tubing (molecular weight cut-off [MWCO]: 12,000 Da) immersed in a 20% solution of PEG in water and dialyzed until the pH reaches around 7. The suspension was diluted with distilled water and bathsonicated for 20 min to increase CNC formation. Lastly, the CNC product was powdered via freeze–drying (-50° C, 2 mbar) overnight, followed by vacuum–drying (24 h, 40°C).

2.3. PU Synthesis. PEO-based PU was synthesized using a two-step bulk polymerization method, as described elsewhere [6]. Briefly, 1.60 g (7.4 mmol) of IPDI was added dropwise to 20 g (2.4 mmol) of Pluronic F-68 under an inert atmosphere at 65°C, followed by the addition of catalyst (0.1 mL of DBTDL). After 2 h of stirring, 1.02 g (4.8 mmol) of o-Tolidine was added, setting the molar ratio of the Pluronic/IPDI/o-Tolidine mixture to 1/3/2. Upon the apparent completion of the polymerization reaction, the PU product was precipitated in water and dried at 80°C under vacuum for 24 h. The number-average molecular weight (M_n) and polydispersity index (PDI) of the product were found to be 81,000 g/mol and 1.6 based on gel permeation chromatography (GPC, Shimadzu 800-series).

2.4. Membrane Preparation. PEBA and PU were dissolved in 70/30 v/v% ethanol/water solution (4 wt%) with the help of bar stirring (6 h, room temperature) and were filtered before use (syringe filter, polytetrafluoroethylene, 1.0 μ m). To maintain the solvent composition, the CNC powder was also dispersed in 70/30 v/v% ethanol/water mixture using sonication and stirring. A series of PEBA- and PU-based MMMs were prepared, varying the CNC filling ratio, that is, 0.2, 0.5, 0.7,

and 1 wt%. CNCs were first primed with respective polymers to suppress interfacial defects by stirring (12 h) and bath sonication. All membranes were cast on nonsticky Petri dishes (made of perfluoroalkoxy alkane) using 0.2 g of polymer with/ without CNCs. As-cast membranes were first predried at 40°C in an oven for 12 h and then subjected to vacuum drying at 75°C for 12 h. The final thickness of the membranes was derived by averaging measurements taken from multiple areas, yielding an approximate thickness of 70 μ m.

To prepare thin-film composites (TFCs), 2 wt.% PEBA and PU solutions containing 1 wt.% CNC nanofillers were spin-coated at 1000 rpm on a PTMSP-coated ceramic porous support. PTMSP gutter layers were made by spin-coating ceramic supports with 2 wt.% PTMSP in cyclohexane. The thickness of the TFC selective layer was ~1 µm as measured by FESEM.

2.5. Nanocellulose and Membranes Characterization. The membranes were characterized by Fourier transform infrared (FTIR) spectroscopy using attenuated total reflectance (ATR) technique (ATR-FTIR, Shimadzu IR Tracer-100) in the range of $4000-600 \text{ cm}^{-1}$ with a resolution of 2 cm⁻¹ accumulating 64 scans per measurement. The crystalline structure of CNC fillers and membranes was investigated by wide-angle X-ray diffraction (WAXD, Rigaku RINT XRD) in the range of $5^{\circ}-40^{\circ}$ with a rotating anode Cu-K_a X-ray generator operated at 200 mA and 45 keV. Differential scanning calorimetry (DSC, 60 Plus, Shimadzu, Japan) was performed under a 10°C/min heating rate over a temperature range of -100 to 250°C. Thermogravimetric analysis (TGA, Rigaku Thermo Plus EVO2, Japan) was performed under a nitrogen atmosphere at a heating rate of 10°C/min over a temperature range of 25-800°C to evaluate the thermal stability of the membranes. The morphology of CNC fillers and membranes was investigated by field-emission scanning electron microscopy (FESEM, JEOL) and tapping-mode atomic force microscopy (AFM, NanoWizard III, JPK Instruments). For FESEM analysis, CNC dispersed in water/ethanol solution was spin-coated on a silicon wafer and dried at 40°C in a vacuum oven, and the membranes were freeze-fractured in liquid nitrogen and sputtered with osmium to prevent charging. Young's modulus (E) and indentation hardness (H) of the prepared films were investigated using a nanoindentation instrument (ENT-2100, Elionix) equipped with a Berkovich diamond tip (radius of 100 nm) at a load of 0.2 mN. Each indent was made up to a maximum depth of ~5 µm. Twelve points in a rectangular configuration were tested on each sample; the average data were calculated by averaging data collected on three samples. The degree of crystallinity (Xc) for the PEO and polyamide 6 (PA-6) phases in PEBA and PEBA MMMs was determined from the area under the endothermic peaks in the DSC thermograms, as follows:

$$Xc = \frac{\Delta H_m}{\Delta H_0} \times 100, \tag{1}$$

where ΔH_m (J·g⁻¹) represents the melting enthalpy of each crystalline phase, and ΔH_0 (J·g⁻¹) denotes the melting

enthalpy of pure crystalline PEO or PA-6, which are 166.4 J·g⁻¹ and 230 J·g⁻¹, respectively. The overall crystallinity of the membranes was calculated by taking into account the PEO/PA weight ratio (60/40 wt%) in the PEBA structure.

2.6. Gas Permeation Measurements. The pure gas permeabilities of the membranes were measured using the variable pressure-constant volume method at 4 bar and 25°C. Gas permeability data for N_2 and CO_2 were recorded separately. The gas permeability (*P*) is calculated based on the following equation:

$$P_i = 10^{10} \frac{273.15}{76} \frac{V}{A \cdot T} \left(\frac{dp}{dt}\right) \frac{l}{\Delta p},\tag{2}$$

where P_i is the permeability of the gas "*i*" through membrane in Barrer (1 Barrer = 10^{-10} cm³ [STP]·cm·cm⁻²·s⁻¹·cm-Hg⁻¹), *V* is the permeate volume (cm³), *A* is the membrane area (cm²), *T* is the operating temperature (K), (*dp/dt*) is the steadystate slope of the pressure increase in the permeate volume (cm-Hg·s⁻¹), *l* is the membrane thickness (cm), and Δp is the pressure difference across the membrane (cm-Hg). The ideal selectivity (α_{ij}) of gas pairs, "*i*" and "*j*," is defined as follows:

$$\alpha_{ij} = \frac{P_i}{P_j}.$$
(3)

The diffusion coefficient (*D*) for each gas was derived by following Equation (4), using the membrane thickness and time lag (θ):

$$D = \frac{l^2}{6\theta},\tag{4}$$

where θ is determined by extrapolating the linear portion of the permeation curve (the steady-state region) back to the time axis (*x*-axis). The point where this extrapolated line intersects the time axis is defined as the time lag.

The solubility coefficients (*S*) were calculated according to Equation (5).

$$S = \frac{P}{D}.$$
 (5)

The constant pressure-variable volume method was utilized to measure the mixed-gas permeation. The membrane was exposed to a CO_2/N_2 (50/50 vol.%, Kyoto Teisan, Japan) mixed gas at room temperature (25°C) with feed pressure at 4 bar. The volumetric flow rate of the feed gas was maintained at 100 mL·min⁻¹ using a digital mass flow controller (Horiba). Helium was employed as a sweep gas at a 50 mL·min⁻¹ flow rate. The permeability and compositions of the gas mixtures that passed through the membrane were determined using an in-line gas chromatograph (GC) (Shimadzu, model 2014) equipped with a thermal conductivity detector (TCD). The GC was fitted with a packed column suitable for separating CO_2 ,



FIGURE 1: Morphology of CNC particles. (a) and (b) Surface SEM images at different magnifications. (c) and (d) Histograms of the length and width of CNC particles, respectively. CNC, cellulose nanocrystal; SEM, scanning electron microscopy.

N₂, and He, with column temperature set to 50°C to optimize separation efficiency. The TCD was operated at 140°C. Calibration was performed using standard gas mixtures to ensure accurate quantification of gas compositions.

The permeance of gas species "i" through the membrane, P_i (Barrer, 1 Barrer = 1×10^{-6} cm³ [STP] cm⁻² s⁻¹ cm-Hg ⁻¹), is calculated by measuring the permeate flow rate (Q_P) and gas compositions using GC according to the formula:

$$P_i = \frac{Q_p x_{p,i}}{A \cdot (p_f x_{f,i} - p_p x_{p,i})}$$

where $x_{p,i}$ represents the volume fraction of component "i" in the permeate gas, $x_{f,i}$ represents the volume fraction of species "i" in the feed gas, A denotes the effective membrane area (cm²), P_f denotes the feed pressure (cm-Hg), and p_p represents the permeate pressure (cm-Hg).

3. Results and Discussion

3.1. CNC Fillers Charge, Microstructure, and Size Distribution. CNC suspensions in water/ethanol solution were stable, with zeta potentials nearing 38 mV. Figure 1 depicts scanning electron microscopy (SEM) images of the CNC particles, along with histograms displaying their size distribution. The CNC synthesized had an average length of 201.9 ± 12.6 nm and a width of 16.5 ± 6.8 nm, resulting in an aspect ratio of 12.2 ± 2.5 .

3.2. Physicochemical Analysis of CNC, PEBA, and MMMs. FTIR was utilized to examine the impact of including CNC nanofillers on the chemical structure of PEBA and PU nanocomposites, as well as to explore potential interactions between the CNC nanofillers and the polymer matrix (Figure 2a and Figure S1). The presence of hydroxyl groups and other charged entities in CNC fillers can potentially enhance the dispersion and promote physical interactions between CNC nanofillers and polymer matrices. Specifically, the surfaces of CNC particles may establish hydrogen bonds through N–H and C=Ogroups, facilitating interactions with rubbery polymers like PU and PEBA chains [25].

The CNC spectrum displays peaks at 3345, 1435, 1315, and 1060 cm⁻¹, representing characteristic cellulose absorption peaks. These peaks correspond to O–H stretching, CH₂ bending, CH₂ rocking, and C–O stretching, respectively [26]. The pristine PU and PEBA film exhibits distinct peaks at



FIGURE 2: FTIR and XRD analyses of nanofillers and membranes. (a) FTIR spectra and (b) XRD patterns of CNC nanofillers, neat PEBA, and CNC-based MMMs. CNC, cellulose nanocrystal; FTIR, Fourier transform infrared; MMM, mixed-matrix membrane; PEBA, poly(etherblock-amide); XRD, X-ray diffraction.

1550, 1637, 1725, and 3300 cm⁻¹, which correspond to specific vibrational modes, including N–H bending, C=O stretching (HNC=O and O–C=O), and N–H stretching vibrations, respectively [16]. Also, The absence of the NCO peak in FTIR spectra (at 2250 cm⁻¹) confirmed the completion of PU synthesis (Figure S1).

The FTIR spectra of the PU, PEBA, and CNC-based MMMs demonstrate a high degree of similarity, with no notable differences observed at low CNC concentrations (e.g., 0.5 wt.%). Conversely, when the CNC concentration was increased to 1 wt.%, notable shifts in the spectral characteristics were observed, primarily resulting from the interactions between polymer chains and CNC nanofillers. Specifically, the N–H stretching band became sharper and slightly shifted towards a lower wavenumber of 3270 cm^{-1} . This change can be attributed to the disruption of interchain interactions within the hard domains of PEBA and PU and the formation of new hydrogen-bonding interactions contribute to the observed spectral shifts in the high CNC concentration samples.

Figure 2b displays the X-ray diffraction (XRD) spectra of CNCs, pure PEBA, and PEBA/CNC nanocomposites. The 2θ angle at 22.9° corresponds to the 200 reflections of cellulose I [25]. In the PEBA/0.5 wt.% CNC sample, at a low CNC content, no distinct peaks of cellulose I were observed. However, as the CNC loading increased, a peak centered at $2\theta = 22.9^{\circ}$ gradually emerged in the XRD pattern of the PEBA/1 wt.% CNC sample. This suggests that the original crystal structure of the CNC nanofillers remained unchanged, indicating the integrity of the CNC structure after being mixed with the PEBA matrix. The addition of CNC into the PEBA matrix resulted in a decrease in the intensity of the reflection peak observed at 20.1° and 24.5°. This decrease indicates a reduction in the crystallinity and packing of the polymer phase in the MMMs compared to the neat PEBA membrane.

3.3. Thermal and Mechanical Analyses of CNC Fillers and MMMs. Incorporating CNC nanofillers into rubbery block copolymers like PEBA and PU can induce changes in their

phase behavior and physiochemical properties (Table S1), which consequently affects the gas transport properties. To investigate this, we analyzed the impact of CNC nanofillers on the thermal properties of PEBA nanocomposite membranes (Figure 3a). The DSC thermogram of pure PEBA revealed typical melting transitions of PEO and PA-6 crystalline phases at ~15 and ~205°C, respectively, along with a low glass transition temperature (T_g) of PEO soft domains at -53°C. As CNC nanofillers were added to the PEBA matrix, increasing the filler loading led to a broadening and reduction in the intensity of the melting peak of PA-6 crystalline domains compared to neat PEBA. This resulted in a decrease in the overall crystallinity of the polymer matrix (Table 1). The strong affinity of the fillers for the PA-6 domains, as discussed in the FTIR section, and their interference with the crystalline regions led to a gradual decrease in the melting temperature of the PA-6 regions with increasing filler concentrations. At a CNC content of 1 wt.%, the melting temperature of the PA-6 regions decreased to 195°C due to the perturbation of hydrogen bonding within the PEBA hard segments caused by the presence of CNC nanofillers.

Thermal stability analysis was conducted using TGA measurements to assess the properties of CNC-based nanocomposite membranes obtained in this study (Figure 3b and Figure S2). CNC alone demonstrated low thermal stability with a noticeable weight loss occurring at ~250°C. However, when CNC was incorporated into PU and PEBA, the TGA curves of the CNC-based nanocomposites exhibited a shift towards higher temperatures, indicating an improvement in thermal stability compared to pure polymer matrices. This enhancement can be attributed to the interfacial interaction between the nanofiller and the polymer matrix. The interaction between the polymer and the filler resulted in a shift in the peak toward higher temperatures for CNC MMMs, indicating a higher level of thermal stability.

Figure 4 displays the results of nanoindentation-based mechanical analyses conducted on neat PEBA membranes and representative CNC-based MMMs. It is evident that even the addition of small amounts of CNC fillers, such as



FIGURE 3: Thermal analyses of nanofillers and membranes. (a) DSC and (b) TGA thermograms of CNC nanofillers, neat PEBA, and CNCbased MMMs. CNC, cellulose nanocrystal; DSC, differential scanning calorimetry; MMMs, mixed-matrix membranes; PEBA, poly(etherblock-amide); TGA, thermogravimetric analysis.

TABLE 1: The crystallinity of neat PEBA and PEBA/CNC MMMs.

M h	$\Delta H_{\rm m} (\mathbf{J} \cdot \mathbf{g}^{-1})$		X _c (%)		
Memoranes	PEO	PA-6	PEO	PA-6	Total
PEBA	20.6	25.4	12.4	11.0	11.6
0.5 wt% CNC	20.3	19.1	12.2	8.3	9.9
1 wt% CNC	19.8	17.8	11.9	7.7	9.4

Abbreviations: CNC, cellulose nanocrystal; MMMs, mixed-matrix membranes; PA-6, polyamide 6; PEBA, poly(ether-block-amide); PEO, polyethylene oxide..



FIGURE 4: Nanoindentation-based mechanical testing of PEBA and CNC-based membranes with respect to the CNC loading. Error bars represent the standard deviation of 12 indents. CNC, cellulose nanocrystal; PEBA, poly(ether-block-amide).

0.5 wt.%, to the PEBA matrix, enhances both Young's modulus and hardness of the membranes. As the filler content increases further, reaching 1 wt.%, Young's modulus and hardness of the membranes continue to improve, reaching ~110% of their initial values, respectively. These improved mechanical properties in the CNC-based membranes can be attributed to the robust hydrogen-bonding interactions at the interfaces between the polymer and filler, as well as the increased rigidity of the PEBA chains.

3.4. Morphological Analysis of the Membranes. FESEM analysis was conducted to examine the dispersion characteristics of CNC within the PEBA matrix and assess their impact on the morphological alterations of the polymer matrix. The obtained cross-sectional SEM images of pristine PEBA and CNC-based MMMs are depicted in Figure 5. The cross-section of the unmodified PEBA matrix displayed a compact and smooth structure devoid of any observable defects (Figure 5a,d). In contrast, the cross-sectional views of the MMMs exhibited discernible fibrillar CNC particles (Figure 5b–f). The presence of CNC fillers became more evident as the CNC loading concentration increased in the cross-sectional analyses.

Notably, even at a CNC loading of 1 wt.%, no noticeable defects were observed at the polymer-filler interface, resulting in the formation of optically transparent films. These findings demonstrate the excellent compatibility between the CNC particles and the PEBA matrix, which is a prerequisite for the fabrication of highly efficient gas separation membranes that are devoid of nonselective voids.

The microphase-separated morphology resulting from the random distribution of soft (PEO) and hard (PA-6) domains within the PEBA structure was observed through

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FIGURE 5: FESEM cross-section images of PEBA and CNC-based membranes at different CNC loadings. (a, d) Neat PEBA. (b, e) 0.5 wt.% CNC. (c, f) 1 wt.\% CNC. The scale bars in panels (a)–(c) represent a length of 10 µm, whereas the scale bars in panels (d)–(f) indicate a length of 100 nm. CNC, cellulose nanocrystal; FESEM, field-emission scanning electron microscopy; PEBA, poly(ether-block-amide).



FIGURE 6: AFM phase images of (a) neat PEBA and (b) MMM with 1 wt% CNC loadings. AFM, atomic force microscopy; CNC, cellulose nanocrystal; MMM, mixed-matrix membrane; PEBA, poly(ether-block-amide).

AFM. Color profiles of phase images provided a visual distinction between the hard and soft domains, with darker and lighter hues corresponding to the hard and soft regions, respectively (Figure 6) [27].

The introduction of CNC into the PEBA matrix resulted in the formation of nanometric aggregates on the membrane surface, leading to a reduction in the size of both the soft and hard domains (Figure 6a,b). The presence of CNC fillers disrupted the crystalline domains of the PEBA matrix, as evidenced by DSC analyses. This disruption increased the mobility of the polymer chains and promoted a greater degree of microphase mixing. This observation is supported by the reduction in the size of soft domains observed in the AFM images.



FIGURE 7: CO_2 permeability and CO_2/N_2 ideal selectivity of (a) neat PEBA membrane and CNC-containing MMMs, (b) neat PU membrane and CNC-containing MMMs at different filler loadings. CNC, cellulose nanocrystal; MMM, mixed-matrix membrane; PEBA, poly(etherblock-amide); PU, polyurethane.

3.5. Gas Transport Properties. At a temperature of 25° C and under a pressure of 4 bar, gas transport experiments were conducted to examine how the inclusion of CNC nanofillers affects the separation performance of the membranes. Figure 7 illustrates the CO₂ permeability and the ideal CO₂/N₂ selectivity of MMMs containing PEBA or PU matrices with varying amounts of CNC. The pristine PEBA membrane demonstrated a CO₂ permeability of ~71 Barrer and an ideal CO₂/N₂ selectivity of ~51 (Figure 7a). These values align with previous findings for pure PEBA membranes [6, 16]. As shown in Figure 7b, the PU matrix exhibited a CO₂ permeability of roughly 62 Barrer and an ideal CO₂/N₂ selectivity of ~43.

With the incorporation of CNC nanofillers, the CO₂ permeability and CO₂/N₂ selectivity of the MMMs showed gradual enhancement. For instance, in PEBA MMMs with 1 wt.% filler, the CO₂ permeability, and ideal CO₂/N₂ selectivity improved to 92 Barrer and 73.6, respectively. Similarly, in PU membranes with 1 wt.% CNC loading, the CO₂ permeability and ideal CO₂/N₂ selectivity reached 78 Barrer and 62.4. Conversely, at higher CNC loadings, specifically 2 wt.%, the CO₂ permeability and ideal CO₂/N₂ selectivity decreased.

Adding impermeable fillers to rubbery polymer matrices typically reduces gas permeability due to the restriction in the diffusion of gas molecules by adding tortuous pathways in the polymer matrix. However, this pattern is not always observed in particle-filled heterogeneous rubbery matrices consisting of hard and soft segments, such as PEBA and PU. In these cases, the presence of functional fillers can disturb the arrangement of polymer chains in the hard segment, leading to an overall increase in the free volume within the polymer phase [28].

The inclusion of CNC filler caused a noticeable alteration in the crystalline structure of the hard segment of the polymer matrix, as observed in DSC thermograms of PEBAbased membranes (Table 1). The presence of CNC could disrupt the alignment of urethane and polyamide hard segments within the PU and PEBA structures. This disruption could enhance the mobility of the soft and hard domains, creating additional gas transport pathways with improved gas diffusivity and permeability (Figures S2 and S3). Furthermore, the addition of CNC fillers improves the adsorption of condensable CO_2 gas onto the particle surface, especially at the interface between the polymer and particles. This heightened adsorption capability results in a higher solubility of CO_2 than N_2 molecules, ultimately enhancing the CO_2/N_2 selectivity (Tables S2 and S3). However, the further addition of CNC had a detrimental impact on the gas properties due to the aggregation of CNC particles. Specifically, samples containing 2 wt.% of CNC lost their transparency and exhibited an aggregated structure, as observed in the AFM image (Figure S3). The agglomerated particles formed compact structures that impeded gas transport.

Gas separation membranes are typically made from TFCs, where a thin selective layer forms on the surface of porous backings. The sub-micron thickness of the selective layer in TFCs makes them particularly susceptible to filler aggregation and nanoscale voids. With its high aspect ratio, nanometric dispersion, and significant influence on enhancing gas transport in MMMs at low loadings, CNC is a suitable choice for developing TFCs. To investigate the possibility of using CNC fillers for making TFC membranes, the optimal concentration of CNC determined from self-standing membranes, that is, 1 wt.%, was used to develop TFC membranes on the surface of porous ceramic support (Figure 8).

The membranes were further tested with binary CO_2/N_2 (50/50 vol.%) mixed gas feed at 25°C and 4 bar. The separation performance of the TFCs is presented in Table 2. The observed CO₂ permeance values for TFCs exhibited a similar pattern to the CO₂ permeability values obtained for thicker membranes, wherein the CO₂ permeance was higher in CNC-filled MMMs compared to unmodified rubbery polymer matrices.

Overall, the incorporation of CNC fillers in the developed TFC membranes resulted in a noteworthy enhancement in CO_2/N_2 selectivity. However, it is important to note that the CO_2/N_2 selectivity measured in mixed-gas conditions was slightly lower than in single-gas measurements. This can be attributed to the competitive sorption of gas molecules and the thinner structure of the TFCs. For



FIGURE 8: FESEM cross-section images of (a) PEBA and (b) PU-based CNC TFCs with 1 wt.% CNC loading. CNC, cellulose nanocrystal; FESEM, field-emission scanning electron microscopy; PEBA, poly(ether-block-amide); PU, polyurethane PU; TFCs, thin-film composites.

TABLE 2: CO_2 permeance and CO_2/N_2 selectivity of PEBA, PU, and CNC-based MMMs.

Membrane	$P_{\rm CO_2}^{a}$	$\alpha_{\rm CO_2/N_2}^{b}$	
PEBA	58.2 ± 41	41.5 ± 3.8	
PU	42.5 ± 31	35.2 ± 3.2	
1 wt% CNC-PEBA	71.0 ± 52	53.2 ± 5.4	
1 wt% CNC-PU	62.3 ± 45	48.1 ± 4.4	

Abbreviations: CNC, cellulose nanocrystal; PEBA, poly(ether-block-amide); PU, polyurethane PU.

^aPermeance (GPU): $\times 10^{-6}$ (cm³[STP]·cm⁻²·s⁻¹. cm-Hg⁻¹). ^bSelectivity.

example, the CO_2/N_2 selectivity of PEBA and PU membranes decreased by almost 18% and 17%, respectively (Figure 7a). Also, the CO_2/N_2 selectivity of PEBA and PU MMMs with 1 wt.% CNC nanofillers decreased by ~14% and ~16%, respectively (Figure 7b). It is important to note that the measured permeance values are significantly lower than the nominal gas permeation unit (GPU) values derived from permeability numbers based on the membrane thickness observed in cross-section SEM images. This is due to the resistances added to the TFCs by incorporating ceramic supports and the PTMSP gutter layer.

To assess the CO_2/N_2 separation efficiency of CNCbased MMMs, the CO_2 separation performance of the developed membranes was compared to Robeson's upper bound (2008) and representative MMMs utilizing PEBA, as documented in previous studies (Figure 9). By introducing CNC nanofillers into the rubbery matrices of PEBA and PU, the membranes experienced substantial performance improvements in CO_2 separation. This advancement in membrane performance significantly narrows the gap between the achieved results and the upper bound, underscoring the promising potential of CNC fillers in the development of exceptionally efficient CO_2 capture membranes.



FIGURE 9: The comparison of CO₂ separation performance of CNCbased MMMs to Robeson's upper bound (2008), representative membranes with 1 wt.% CNC loading and PU or PEBA matrices are denoted by red and green triangles. The circles represent the state-of-the-art PEBA-based MMMs reported in the literature; silica, [29] GO, [30] IL-GO, [30] MWNTs-NH₂, [31] MoS₂, [32], MXene, [33] ZIF-7, [34] ZIF-8, [35] UiO-66-NH₂, [36] COF-5, [37] PEG-Microcapsules, [38] zeolite-NaX, [39] and fumed silica [40]. CNC, cellulose nanocrystal; MMM, mixed-matrix membrane; PEBA, poly(ether-block-amide); PU, polyurethane.

4. Conclusions

In summary, this study presents the design of a highperformance nanocomposite membrane for CO_2 separation by incorporating CNC nanofillers into PEO-based polymer matrices. The results demonstrate that even at low loading of CNC nanofillers (i.e., 1 wt.%), the CO_2 separation performance of these polymers can be significantly enhanced. Through varying the amount of CNC nanofillers, we were able to optimize the CO_2 separation performance of the MMMs. The CNC-filled membranes exhibited outstanding CO_2/N_2 selectivity, reaching values of up to 70, and remarkable CO_2 permeability, reaching up to 90.

Furthermore, our results indicate that the low concentration of CNC fillers at ~1 wt.% improved the thermal and mechanical properties of the membranes. The phase imaging study of the membranes revealed that the microphase separation of the polymer matrix, facilitated by hydrogen-bonding interactions between the CNC nanofillers and polymer chains, played a key role in these improvements.

Additionally, the low aspect ratio of the CNC fillers, coupled with their efficiency at low loading, enabled the development of defect-free TFC membranes with a micron-sized selective layer. The TFC membranes achieved a CO_2 permeance of ~580 GPU and a CO_2/N_2 selectivity of ~41. These advancements contribute to the development of highly efficient membranes for CO_2 capture, holding promise for future sustainable separation processes.

Data Availability Statement

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflicts of interest.

Author Contributions

The research idea was conceived by S.N. and B.G. The study was designed by S.N., B.G., and E.S. with the feedback of H.E.K. S.N. conducted most of the experimental work and prepared the initial draft of the manuscript. B.G. and H.E.K. performed manuscript review and editing. Data analysis was supported by H.E.K., A.P.I., D.Q., and M.M.I. Supervision was provided by B.G. and E.S. All authors contributed to the discussion of results and refinement of the manuscript.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. (*Supporting Information*) Figure S1. FTIR analyses of PU and PU-CNC MMMs. Figure S2. TGA thermograms of neat PU and CNC-based MMMs. Figure S3. AFM phase images of PEBA-based MMM with 2 wt% CNC loading. Table S1. Physiochemical properties of PEBA and PU in this study. Table S2. CO₂ and N₂ diffusivity and solubility coefficients of PEBA and PEBA/CNC MMMs. Table S3. CO₂ and N₂ diffusivity and solubility coefficients of PU and PU/CNC MMMs.

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