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Research article

# Investigations on the effect of halloysite nanotubes loading on the physicochemical properties of cellulose acetate/polysulfone asymmetric membrane

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**Abstract.** Membrane-based gas separation offers practical advantages for hydrogen (H<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) separation for steam methane reforming units. Modification of membrane materials can optimize membrane performance. In this study, the central focus is on investigating the effect of different loadings of halloysite nanotubes (HNTs) (0, 0.5, 1.0, 1.5, and 2.0 wt%) incorporated into a blend of cellulose acetate (CA) and polysulfone (PSF) polymers with the aim of improving the membrane properties. The Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) results confirmed that the primary functional groups of PSF and CA remained intact upon HNTs incorporation, with no distinct HNT peaks altering the main chemical functionalities. Field emission scanning electron microscopy- energy dispersive X-ray spectroscopy (FESEM-EDX) analyses showed that low concentrations of HNTs (0.5 wt%) improved surface smoothness and reduced macrovoids, beneficial for gas separation. Cross-sectional images of FESEM micrographs showed no evidence of obvious agglomeration, suggesting a good dispersion of HNTs. From the X-ray diffraction (XRD) analysis, all the membrane samples retained an amorphous structure, indicating that the incorporation of HNT has less effect on the polymer chain properties of the membranes.

Keywords: membrane, nanocomposite, halloysite, clay, nanoparticle

## 1. Introduction

The demand for energy around the world is rising as people's daily routines are governed by energy-driven appliances. Increased demand for energy can be attributed to rapid automation, improved living standards, and rising worldwide per capita consumption. To this day, fossil fuels continue to play a significant role (80%) in meeting the world's energy needs. However, there is a pressing need to explore cleaner energy alternatives due to environmental concerns, including pollution, global warming, and fossil fuel sustainability challenges. Numerous alternative fuels are proposed to address environmental and energy

\*Corresponding author, e-mail: <u>maizura@ums.edu.my</u> © BME-PT supply challenges, with hydrogen  $(H_2)$  offering the greatest potential in these areas [1].

 $H_2$  can be used in various applications, including as a fuel for internal combustion engines and in fuel cells to provide electricity.  $H_2$  appeals lie in its ecofriendly characteristics and versatility, as it emits no harmful greenhouse gases when used to produce energy, and its combustion produces a significant amount of energy while emitting only water as a byproduct. However, when producing hydrogen as an alternative fuel, carbon dioxide can be involved in the process through various methods. The most common method for producing hydrogen is natural

gas reforming, where natural gas is reacted with high-temperature steam to produce a mixture of hydrogen, carbon monoxide, and a small amount of carbon dioxide. One example is the widely employed industrial method known as steam methane reforming (SMR), which is predominantly utilized for generating hydrogen using methane as its main raw material, commonly sourced from natural gas. SMR accounts for over 95% of global hydrogen production [2]. The process begins with methane undergoing a reaction with steam in the presence of a catalyst at elevated temperatures to generate both hydrogen and carbon monoxide. The carbon monoxide is then subjected to the water-gas shift reaction to enhance the hydrogen output and decrease the carbon monoxide content. Despite the water-gas shift reaction diminishing the carbon monoxide content, it concurrently produces carbon dioxide (CO<sub>2</sub>) as a resultant byproduct. Therefore, while the primary aim of steam methane reforming is hydrogen production, the process inevitably generates CO<sub>2</sub> as a co-product. The coexist characteristics and with hydrogen can impact fuel quality in several ways, which include affecting the calorific value, combustion characteristics and contributing to corrosion in storage and transportation systems. Even small amounts of CO<sub>2</sub> can significantly affect performance, for instance, its effects on lowering the heating value of fuel. This makes an effective separation of CO<sub>2</sub> crucial to maintain high-quality hydrogen for application [3]. Plus, the presence of  $CO_2$  can contribute to indirect warming by increasing the amounts of other greenhouse gases. Hence, the need for effective separation techniques becomes more evident.

Numerous advanced methods are available to separate hydrogen and carbon dioxide. Some of the conventional methods used to separate hydrogen are pressure swing adsorption (PSA), amine absorption, low-temperature separation (cryogenic separation), metal hydride (MH) method, and palladium membrane absorption [4]. However, the drawbacks of these conventional methods include high energy consumption, high costs, environmental impact, complexity, limited efficiency, and challenges in scaling up to industrial applications [5]. Membranes, by definition, are thin and selective barriers that separate fluids based on specific properties. More than 180 years ago, John Mitchell investigated mixtures of hydrogen and carbon dioxide using polymeric membranes. Mitchell observed that different gases could pass through rubber membranes, and the rate of flow was distinct for each gas. Since then, the development in this field has continued over the following decades [6]. Gas separation membranes function through selective permeation across their surfaces, with the permeation rate of each gas determined by its solubility and diffusion rate within the membrane. Polymeric membranes are gaining popularity in industrial gas separation applications due to their cost-effectiveness, strong selectivity, and ease of processing [7]. Their gas separation capabilities have been recognized for over a century.

Cellulose acetate (CA) has been explored for various membrane applications, including hydrogen gas separation. The use of CA as a membrane material is attributed to its abundance, cost-effectiveness, hydrophilic nature, mechanical and thermal properties, renewability, and biocompatibility [8]. However, the performance of cellulose acetate in terms of gas separation needs further improvement to enhance its suitability for specific applications. Another material widely used in membrane fabrication is polysulfone (PSF). PSF, a thermoplastic polymer, has been extensively studied for gas separation processes owing to its good chemical stability, permeability, selectivity, and mechanical strength [9]. It can be further modified, for example, by blending it with other materials or incorporating mixed-matrix membranes (MMMs) to enhance its gas separation properties. In addition to that, halloysite nanotubes (HNTs) are attracting attention for gas separation due to their tubular structure, high aspect ratio, and advantageous physical and chemical properties [10]. HNTs are naturally occurring aluminosilicate nanotubes with a hollow tubular structure and high aspect ratio. They have been studied for various applications, including gas separation, due to their unique properties [11]. The use of HNTs in membrane technologies holds promise for enhancing the efficiency and selectivity of gas separation processes. Several studies have proven that the incorporation of HNTs into membranes improves the permeability and selectivity of gas separation [12– 14]. The improvement in the gas separation was due to the sieving effects and tortuous path created by the dispersed nanoparticles, which makes it difficult for the unwanted gas to pass through. Besides, the incorporation of the HNTs could change the polymer chain packing, consequently increasing the diffusivity of the gas.

Hence, this work aims to focus on investigating the membrane's functional group, crystal structure, and morphology based on different weight percentages of halloysite nanotubes in conjunction with blended polymers, CA and PSF.

### 2. Methodology

### 2.1. Materials

The polymers employed in this study include PSF (25135-51-7) – weight average molecular weight  $(M_w) \sim 35\,000$  by light scattering (LS), number average molecular weight  $(M_n) \sim 16000$  by membrane osmometry (MO), obtained as transparent pellets and CA (9004-35-7),  $M_{\rm n} \sim 30\,000$  by gel permeation chromatography (GPC), in powder form, were both supplied by Sigma Aldrich Co. from Saint Louis, USA. The filler, HNTs (1332-58-7), was also procured from the same supplier. Meanwhile methanol for analysis EMSURE® ACS, ISO, Reag. Ph Eurmethanol (67-56-1) was obtained from Millipore Sigma-Aldrich Ireland Limited, Ireland, UK, to eliminate any residual solvent from the membrane. N-methyl-2-pyrrolidone (NMP) (872-50-4) with a purity of 99.5% served as the solvent and was also procured from Sigma Aldrich Co. from Saint Louis, USA.

#### 2.2. Membrane synthesis

The membrane preparation protocol in this work was adapted from the literature [15, 16]. The measured PSF was dried in an oven at 40 °C for 24 h to eliminate any moisture content. PSF and CA were dissolved in NMP, the solvent, with a ratio of 25:75 (PSF/CA:NMP). The mixture was stirred at a constant speed of 215 revolutions per minute [rpm] using the motor stirrer for 24 h to ensure complete dissolution. The bottle cap needs to be sealed to prevent any evaporation during the overnight period. Upon the completion of the mixing, the mixture was ready to be placed into the ultrasonicator (40 kHz, WITEG WUC-A02H, Germany) to remove air bubbles for 1 h. Then, a small amount of the dope solution was placed onto a glass plate, and the solution was spread evenly. The thin film was immersed in a water bath and soaked in methanol for 4 h to remove any remaining solvent. Lastly, the membrane was dried for 3 days. The same protocol was used to prepare the mixed matrix membrane, but as a first step before dissolving PSF and CA, the filler, in this case, HNTs, was mixed with NMP to avoid agglomeration. Then, PSF and CA were added to the solution mixture. The mixture was stirred to obtain a homogeneous solution [15]. Similar phase inversion and drying processes were employed for the solution. Materials were produced with different HNT content (0.5; 1.0; 1.5 and 2.0 wt%). The materials are marked as follows: PSF/CA/XHNT, where X is the HNT content in wt%.

#### 2.3. Membrane characterization

# **2.3.1.** Fourier transform infrared spectroscopyattenuated total reflectance (FTIR-ATR)

The Fourier transform infrared-2D instrument, specifically, the PerkinElmer Frontier (PerkinElmer Inc., Waltham, USA), was utilized to analyze the chemical composition and molecular interactions between polymers, which can impact gas separation. The frequency range employed is between 4000 and 400 cm<sup>-1</sup> resolution, with a total of 4 scans. The samples were finely crushed before being placed onto a scanning plate. Subsequently, absorbance spectra were generated and displayed on a computer screen.

# 2.3.2. Field emission scanning electron microscopy-energy dispersive X-ray spectroscopy (FESEM-EDX)

The membrane's surface and cross-section morphologies and elemental analysis were studied by using the Field emission scanning electron microscope-energy dispersive X-ray spectroscopy (FESEM-EDX) with Jeol JSM-7900F (JEOL Ltd., Tokyo, Japan Japan). The samples were sliced into small membrane pieces measuring  $5 \times 5$  mm using a microtome knife prior to the analysis. These samples were then mounted onto the sample stubs and coated with platinum using a sputter-coater for 60 s at a current of 40 mA.

### 2.3.3. X-ray diffraction (XRD)

This analysis was utilized to investigate the impact of different loadings of HNTs in the membrane. The X-ray diffractometer (XRD) from Rigaku Smartlab (Tokyo, Japan) was used to obtain the XRD patterns to describe the changes in the phase structure for neat and mixed matrix membranes because of the incorporation of HNTs.

#### 3. Results and discussions

# 3.1. Determination of functional group by using FTIR-ATR

Figure 1 presents the FTIR spectra of PSF/CA, PSF/CA/0.5HNT, PSF/CA/1.0HNT, PSF/CA/1.5HNT, and PSF/CA/2.0HNT membranes. Firstly, the presence of CA is determined by the strain vibrations of functional groups. These include the carbonyl (C=O) group, the ester linkage (C–O) of the acetyl group, the carbon-hydrogen (C–H) bonds, and the aryl ether linkages [17].

In Figure 1, the functional group of C=O is shown at the wavenumber range of around 1740 to 1748 cm<sup>-1</sup>, while C–O is depicted around 1041.4 to 1074.5 cm<sup>-1</sup>, and aryl ether is depicted in the range of 1234 to 1236 cm<sup>-1</sup>. The –CH<sub>3</sub> group asymmetric stretching is shown around the range of 2965 to 2968 cm<sup>-1</sup>. This range agrees with the research of Douna *et al.* [19], which also confirmed the presence of C–O, –CH<sub>3</sub>, and C=O at wavenumbers of 1251, 2942, and 1736 cm<sup>-1</sup>, respectively. Additionally, the aryl ether range is confirmed by the research [17], where the typical range for aryl ether of cellulose acetate is from 1329 to 1210 cm<sup>-1</sup>.

However, in the cellulose acetate, O–H may be present due to incomplete acetylation of cellulose, and some O–H groups from the cellulose backbone remain unreacted. The presence of hydroxyl groups can reduce the permeability of gases through the membrane. This is because the hydroxyl groups can create additional interactions with the gas molecules, for instance, increasing the resistance to gas transport, in this case, decreasing permeability and also enhancing the selectivity for certain gases [18]. From the results of the FTIR analysis, there is a clear peak at the wave number around 3609 to 3413 cm<sup>-1</sup> which is ascribed to the O–H group of CA. This pattern is



Figure 1. FTIR Spectra of the fabricated membranes.

similar to a result of CA/PSF spectra where a wave number for O-H absorption band was detected at the wavenumber of 3657 to 3213 cm<sup>-1</sup> [19].

Furthermore, the stretching frequencies around 1367 to 1366 and 1169 cm<sup>-1</sup> correspond to the asymmetric and symmetric vibrations of the sulfonyl (S=O). The aryl ring stretching is observed at 1487 cm<sup>-1</sup>, confirming the presence of PSF in the membrane and consistent with findings [19]. The interaction and miscibility of PSF with the CA matrix are confirmed by the presence of the C=C bond of aryl around 1585 to 1584 cm<sup>-1</sup>, which is similar to the literature, where the interaction of PSF with CA is detected around 1581 to 1594 cm<sup>-1</sup> [19]. As the number of groups increases, the peak area corresponding to bond vibrations increases.

For halloysite nanotubes (HNTs), characteristic peaks are expected around 3693 and 3621 cm<sup>-1</sup>, corresponding to the O-H stretching of the inner-surface hydroxyl groups and the O-H stretching of the inner hydroxyl groups, respectively [15]. A study also shows two intense peaks at 3690 and 3620 cm<sup>-1</sup> in the HNT spectrum, corresponding to O-H group vibrations [20]. However, the spectra in Figure 1 do not show these characteristic peaks of HNT. The absence of these peaks may be due to the low concentration of HNT incorporated into the PSF/CA membranes, making the intensity of the characteristic peaks around 3690 and 3620 cm<sup>-1</sup> too weak to detect. This explanation is supported by a study which investigates polyaniline in situ/ modified halloysite nanotubes [21]. It shows similar patterns where, at concentrations of 0.5, 1.0, and 2.5 wt% of Polyaniline (PANi)-HNT/PSF membranes, no visible characteristic peaks of HNT are present due to the low amount of PANi-HNT. Therefore, Table 1 will summarize the FTIR spectra analysis of the functional group's presence in the membranes.

The FTIR spectra shows different levels of light transmission through the membranes, as indicated by the finding that PSF/CA/2.0HNT exhibits the maximum transmittance and PSF/CA/0.5HNT displays the lowest. The variations in the amounts of halloysite nanotubes (HNTs) added to each sample account for this discrepancy. Because HNTs have hydroxyl groups on their surface, they can form hydrogen bonds with PSF and CA to interact, which may change the membrane's overall structure and composition. The greater abundance of HNTs, which may affect the concentration of O–H groups seen in

Functional group	Wavenumber range [cm <sup>-1</sup> ]	Presence of	Reference
C=O	1740–1748	CA	[17, 19]
C–O (ester)	1041.38-1074.5	CA	[19]
Aryl Ether	1234–1236	CA	[17]
CH <sub>3</sub> (asymmetric stretch)	2965–2968	CA	[19]
О-Н	3609–3413	CA and HNT	[18, 19]
S=O (asymmetric and symmetric stretch)	1357–1366 and 1169	PSF	[19]
Aryl ring stretch	1487	PSF	[19]
C=C (aromatic ring)	1585–1584	PSF	[19]

Table 1. FTIR spectra analysis of functional groups in membranes.

FTIR spectra and other membrane properties, is most likely the cause of the enhanced transmittance in PSF/CA/2.0HNT. From the spectra of the polymers, it can be seen that as the HNT content increases, there is an increase in the peak area around 3500 cm<sup>-1</sup>, which can be attributed either to the presence of residual moisture in the polymer or to an increase in the proportion of OH groups.

#### **3.2.** Morphology of the membrane

The incorporation of HNTs into the polymer matrix can influence the surface morphologies of the resulting membrane to some extent [22]. The impact of adding HNTs on the morphological properties of asymmetric membranes can be seen through the presence, dispersion, aggregation, and phase separation of the nanofillers [12]. According to the FESEM surface image in Figure 2a the surface of the neat PSF/CA membrane appears to be rough. A study investigated the surface morphology of CA/PSF membranes and found that at low concentrations of PSF, the surface exhibited a dense and smooth morphology without any defects [19]. However, at higher concentrations of PSF, some particles were observed on the surface, contributing to a rougher texture. In this study, the amount of PSF is higher compared to CA, which may explain the similar observation.

In addition, the features observed on the surface of the neat PSF/CA membrane might be dust particles or other contaminants rather than intrinsic morphological structures. These many small, scattered particles could have been introduced during the sample preparation or imaging process. As depicted in EDX images of surface sample PSF/CA in Figure 3a, there is a presence of chlorine at 0.1 atomic percent (At%) detected in the EDX spectrum, which can be considered as foreign material in the membrane. This is because chlorine is not typically a component of the PSF/CA membrane materials, so its presence suggests contamination. This contamination could have originated from various sources, such as the environment or the equipment used for membrane preparation for analysis. Therefore, the detected chlorine can be attributed to the impurities on the surface of the membrane.

In Figure 2b, the surface of the membrane with 0.5 wt% HNT exhibits a smoother surface morphology. Since this observation aligns with several studies reporting that the addition of HNTs to polymer membranes can decrease surface roughness, we postulated a similar conclusion for our samples, too [23, 24]. Additionally, similar observations were also reported whereby the top surfaces with denser but smaller pore sizes were obtained by adding low amounts of HNTs (0.2 and 0.5 wt%) to the casting solution [16]. The study indicates that the increase in hydrophilicity at low HNTs loading was not sufficient to significantly accelerate solvent/nonsolvent demixing during membrane formation. Furthermore, the reduction in pore size at low HNTs loading may indicate good compatibility and strong interaction between the polymer and HNTs. The presence of hydroxyl groups on the HNTs surface probably helps to form multiple hydrogen bonds with PSF, thereby improving the compatibility and interaction overall. Besides, a similar pattern was observed, where incorporating 0.5 wt% HNT into the polymer matrix resulted in the absence of significant cavities [12]. This effect is attributed to the fine dispersal of HNTs within the polymer matrix and the strong adhesion between HNTs and the polymer, preventing the formation of voids or cavities around the nanotubes. As shown in Figure 2b, the number and size of macrovoids have decreased, indicating improved membrane properties. The reduction in macrovoids suggests a more uniform and defect-free structure, which can enhance the membrane's mechanical strength and overall performance. No presence of



Figure 2. FESEM surface images for a) PSF/CA, b) PSF/CA/0.5HNT, c) PSF/CA/1.0HNT, d) PSF/CA/1.5HNT, and e) PSF/CA/2.0HNT.

HNTs is observed on the membrane's surface. Therefore, the EDX spectrum in Figure 3b shows only carbon, oxygen, and sulfur components, which originate from the PSF and CA.

For 1.0 wt% HNT (Figure 2c), the surface of the membrane shows more visible spherical structures (in the circle) compared to the previous membrane (0.5 wt% of HNTs). Since the elemental analysis did not indicate the presence of HNT or any impurities,

to be specific, we postulated that visible spherical structures could have originated from the small fragments of polymer samples during the sample preparation. Despite this increased polymer-clay interaction due to the higher loading, the dispersion of HNTs seems fairly homogeneous, as there are no large aggregates observed.

On the other hand, the FESEM images of the surface of the membrane with 1.5 wt% HNT (Figure 2d)

show well-defined spherical structures, which are the macrovoids or air bubbles that formed during the membrane casting process. They are evenly distributed across the surface and are a dominant feature of this membrane. Apart from the spherical structures, the rest of the surface appears relatively smooth and uniform. There are no distinct particles or clusters of halloysite nanotubes visible in this image. As a result, the only components displayed in the EDX spectrum in Figure 3d are PSF and CA.

On the other hand, the overall surface of the PSF/ CA/2.0HNT membrane, as shown in Figure 2e, exhibits a highly irregular and textured morphology, indicating substantial changes to the membrane's uniformity due to the addition of HNTs. The image reveals numerous defects or macrovoids on the membrane surface, more than what is observed with other HNTs loadings. This may be attributed to the high concentration of HNTs leading to agglomeration, resulting in larger particles that can create macrovoids. Another potential reason is the inadequate dispersion of HNTs in the polymer matrix. This is consistent with a finding that high HNT loadings resulted in large pores on the top membrane surface [16]. The study explains that this occurs because the hydrophilicity of the casting solution significantly increases



Figure 3. EDX Spectrum of a) PSF/CA, b) PSF/CA/0.5HNT, c) PSF/CA/1.0HNT, d) PSF/CA/1.5HNT, and e) PSF/CA/2.0HNT.

with higher HNT concentrations. This heightened hydrophilicity facilitates a rapid solvent-nonsolvent exchange when the cast polymer film is immersed in the coagulation bath, accelerating polymer precipitation and leading to the formation of larger pores in the membrane samples. Consequently, the observed pores in Figure 2e suggest that the incorporation of HNTs affects pore formation and distribution. Overall, the high concentration of HNTs has disrupted the membrane formation, significantly altering its structural and surface properties.

Despite the high concentration of HNTs in the dope solution, the EDX analysis, as shown in Figure 3e, does not detect HNTs on the membrane surface. This could imply that the HNTs might be evenly distributed throughout the polymer matrix instead of being concentrated on the surface. This uniform dispersion within the matrix could make it difficult for the EDX analysis, which scans specific surface areas, to detect the HNTs. Also, the concentration of HNTs on the surface may be below the detection threshold of the EDX analysis in the areas that were scanned.

The cross-sections of all produced asymmetric CA/PSF membranes show two different layers, as demonstrated in the FESEM pictures at 150× magnification in Figure 4. These layers consist of a dense skin layer and a supporting substructure. The impact of polymer concentration on the morphological features of the asymmetric membrane is commonly observed by measuring the thickness of the skin layer and the formation of macro-void structures in the porous substructure. As depicted in Figure 5, the neat membrane, composed solely of PSF and CA, exhibits a small, dense layer with teardrop-like structures embedded within the porous structure. Meanwhile, the asymmetric cross-section morphology becomes somehow different after the incorporation of varying amounts of HNTs into the PSF/CA membranes.

For instance, membranes with varying loadings of halloysite nanotubes exhibit an increase in the thickness of the dense skin layer as the weight percentage of halloysite nanotubes increases. As shown in Figure 6, the thickness of the dense skin layer for the neat membrane is 0.400  $\mu$ m. MMMs with 0.5 wt% HNT show an increase in thickness to 0.457  $\mu$ m, representing a 14.2% increase compared to the neat membrane. MMMs with 1.0 wt% HNT exhibit a thickness of 0.486  $\mu$ m, which is a 21.4% increase. For MMMs with 1.5 wt% HNT, the membrane skin

layer cannot be detected, suggesting a potential disruption or inconsistency in the formation of the skin layer at this concentration. Finally, MMMs with 2.0 wt% HNT have a dense skin layer thickness of 0.865 µm, marking a substantial increase of 116.2% compared to the neat membrane. As discussed before, the increasing thickness of the dense skin layer with higher HNT concentrations can be attributed to the improved distribution and strong interaction of HNTs within the polymer matrix. This homogeneous distribution and strong interaction reduce the rate of solvent/nonsolvent exchange during the membrane formation process. Consequently, this leads to a denser and thicker skin layer, as the incorporation of HNTs slows down the phase separation, allowing more time for the formation of a thicker dense layer [16].

While the dense top layer is responsible for selectivity, the bottom layer, consisting of macro-voids and finger-like pores, is responsible for providing mechanical support. The change in finger-like pore size and pore amount will be caused by the addition of HNTs. Figure 5 shows the membrane at  $3000 \times$  magnification, which clearly reveals the effect on the macropores and the finger-like pores. As seen in Figure 5a, in the neat PSF/CA membrane, the structure is characterized by finger-like pores that extend vertically. The pores appear to be open and well-defined, with clear pathways and larger spaces between them. This open structure facilitates the flow of substances through the membrane.

Unlike the neat membrane, those incorporated with HNTs display noticeable structural changes. As the HNT content increases from 0 to 2.0 wt%, the PSF/CA membrane transitions from having open, well-defined finger-like pores with prominent horizontal macropores to a much denser, less porous structure. The finger-like pores shorten and become more compact, and the horizontal macropores gradually vanish. A similar pattern where increasing filler loading, shrinking in tear-drop size and expansion of sponge-like structure was observed [21]. Excellent interaction between this HNT and PSf matrix is well predicted owing to the modification of the surface of the filler with PANi. Therefore, the observed changes in membrane morphology can be attributed to the excellent interaction between the HNTs and the polymer matrix. This occurs because adding nanomaterials to the membrane casting solution raises its viscosity, which impacts the membrane's

a) b) c) d) 100 µm JE0

**Figure 4.** 150× magnification FESEM images of the a) PSF/CA, b) PSF/CA/0.5HNT, c) PSF/CA/1.0HNT, d) PSF/CA/1.5HNT, and e) PSF/CA/2.0HNT.

morphology by altering the liquid exchange rate during phase inversion [25]. With a higher amount of HNTs, the viscosity significantly increases, slowing down the exchange rate and resulting in a denser internal membrane structure.

e)

# 3.3. Determination of phase structure by using XRD

The structural analysis of the blended polymeric membranes is investigated using the X-ray diffraction technique. The result of this technique will be



Figure 5. 3000× magnification FESEM images of the a) PSF/CA, b) PSF/CA/0.5HNT, c) PSF/CA/1.0HNT, d) PSF/CA/1.5HNT, and e) PSF/CA/2.0HNT.

displayed as a plot of signal intensity versus various diffraction angles at particular two theta positions. Based on the angle at which the incident X-ray beam is diffracted, these two theta positions show the distance between crystals or atoms in the sample. Each peak's strength corresponds to the number of



**Figure 6.** 10000× magnification FESEM images of the a) PSF/CA, b) PSF/CA/0.5HNT, c) PSF/CA/1.0HNT, d) PSF/CA/1.5HNT, and e) PSF/CA/2.0HNT.

molecules in that specific phase or spacing. Consequently, a greater peak intensity denotes a greater concentration of crystals or molecules with that particular spacing [26]. Generally, the microstructure of polymers is composed of both crystalline and amorphous areas. High-intensity, sharp peaks in the XRD spectrum indicate the crystalline portion of the polymer, whereas broad, lower-intensity peaks attest to its amorphous portion [27]. Figure 7 shows the XRD spectra of the fabricated membranes. The pattern of the membrane is similar to each other where for all membranes, a single spread diffraction peak is observed. The peaks located at  $2\theta = 17.98$ , 18.01, 18.02, 18, and 17.99° for PSF/CA, PSF/CA/0.5HNT, PSF/CA/1.0HNT, PSF/CA/1.5HNT, and PSF/CA/2.0HNT, respectively. These peaks are attributed to the semi-crystalline nature of the material (Douna *et al.* [19]). This result corresponds with research where the broad peak of PSF can be seen at  $2\theta = 18^{\circ}$  [19, 21].

XRD spectrum of pristine CA shows two large diffuse amorphous peaks at diffraction angles of  $2\theta =$ 10 and 17°, and three sharp crystalline peaks at  $2\theta =$ 22, 26, and 29°. Because of the strong intermolecular contacts (hydrogen bonding) between the acetyl and hydroxyl groups, CA is a semi-crystalline polymer with poor crystallinity [19]. Therefore, in this XRD spectrum, no peak of CA was observed, suggesting that the single spread diffraction peak of PSF is more dominant.

For HNT, characteristic peaks of HNT at  $2\theta = 13$ , 20.5, and 29° [21]. However, the research also notes that in the MMMs, which are PANi-HNT/PSF membranes, HNT peaks were not observed. This is attributed to the low filler concentration in the polymer matrix, making detection difficult. The concentrations for PANi-HNT were 0.5, 1.0, and 2.5 wt%, which are approximately the same as the weight percentages in this research.

In Figure 7, from the XRD patterns of PSF/CA/ HNT-based membranes, the peak width and positions are quite similar, with minimal intensity differences between the samples. In general, the XRD patterns for all the samples show a broad peak at  $2\theta =$ 9–36°, which indicates an amorphous structure. The PSF/CA/1.0HNT sample exhibits a slightly higher peak intensity postulated because of the higher



Figure 7. Stacked XRD spectra.

dispersion, which increases the basal spacing within the polymer matrix. As a conclusion, the amorphous structure of PSF/CA/HNT-based membranes, which was confirmed from the XRD patterns, was consistent with other studies with very low loadings of inorganic fillers.

#### 4. Conclusions

This study observed the performance of mixed matrix membranes (MMMs) composed of CA, PSF, and different weight percentages of HNTs for CO<sub>2</sub> and H<sub>2</sub> separation. The main objective was to improve the mechanical properties and gas separation efficiency of these membranes by incorporating HNTs into the polymeric matrix. The study proved the existence of cellulose acetate and polysulfone in the membranes by identifying typical peaks for functional groups such as carbonyl (C=O), ester (C-O), aryl ether, and C-H stretching vibrations. The presence of hydroxyl (O-H) groups showed inadequate acetylation of CA, which could decrease gas permeability. Peaks for sulfonate (S=O) and aryl ring stretching indicated the presence of PSF. However, no identifiable peaks for HNTs were found, perhaps due to their low concentration, as previously reported.

Morphological investigation using FESEM revealed that the pure PSF/CA membrane had a rough surface with extensive macrovoids, which could affect gas separation performance. The addition of HNTs produced smoother membrane surfaces and fewer macrovoids, particularly at 0.5 wt% HNT loading. At higher HNT concentrations (1.0 wt% and above), observable spherical shapes and imperfections indicated alterations in membrane morphology caused by phase separation and probable HNT aggregation. In addition, EDX analysis revealed only PSF and CA elements, with no detectable HNTs on the membrane surface, indicating a homogeneous dispersion of HNTs within the polymer matrix.

The phase structure study by XRD demonstrated a single broad diffraction peak around  $2\theta = 18^{\circ}$ , indicating the amorphous nature of PSF. The lack of discrete peaks for CA and HNTs indicates that the PSF's amorphous structure dominates the diffraction pattern. The strength of the XRD peaks varied according to HNT concentration, which shows slightly different intensities. However, the addition of HNTs did not significantly contribute to any changes in the polymer chain retaining its amorphous structure.

This study demonstrated the importance of HNTs loading in determining the membranes' structural, morphological, and crystalline properties by carefully analyzing FTIR-ATR, FESEM, and XRD data. In conclusion, we found that adding HNTs into CA/PSF membranes did not alter their physicochemical properties of the membranes significantly postulated due to the low concentration of HNTs. However, it is presumed that HNTs were well dispersed in the polymer matrix since there were visible agglomerations. For future works, it would be necessary to determine the gas separation efficiency despite the minimal changes in the physicochemical properties to draw a solid conclusion. This study serves as a platform for further investigation and development of enhanced MMMs adapted to specific industry requirements.

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