

Carbon Nanotubes in Nanocomposite Mixed-Matrix Membranes

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Carbon nanotubes (CNTs) are a popular material for gas separation because their walls are naturally smooth, allowing for faster gas transit than other inorganic fillers. It also has excellent mechanical strength, allowing membranes to work under high pressure. Although CNTs have superior qualities to other inorganic fillers, incorporating them into a polymer matrix is difficult due to CNTs' strong van der Waals forces, which cause agglomeration. CNT dispersion must be addressed if the full potential of CNTs is to be realized.

Keywords: mixed-matrix membranes ; carbon nanotubes (CNTs) ; nanocomposite ; gas separation ; membrane technology

1. Carbon Nanotubes (CNTs)

Endo first synthesized carbon nanotubes (CNTs) in 1976 before Iijima worked on the detailed structure characterization in 1991 [1]. Iijima discovered multi-walled nanotubes (MWNTs) in carbon soot made by the arc-discharge method. Two years later, single-walled nanotubes (SWNTs) were discovered by Bethune and coworkers using the same method [2]. CNTs are divided into single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). SWNTs consist of a graphene sheet rolled over into sp^2 bonded carbon atoms with a diameter of about 1.4 nm, similar to a C_{60} bucky-ball [3][4]. Sometimes, the tubule diameter is too small and exhibits the effects of one-diameter (1D) periodicity. MWNT is a concentric cylinder with an interlayer spacing of 3.4 Å and a diameter typically around 10–20 nm.

SWNT is formed when the beginning of the graphene sheet is folded over so that it touches the end of the (m,n) lattice vector, thus obtaining an (m,n) nanotube. Hence, the (m,n) indices determine the diameter and chirality of the nanotube. Both diameter and chirality of a nanotube are important in determining the properties of a nanotube, as a slightly different angle may change the properties of SWCNTs from a metal to a semiconductor. If the (m,n) has a difference of multiple three, the SWNT is said to be metallic; if the difference of (m,n) is not a multiple of 3, it possesses semi-conductor characteristics [5]. Unlike MWCNTs, the atoms of SWCNTs form a single covalently bound array. Because of this difference, SWCNTs have been used over MWCNTs in electric components due to their distinct electrical and optical properties.

Properties of CNTs vary depending on the chirality in terms of the angle and vector of rolled-up directions. In terms of mechanical strength, CNTs with high flexibility and strength and high stiffness are known for their superiority over graphite fibers. This is because of the strongly bonded sp^2 C=C and their high aspect ratio. The yield strength of CNTs was reported as ~0.64 TPa compared to steel at ~300 MPa, with CNTs being only one-sixth the weight of steel. Incorporating CNTs into the polymer matrix has been proven to increase mechanical strength. For instance, 1 wt. % of MWCNT addition to polystyrene/MWCNT nanocomposite films increased the break stress and tensile strength by about 25% and 40–42%, respectively [6]. Nonetheless, most studies reported a decrease in nanocomposites' impact toughness, and only a few studies reported an increase in the impact toughness. A recent study confirmed that when 1 wt.% CNTs were incorporated with polyethylene, ductility and toughness increased by 104% and 150%, respectively [6].

CNTs incorporated in the polymer matrix show a desirable enhancement in thermal strength. The constraint effect on polymer segments and chains found in CNTs enables an upgrade in the glass transition temperature (T_g) and the melting and thermal decomposition temperatures of the polymeric matrix. A study reported that the addition of 3 wt.% SWCNTs to epoxy increased its thermal conductivity up to 300% [6].

2. CNT-Polymer Nanocomposites

Due to the intrinsic smoothness of MWCNTs, CNTs in MMMs contribute to the highly rapid transport of gases and mechanical properties compared to other inorganic fillers [7]. Additionally, carbon nanotubes have significantly greater permeability and selectivity than any other recognized inorganic materials. When carbon nanotubes are combined with certain polymers, their permeability can be considerably enhanced by increasing their diffusion coefficients. CNT MMM development has accelerated significantly in recent years, particularly in gas separation [8][9] and water treatment [10][11]. The interfacial interactions between the carbon nanotubes and the polymer and their dispersion in the polymeric matrix affect the overall performance of CNT MMMs [12].

2.1. Dispersion of CNTs

Although carbon nanotubes have superior properties to other inorganic fillers, their applicability in mixed-matrix membranes for large-scale industries remains uncertain due to their inert chemical characteristics and incapability to disperse in typical organic solvents [13]. This is due to the properties of CNTs, which have very strong van der Waals forces between them. They tend to agglomerate and form tight bundles; hence, homogenous dispersion in the polymer matrix is difficult to obtain [3]. This has been the biggest challenge in developing CNT MMMs in producing defect-free membranes. The dispersion state of carbon nanotubes in various solvents is frequently used to better understand the carbon nanotube–solvent interaction and identify new approaches to improve their dispersion [6]. Improved dispersion of CNTs can be approached either by physical (ultrasonication, ball-milling, extrusion, and high shear mixing) or chemical methods. Chemical methods, also called CNT functionalization, include covalent and non-covalent methods.

2.1.1. Covalent Functionalization

Covalent functionalization alters the translational symmetry of carbon nanotubes by modifying sp^2 carbon atoms to sp^3 carbon atoms [14]. There are two methods for functionalizing carbon nanotubes: modifying surface-bound carboxylic acid groups or directly attaching reagents to the side walls. During the oxidation process, functional groups such as $-COOH$, $-OH$, $-F$, and $-NH_2$ are formed on the surface of carbon nanotubes. The most frequently used method is to treat the surface with strong inorganic acids. The functional groups on the surface of the carbon nanotubes were attached during the treatment to improve their compatibility with the polymer matrix [15]. Due to the attachment, the hydrophobic nature of carbon nanotubes is diminished, and they become hydrophilic, allowing for homogeneous dispersion of the functionalized MWCNTs in a broad range of organic solvents.

Ghaemi et al. [16] used phase inversion induced by immersion precipitation to prepare amine-functionalized MWCNTs/PES membranes. Chemically, pristine MWCNTs were treated with a mixed acid (sulfuric acid (H_2SO_4) and nitric acid (HNO_3)) solution at a 3:1 volume ratio. Before filtering, the solution was stirred for 1 h at 90 °C. The carboxylated MWCNTs were dried for 1 h in a vacuum oven at 100 °C. They were then added to a mixture of 1,3-phenylenediamine (mPDA) and DMF solvent and stirred for 96 h at 70 degrees Celsius. SEM analysis revealed that amine-functionalized MWCNTs had thicker structures than pristine MWCNTs, particularly at the end caps of CNTs, increasing membrane hydrophilicity. The addition of functionalized MWCNTs significantly increased the membrane's surface hydrophilicity. Additionally, FTIR demonstrated the presence of amine functional groups on the surface of MWCNTs. They explained that incorporating f-MWCNTs into PES membranes improved the performance and antifouling properties. Covalent functionalization has been proven to increase the solubility and dispersion of CNTs in the polymer matrix. Nonetheless, this technique that requires alteration of structural properties of CNTs during sonication, oxidation, and acid treatment may impede the full potential of CNTs. Thus, non-covalent functionalization is an alternative to functionalized CNTs without forming chemical bonds.

Amirkhani et al. [17] grafted functional groups ($-COOH$, $-NCO$, and $-H_2$) on the surface of MWCNTs, which were then incorporated into PEBAX matrix at 0.1–1 wt.% loading. Here, 4,40-diphenylmethane diisocyanate (MDI) was used to functionalize MWCNTs into MWCNT- $COOH$, MWCNT- NCO , and MWCNT- H_2 was synthesized by adding distilled water to the synthesized MWCNT- NCO . The optimal performance of permeability and selectivity differed for various functional groups based on the loading conditions with MWCNT- $COOH$ at 0.75 wt.% loading, MWCNT- NCO (0.3 wt.%), and MWCNT- H_2 (0.5 wt.%). The performance of membranes improved with increasing loading until it reached the optimum point, after which the addition of MWCNTs caused filler agglomeration and poor performance. MWCNT- NCO had the highest permeability for all gases with CO_2 at 148.86 barrer, followed by CH_4 (5.14) and N_2 (1.42). Incorporating functionalized groups disrupted polymer chain links and affected interfacial interactions and chain mobility, thereby affecting the fractional free volume (FFV) and polymer density. It has been demonstrated that -NCO groups enhance the inter-chain interaction of MWCNT- NCO membranes with the highest T_g relative to other membranes, resulting in high permeability and selectivity.

Singh et al. [18] prepared PSF-based MMMs incorporating PEG-grafted CNTs as inorganic fillers with loading varying from 2.5–7.5 wt.% via initial solvothermal mixing followed by solvent casting. A uniform dispersion achieved up to a certain filler loading contributed to the high permeability result. Moreover, MMMs demonstrated a 12.5% increase in mechanical strength compared to pure PSF.

2.1.2. Non-Covalent Functionalization

Non-covalent functionalization has no detrimental effect on the properties of carbon nanotubes because it involves the adsorption of chemical moieties onto the surface wall of the carbon nanotubes. As a result, it does not affect the final properties of carbon nanotubes. This method utilizes surfactants, biomacromolecules, or polymer wrapping. Hydrophobic micelle components surround the nanotubes. When the hydrophobic portion of the amphiphilic consists of an aromatic group, the interaction becomes stronger.

The specific reaction between polymers and CNTs is the wrapping mechanism [14]. Mousavi et al. [19] fabricated PEBAX-1657/chitosan-wrapped MWCNTs on an ultra-porous polyethersulfone (PES) substrate. The MWCNTs were functionalized using carbohydrate polymer chitosan using the simple-mixing method. Chitosan was dissolved in acetic acid/water (2:98%). Polymers that wrap around CNTs are also known as supramolecular complexes. In this case, π

-stacking interaction between the polymer and nanotubes surface is responsible for the close association of the structures. The addition of chitosan increases the adsorption capacity of the membrane, thereby increasing its antifouling property. Additionally, SEM images demonstrated a well-coated PEBA layer on a porous PES support and uniform dispersion of f-MWCNTs within the PEBA matrix.

Rajashree et al. [20] wrapped carbon nanotubes with carboxymethyl chitosan (CMC) via wet grinding-assisted sonication. The nondestructive walls of CNTs observed in FETEM analysis indicated the polymer wrapping did not affect the CNTs' integral architecture. Raman spectroscopy analysis also suggested that the G-band shifted to a greater wavenumber of 1590 cm^{-1} from 1575 cm^{-1} , subsequently wrapping with CMC, whereas the D-band had a negligible spectral shift. The intact position observed in the D-band suggested that CMC had not bonded covalently to CNTs. The increase in the G-band wave number resulted from the field disturbance caused by the CMC coating on the CNTs. This indicates that CMC and CNTs interact strongly.

A non-wrapping mechanism is another approach to the non-covalent functionalization of CNTs. In this case, copolymers are introduced as the stabilizers to disperse CNTs in the solvents. Fernandes et al. [21] suggested that the triblock copolymer, Pluronic F127, adsorbed to CNTs via a non-wrapping mechanism, and a central hydrophobic polypropylene oxide block flanked by hydrophilic polyethylene oxide blocks acted as the physical barrier to form a stable dispersion of SWNTs and MWNTs. Nonetheless, the non-covalent attachment of molecules may be weak, which will lead to the low efficiency of carbon nanotubes loading into the polymer matrix.

2.2. CNT–Polymer Mixed-Matrix Membrane in Gas Separation

CNT MMMs can be applied in various gas separation processes, including the separation of carbon dioxide, oxygen-nitrogen separation, and hydrogen separation. Hussain et al. [22] incorporated MWCNTs into polymer-blended CA/PEG membranes with 5–15 wt.% loading. Membranes with a loading of 10 wt.% had the best dispersion of filler particles and polar ether groups, resulting in increased crystallinity. The molecular sieving property of filler particles allowed for the highest CO_2/CH_4 selectivity. At higher loading of CNTs, agglomeration of CNTs occurred, creating non-selective voids between fillers and the polymer matrix. The addition of MWCNTs increased the thermal stability of membranes, allowing a $290\text{ }^\circ\text{C}$ operating temperature, making it industrially very useful where separation occurs at higher temperatures. Akshay et al. [23] developed a hollow fiber membrane using PES and carboxylated CNTs. The membrane showed excellent mechanical strength; Young's modulus increased from $268.1 \pm 4.1\text{ MPa}$ for pristine PES to $409.1 \pm 4.5\text{ MPa}$ for PES–CNT membranes. This resulted from the enhanced interfacial compatibility between oxygen-containing functional groups on carboxylate CNTs and sulfone groups on the PES matrix.

Yousef et al. [24] prepared PES/CNT membranes and recorded the separation performance of CO_2 , CH_4 , N_2 , and H_2 gases. These authors varied the CNT loading (0.01–0.03 wt.%), pressure (1–6 bar), and temperature (20, 40, and $60\text{ }^\circ\text{C}$). N_2 recorded the highest permeability at 10.5–15.4 barrer followed by H_2 (8.4–12.1 barrer), CO_2 (8.8–14.2 barrer), and CH_4 (3.4–5.6 barrer). Permeability increased as the temperature increased due to the plasticization effect on PES. The behavior and character of the gases changed with the applied heat. The membrane loaded with 0.02 wt.% carbon nanotubes had lower permeability than 0.01 and 0.03 wt.% carbon nanotubes. This was due to the uniform distribution of carbon nanotubes in the sample, which increased the matrix's crystallinity degree by partially aligning the molecular

chains and forming lamellae regions, obstructing gas transport through the membrane. Membranes with 0.01 and 0.03 wt.% CNTs loading had a random distribution of CNTs, decreasing the crystallinity degree and disrupting the PES chains, thus having a better permeability. Selectivity values of CO_2/CH_4 and CO_2/N_2 were 1.62 and 0.87, respectively.

Yu et al. [25] used carbon nanotubes to reinforce Pebax-1657 polymer membranes. The CO_2 permeability increased as the CNT content increased and reached a maximum of 5% wt CNTs. The increased gas permeability explained the increased gas diffusivity of carbon nanotubes. The mechanical strength of membranes was determined, and the tensile modulus increased by 43% when 5 wt.% single-wall carbon nanotubes (SWNTs) were added and by 24% when 5 wt.% multi-wall carbon nanotubes were added (MWNTs).

Dai et al. [26] investigated the CO_2 separation properties of Pebax/carbon nanotube–polyethylene glycol hybrid membranes. CO_2 permeability was 369.1 barrer with CO_2/N_2 selectivity of 110.8 for a hybrid membrane containing 3 weight percent CNT–PEG, surpassing the CO_2/N_2 Robeson upper limit. Lee et al. [27] used the wet phase inversion approach to integrate dispersant-functionalized multiwalled carbon nanotubes (MWCNTs–F) into a polymer matrix of varied molecular weight (70,000 with 12,000, 30,000, and 65,000 Mn). CO_2 had a selectivity of 17.09 for N_2 and permeance of 341.15 for CO_2 .

Shin et al. [28] studied the performance of 0.1 wt.% functionalized MWCNTs incorporated with 4 wt.% cellulose acetate butyrate (CAB), and the effect of different loadings from 0.2–1.2 wt.% was observed. The membrane was evaluated using a CO_2 and N_2 single permeation test. The findings indicated that the MMM comprises CAB polymer and 0.1 wt.% MWCNTs performed better in CO_2/N_2 selectivity, with a value of 2.887. Farid et al. [17] grafted several functional groups (–COOH, –NCO, and –NH₂) onto the surface of MWCNTs before incorporating them into a poly(ether-block-amide) (PEBAX) polymeric matrix. MMMs' CO_2 permeability and ideal CO_2/N_2 and CO_2/CH_4 selectivity were compared to the plain membrane. The findings indicated a significant increase and exceeded the CO_2/N_2 Robeson upper limit under 4–10 bar in the temperature range of 15–55 °C. MMMs with all three kinds of functional groups exhibited increased CO_2 permeability and CO_2/N_2 and CO_2/CH_4 selectivity compared to pristine MWCNTs, demonstrating the strong adherence of functionalized MWCNTs to the polymer matrix.

The third component is an additive that can further enhance the performance of MMMs. Low-molecular-weight components such as diethanolamine (DEA), amine, ionic liquids, and chitosan are often used as additive to promote homogenous dispersion of inorganic fillers in the polymer matrix. Murali et al. [29] prepared MMMs using Pebax-1657 and MWCNTs with the addition of 2,4-toluylene diisocyanate (TDI) to study the gas permeation properties of O_2 , H_2 , CO_2 , and N_2 gases. The CNT loading was varied to study the effect of loading on the permeability of the membranes. The selectivity of a cross-linked 2% MWNT Pebax membrane for the CO_2/N_2 gas pair was increased from 83.2 to 162 with increasing input pressure (1–3 MPa). The incorporation of MWNT increased the free volume. The cross-linking with TDI reduced the polymer's ion exchange capacity.

Moghadassi et al. [30] reported studies on functionalized carboxyl-MWCNTs incorporated with a polycarbonate (PC)/polyethylene glycol (PEG) polymer matrix at different loading ratios (1, 2, 5, and 10 wt.%). CO_2 gas with a small kinetic diameter had the highest permeability result. For N_2 and CH_4 gases, the permeation process is similar to diffusion via the inner surface of carbon nanotubes. Hence, a higher loading rate of MWCNTs promoted the diffusion of the gases. As a result, the selectivity of CO_2/CH_4 and N_2/CH_4 increased as the loading rate of MWCNTs increased. Selectivity started to show a decrease at a loading rate of 5 wt.% due to the trade-off of rapid diffusion of large gas molecules. The highest CO_2/CH_4 selectivity at 2 bar pressure and 25 °C was 27.38 for 5 wt.% of functionalized carboxyl-MWCNTs. Moghadassi et al. [31] also studied a cellulose acetate (CA)/styrene-butadiene rubber (SBR) blend polymer with both raw and functionalized MWCNT mixed-matrix membranes for the same types of gases. Permeabilities of gases increased with the increase of the CNT loading ratio. Some CNTs act like pinholes when vertically aligned to the membrane surface and create chances for diffusion mechanisms. The number of pinholes increases as the loading ratio increases, resulting in increased permeability. The increase in MWCNTs also increases FFV due to solution heterogeneity, creating voids between polymer chains and MWCNTs. The interaction between modified CNTs and polymer chains creates an interfacial zone that increases the relative sorption of gases; hence, permeability increases. However, the permeability was constant when the modified CNT loading ratio was higher than 0.65 wt.% due to adsorption stopping. Carboxylic groups that form on the surface of the filler material may act as a barrier to the entry of the nanotubes.

Dilshad et al. [32] studied the impacts of pressure on cross-linked polyvinyl alcohol (PVA)/polyethylene glycol (PEG) membranes tethered with surface-engineered multi-walled carbon nanotubes (SE-MWCNTs). The permeation of pure CO_2 , N_2 , and CH_4 was recorded. They discovered that a membrane-tethered with 0.5 wt.% SE-MWCNTs did not exhibit an abrupt increase in permeability and a significant decrease in gas selectivity up to 20 bar pressures, demonstrating that

the membrane was not plasticized under mixed gas circumstances or at high pressure. At higher loading of SE-MWCNTs with 0.75 wt.%, the permeability and selectivity of all gases decreased sharply due to the occurrence of interfacial voids. This occurred due to MWCNTs agglomerating at higher loads due to the Van der Waals interaction forming dense bundles with an uneven orientation. The performances of these membranes are tabulated in **Table 1** to highlight the permeability and selectivity of membranes under different parameters.

Table 1. Different MMMs' permeability and selectivity in gas separation.

Membranes	Pressure (bar)	Loading Ratio (wt.%)	Permeability				Selectivity		Refs.
			CO ₂	N ₂	CH ₄	H ₂	CO ₂ /CH ₄	CO ₂ /N ₂	
PES/MWCNT	2	1	3.2	0.15				22	[8]
	2	3	3.5	0.17				21	
	2	5	4.5	0.21				21	
	2	10	3.5	0.19				18.5	
Matrimid/MWCNT	2	2	13	0.84	0.81		16	15.5	[33]
	2	5	15	1	1		15	15	
	2	8	18	1.29	1.38		13	14	
	2	10	11	0.85	0.92		12	13	
PEBAX/MWCNT with TDI	1	2	3.54	0.03		2.51		83.2	[29]
	1	5	17.47	0.21		7.18		84.5	
PEBAX/MWCNT-NH ₂ with GTA	20	1	1408			213			[34]
PEBAX-MWCNT crosslinked	10	2							
	10	5							
PEBAX/CNT-COOH	10	0.75	132.30	1.55	5.47		24.18	85.32	
PEBAX/CNT-NCO	10	0.3	148.86	1.42	5.14		28.95	104.92	[17]
PEBAX/CNT-NH ₂	10	0.5	139.52	1.46	5.31		26.28	95.62	
PC-PEG/ MWCNT-COOH	2	1	8.35	0.18	0.28		25.73	28.19	
	2	2	12.53	0.26	0.37		26.59	27.45	[30]
PC-PEG/MWCNT-COOH	2	5	15.47	0.31	0.46		27.38	25.42	
	2	10	20.32	0.39	0.57		27.28	25.37	
	1	0.5	115.57	0.57	1.41		82.26	202.75	
PVA-PEG/MWCNT	5	0.5	107.78	0.55	1.38		77.88	195.96	
	10	0.5	104.5	0.54	1.35		77.35	193.52	[32]
	15	0.5	101.12	0.52	1.32		76.49	194.46	
	20	0.5	99.62	0.51	1.33		76.45	195.33	

3. CNT MMMs Gas Separation Application

CNT is one of the interesting components of an inorganic filler in membrane technology. As mentioned above, some innovative approaches to CNT MMMs should be assessed or improved to maximize the full potential of CNTs. In addition, coupling membrane separation with other assistant methods, including adsorption, catalysis, and electrochemistry, is worthy of further investigation [35]. CNT MMMs have demonstrated great promise in gas separation; consequently, they have been explored as a potential approach. With a good understanding of the behavior and characteristics of CNT MMMs, the performance of membranes in terms of permeability and selectivity shall increase rapidly.

One application of CNT MMMs is natural gas purification [36]. Natural gas consists mainly of CO₂ as its impurity and must be removed to meet the pipeline specifications. Commonly, in the last few decades, amine absorption technologies have been preferred due to their high selectivity, up to 99.0 %. However, this technology requires high capital and operation costs and large floor areas. Nonetheless, in recent years, membrane technologies have started penetrating the market as the performance of membranes has improved over time. CO₂ gas possesses condensability and quadrupole moments, making it plausible to use as a selective surface flow or adsorption as its separating mechanism for CO₂/CH₄ separation. According to molecular dynamics simulations, the gas penetration rates inside the one-dimensional pores of carbon nanotubes are orders of magnitude greater than those in any other known microporous material [37]. As a result, one-dimensional nanochannels made of carbon nanotubes can serve as CO₂ transportation highways, accelerating CO₂ permeation across the membrane.

Cheng et al. [38] fabricated SWNTs with triptycene-containing polyimide with various loading of nanotubes from 2–15 wt.%. Here, a polyimide containing hierarchical triptycene units (6FDA-TP) was utilized. The triptycene units may introduce π - π stacking and nanostructures shape-fitting interactions with CNTs, thereby facilitating the configuration of desirable interface morphology in composite membranes. They showed significant improvement in CO₂ with 144 barrer, a 144% increase compared to membranes without CNTs. Recognizing the trade-off between permeability and selectivity, there was a slight decrease in selectivity, but it remained within the acceptable range. Dan Zhao et al. [39] prepared MMMs based on Pebax-1657 and carbon nanotubes (CNTs) via the solution-casting method. Glycerol triacetate (GTA) was added as the third component, which enhanced the solubility coefficient. It was reported that the gas permeability of MMMs increased linearly with the addition of CNTs. This might be because carbon nanotubes carry gas more quickly than any other known material owing to their intrinsic smoothness. Moreover, with the addition of GTA as an additive, the permeabilities of CO₂ increased significantly. The highest achieved permeability was at 1408 barrer, with the highest concentration of GTA 10 times higher than that of pristine Pebax.

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