



# Polyaniline in situ modified halloysite nanotubes incorporated asymmetric mixed matrix membrane for gas separation



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## ABSTRACT

The embodiment of polyaniline in situ modified halloysite nanotubes (PANI–HNTs) on the gas permeation properties of CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub> gases in polysulfone (PSf) membrane has been investigated. Halloysite nanotubes (HNTs) were modified by in situ polymerization of aniline. Asymmetric mixed matrix membranes (MMMs) were synthesized by varying the PANI–HNTs concentrations of 0.5–2.5 wt.% of polymer in the PSf solutions. The MMMs were characterized by SEM, ATR-IR, DSC and XRD. Membrane characterization reveals the structural change of the filler and interaction of PANI with PSf polymer matrix. The permeance of pure gases and the ideal selectivities were determined using an indigenously built high-pressure gas separation manifold. Increasing the PANI–HNTs incorporation in polymer enhanced the permeance of CO<sub>2</sub> from 17.4 to 68.4 GPU, CH<sub>4</sub> from 0.8 to 4.8 GPU, O<sub>2</sub> from 3.9 to 18.8 GPU and N<sub>2</sub> from 0.7 to 3.1 GPU, respectively. The use of PANI–HNTs loaded PSf membranes provides a means for separation of CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub>.

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## 1. Introduction

Membrane technology is an emerging field for the separation of gaseous mixtures owing to low running costs, simple operating procedures and high separation efficiency [1–3]. Robeson had developed the concept of the upper bound curve for polymeric membranes, which generally undergo a tradeoff limitation between permeability and selectivity [4]. Membrane researchers therefore have strived to develop novel materials to exceed the ‘upper bound’ limitation, which lead to the evolution of organic–inorganic hybrids, commonly called mixed matrix membranes (MMMs). In this approach, superior gas separation properties of inorganic fillers, for instance zeolites, carbon molecular sieves, nanotubes, nanosized particles, combine with desirable mechanical properties and economical processability of polymers [5,6]. Although a great deal of effective practical and fundamental research studies has been reported, the development of new materials of MMMs is still anticipated [7,8]. The major factor for the successful MMMs development is heavily dependent on the selection of inorganic fillers.

Key challenging aspect in the preparation of MMM is the interaction or bonding between the polymer matrix and filler particles.

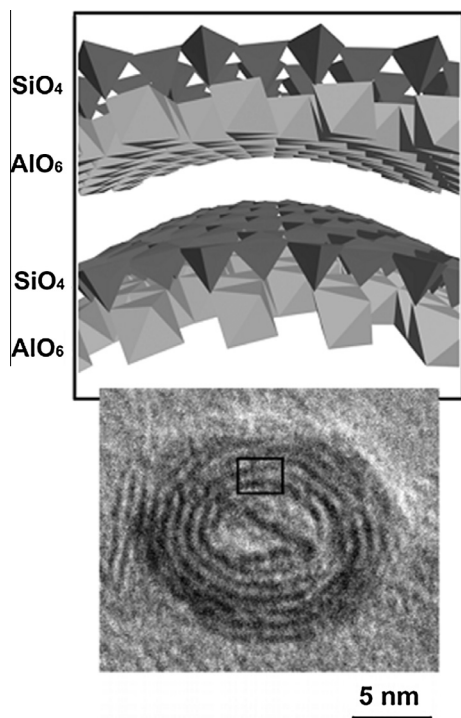
Undesirable voids may be formed at filler and polymer interfaces if the polymer chains do not interact with the filler particles, which in turn leads to reduction in membrane performance. To overwhelm this issue, fillers are modified to facilitate good interfacial interaction between polymer and filler. Several researchers have been working to modify the filler for better interaction of polymer and filler to achieve high performance MMMs [9–13].

Clay, which is inorganic filler that differs significantly from molecular sieves as the inorganic disperse phase, is a fascinating alternative for MMMs. Halloysite, Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>·2H<sub>2</sub>O, is a naturally occurring clay mineral which is mostly composed of multi-walled nanotubular-shaped crystals and characterized by high specific surface area [14,15]. It has been reported as new promising nanofiller to reinforce polymers [16–20]. Halloysite nanotubes (HNTs) results from the wrapping of the clay layers around themselves to form hollow cylinders under appropriate geological conditions. The wrapping process is due to mismatch in the cyclicity among the oxygen sharing tetrahedral SiO<sub>4</sub> sheets and the neighboring octahedral AlO<sub>6</sub> sheets in the 1:1 layer [21–23]. Fig. 1 represents multi-walled structure of halloysite nanotubes as a combination of AlO<sub>6</sub> octahedra with SiO<sub>4</sub> tetrahedra [14].

In our earlier work, asymmetric MMMs were fabricated by loading raw and modified HNTs into the polyetherimide polymer matrix to investigate the gas separation properties [23–25]. In the present work, PANi was chosen to modify the HNT in the

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**Fig. 1.** Structure of halloysite nanotubes as a combination of  $\text{AlO}_6$  octahedra with  $\text{SiO}_4$  tetrahedra [adopted from Ref. [4]].

preparation of MMMs for the gas separation studies. PANi was selected due to the easily available monomer, synthesis, environmental stability, simple doping/de-doping chemistry and solubility in highly aprotic solvents [26]. Polyaniline is one of the promising conducting polymers, which exhibits gas separation performance as good as conventional polymers [27]. Apart from these PANi/PSf membranes had been using for different applications such as fuel cell and ultrafiltration, because of superior interaction between PSf and PANi.

A literature survey reveals the absence of previous studies on gas permeation characteristics of polyaniline in situ modified halloysite nanotube (PANi–HNT) loaded polysulfone (PSf) for fabricating MMMs, which forms the focus of this investigation. MMMs are characterized by SEM, XRD, DSC and FTIR. Gas permeation studies are conducted with pure gases such as  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{O}_2$  and  $\text{N}_2$ . The extent of filler incorporation on the membrane characteristics and gas separation performance was evaluated.

## 2. Experimental

### 2.1. Materials

Polysulfone (PSf Udel-P3500) was procured from Amoco Chemicals. N-methyl-2-pyrrolidone (NMP), HCl, aniline and ethanol solvents were supplied by Merck. Tetrahydrofuran (THF) was obtained from QReC. All the chemicals purchased in reagent grade purities were used as received without purification. HNT and ammonium peroxydisulfate were procured from Aldrich. PSf pellet and HNT powder were pretreated in a vacuum oven at  $60^\circ\text{C}$  for 24 h to remove the residual moisture. Table 1 gives the specifications of HNT.

### 2.2. Modification of HNT by in situ polymerization by PANi

Zhang et al. synthesized polyaniline coated HNT using in situ polymerization technique. In the present study, the same

**Table 1**  
Specifications of HNT.

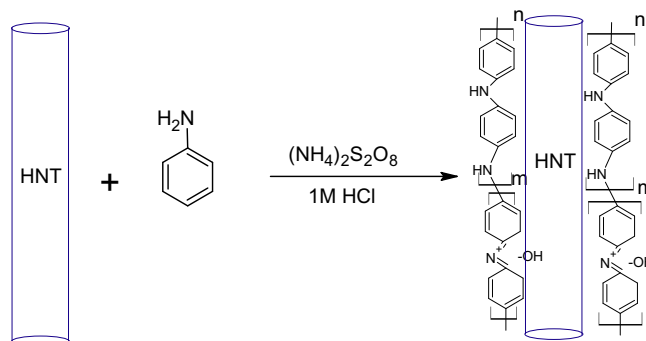
Internal diameter	30 nm
Length	0.25–4 $\mu\text{m}$
Density	2.136 $\text{g}/\text{cm}^3$
Color	Gray

procedure was followed to modify HNT as described elsewhere [28]. Process conditions were controlled to circumvent the effect on HNT. 1.5 g of HNT was added to 100 ml of distilled water and subjected to sonication for uniform dispersion. Mixture of 3 ml aniline and 270 ml of 1 M HCl was added to HNT aqueous solution with continuous stirring at  $10^\circ\text{C}$ . Temperature plays a significant role to avoid fast dissociation of the acid, which shows the effect on HNT. A pre-calculated mixture of 7.5 g ammonium peroxydisulfate in 300 ml of 1 M HCl was gradually added to the reaction mixture over a period of 90 min. The polymerization reaction was maintained for 4 h at room temperature without any interruption. Dark colored, PANi modified HNT, was filtered and washed with distilled water for several times. Finally, the product was stirred in liquid  $\text{NH}_3$  gently for 30 min to remove the residual acid content and neutralize the compound. Thus, obtained PANi–HNT was dried in oven at  $70^\circ\text{C}$  for 48 h to remove the moisture content. Fig. 2 illustrates the schematic representation of in situ modification of HNT by PANi. Modification was confirmed by ATR-IR and XRD.

### 2.3. Dope solution preparation

For the pristine PSf membrane, 27 wt.% PSf polymer pellets was added to 34 wt.% NMP (non-volatile solvent) and 34 wt.% THF (volatile solvent). Initially, 1/3rd of the polymer pellets were added to the solvent mixture. After the complete dissolution of pellets, remaining polymer was gradually added. The polymer was dissolved with vigorous stirring over a period of 24 h. After ensuring that polymer was completely dissolution, 5 wt.% ethanol (non-solvent) was added to the dope solution and subsequently stirred for 3 h.

For the MMMs, same dope formulation aforementioned was followed by varying the PANi–HNT content from 0.5 to 2.5 wt.% of the PSf polymer. Fig. 3 shows the schematic representation of possible interaction in dope solution. Particularly for asymmetric MMMs, uniform distribution of the filler particles has always been the challenging problem in the preparation of a successful membrane. In the present case, for better dispersion of filler, the calculated amount of 0.5 wt.%, 1 wt.% and 2.5 wt.% PANi–HNT powder was added to the binary solvent mixture (NMP and THF) and the suspension was subjected to stirring for 30 min and followed by sonication for 90 min at  $50^\circ\text{C}$ . The filler was then subjected to priming



**Fig. 2.** Schematic representation of in situ modification of HNT by PANi.

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