Mixed matrix membrane incorporated with large pore size halloysite nanotubes (HNT) as filler for gas separation: Experimental

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ABSTRACT

This study investigated the gas separation and transport properties of asymmetric mixed matrix membranes (MMM) fabricated from polyetherimide (PEI); Ultem 1000 incorporated with raw and modified halloysite nanotubes (HNT) as filler. The modified HNTs; S-HNTs were prepared by treating HNTs with N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane (AEAPTMS). FESEM, XRD, FTIR, TGA, DSC and pure gas permeation testing were used to characterise the S-HNTs and the fabricated MMMs. In the first part of the experiments, the effect of dope preparation factors such as: ultrasonic sonication period, filler wetting period and priming period were investigated. In the second part, the influence of silane concentration on the fabricated MMMs was studied. Results showed that, increasing the silane concentration, led to higher tendency in HNT agglomeration which resulted in poor separation properties but permeability enhancement. In the last part, the effect of S-HNTs loading was experienced. Our observations showed that the dispersion of nanoparticles decreased with an increase in the S-HNTs loading. Accordingly, 0.5% loading of silylated-HNT yielded the optimum MMMs in terms of permeability (27% increase) and selectivity (8% increase).

1. Introduction

The ever-increasing needs in developing the membrane performance for the purpose of gas separation have led to an increase in demand of novel materials and new methods. Mixed matrix membranes (MMMs); a combination of polymers and inorganic materials, have the potential to be considered a promising answer to this demand. Polymeric membranes have excellent processability, good intrinsic transport properties and low cost. On the other hand, inorganic membranes are capable of discriminating gas species even in severe temperature and pressure conditions and aggressive environments. However, their use is still limited for reproducibility problems in the preparation step, as well as lifetime and high cost [1–3]. MMMs are heterogeneous membranes in which inorganic fillers are dispersed in a polymer matrix [4–24]. The concept of MMM combines the advantages of each phase: high selectivity of the dispersed fillers and desirable mechanical properties and economical processability of polymers.

MMMs are very effective in gas separation processes (for example: separation of oxygen–nitrogen mixture, purification of natural gas by removing carbon dioxide). The inorganic fillers used in MMMs are mostly porous molecular-sieve type materials, including zeolites [13–15] and carbon molecular sieves [5,11,25].

There are many other fillers than zeolites and CMSs and our attempt is to classify these fillers into two distinct categories. The first one, called Type 1, is featured by their intrinsically high separation capacities like molecular sieves. Their sizes are, at least from the open literature [5,6,8,10,13,14,16,17,23–25], mostly in the micro-meter scale. This type of fillers is more traditionally used. The Type 2 fillers, on the other hand, are featured by intrinsically low separation capacities and they are mostly in the nano-meter scale. Examples are non-porous silica [26–31], large pore size zeolites [32–34], carbon nanotubes (CNT) [35–37] and metal organic frameworks (MOF) [38,39]. These fillers are more untraditional. In comparison to the first Type, a larger interfacial area between the fillers and the polymer matrix per unit volume of the fillers can be achieved for the second Type, since the fillers are nano-sized.

Another difference between the membranes in which Type 1 fillers and Type 2 fillers are incorporated (called Type 1 MMM and Type 2 MMM, respectively hereafter) is the thickness of the membrane. The polymer matrix of the Type 1 MMM normally consists of a dense homogeneous film as thick as more than 1 μm, to allow complete embedment of the fillers. The Type 2 MMM, on the other hand, can have an asymmetric structure with a skin layer of less than 1 μm and is prepared by the phase

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inversion technique, It is needless to say that Type 2 MMM has more practical usefulness since it allows high permeation rate.

During the last decades, little attention has been devoted to aluminosilicate mineral clays. While clays (particularly Montmorillonite) were incorporated as filler, in most cases, for fabricating nano-composite polymers either to enhance the mechanical/physical properties or for food packing purposes, fewer works have been done for gas separation purposes. The transport features of EVA/clay(cloisite Na$^+$) nanocomposites containing different filler loadings were investigated by Kumar et al. [40]. According to them, nanocomposites exhibited lower permeability to the tested gases; oxygen and nitrogen, due to the enhanced polymer/filler interaction. However, the permeability increased at higher filler concentrations. This was explained in terms of the aggregation of filler particles at higher concentrations. Clay-polydimethylsiloxane (PDMS) MMMs were prepared by Defontaine et al. [41] using two natural clays (sepiolite and montmorillonite) as fillers. Their MMMs yielded an increase in selectivity but decrease in permeability. It is known that, clays are cheep, abundantly available, possessing a vide variety of structures. Hence, the investigation of materials in the clay family, such as: montmorillonite, kaolinite and imogolite, as fillers in the polymer/inorganic MMM offers a new and attractive research area.

The objective of the present work was to investigate the possibility of using a member of the clay family, known as halloysite as a filler in polyetherimide (Ultem) composite membranes. Holloysite consists of nano-tubes (HNTs) with an internal diameter of 10–100 nm and a length of 0.25 to 4 μm. Thus, it satisfies the requirements to be Type 2 filler. It was attempted to investigate the significant parameters which influence the produced MMM separation and transport properties such as: ultrasonic sonication period, filler wetting period, filler priming period. Furthermore, N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane (AEAPTMS) was applied to the HNTs as a compatibilizer. The effects of the AEAPTMS concentration and the filler loading in the casting dope on the gas separation performance were studied. FESEM, XRD, TGA, DSC, FTIR and pure gas permeation testing were conducted to characterize the laboratory made MMMs. To the best of our knowledge, there is no documentation on the use of HNTs clay to fabricate a MMM in conjunction with a glassy polymer for gas separation purposes.

2. Experimental

2.1. Materials

A commercial Ultem® 1000 polyetherimide, purchased from GE plastic, USA was chosen as the polymer matrix phase. Two solvents were used; N-methyl-2-pyrrolidone (NMP) as non-volatile solvent supplied by Merck and tetrahydrofurane (THF) as volatile solvent purchased from QReC. Ethanol, used as non-solvent, was supplied by Merck. The inorganic filler, halloysite nanotube (HNT) clay, was purchased from Aldrich. The tube dimension of HNT is 30 nm × 0.25–4 μm. N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane (AEAPTMS) having a molecular formula of $NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$ (Mw = 222.36), was used for the chemical modification of HNT and was purchased from Merck. Toluene was purchased from Merck. Prior to any use, PEI and HNT nano-
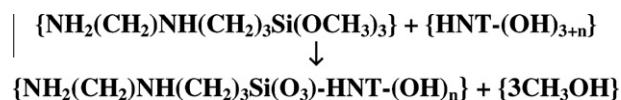
$$\{NH_2(CH_2)NH(CH_2)_3Si(OCH_3)_3\} + \{HNT\text{-}(OH)_{3+n}\}$$
$$\downarrow$$
$$\{NH_2(CH_2)NH(CH_2)_3Si(O_3)\text{-}HNT\text{-}(OH)_n\} + \{3CH_3OH\}$$

Fig. 1. Schematic representation of silylation of HNT by AEAPTMS.
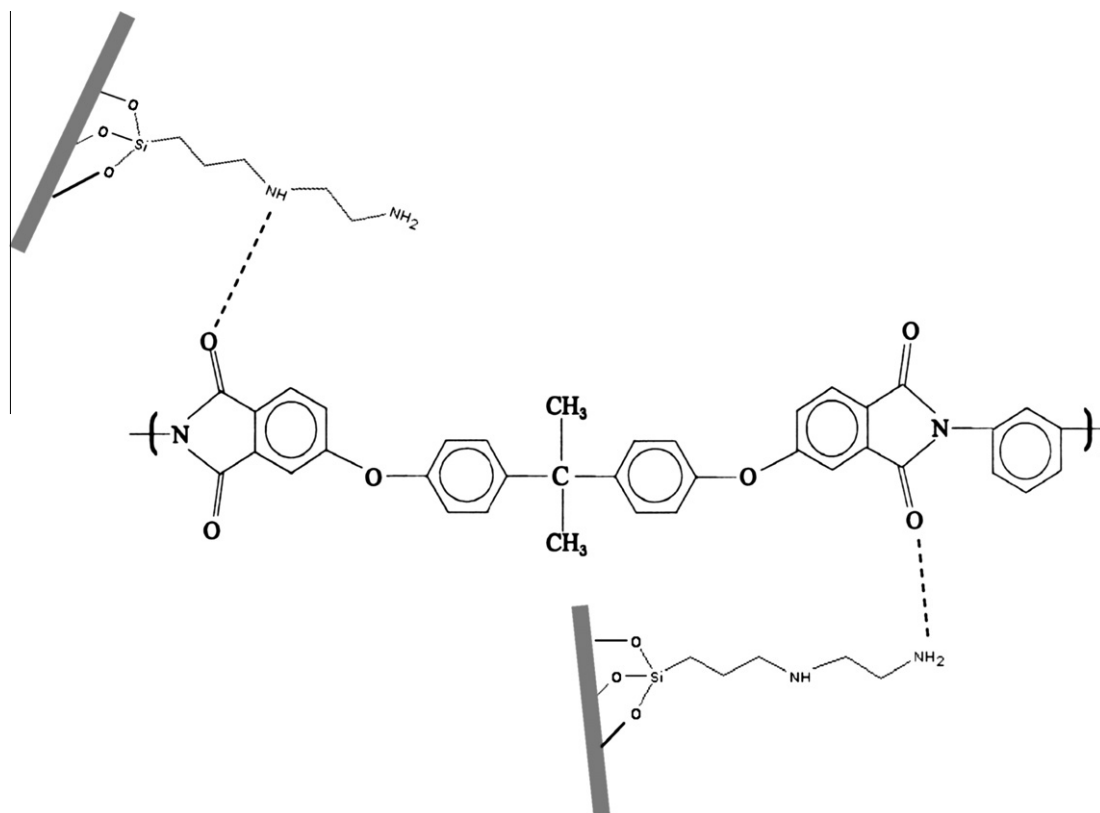
Fig. 2. Hydrogen bonding (broken lines) between PEI and S-HNT.