



Mixed Matrix Hollow Fiber Membranes with enhanced gas permeation properties



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ABSTRACT

In this study, both the structural and gas permeation properties of mixed matrix asymmetric hollow fiber membranes were investigated. The average outer and inner diameters of the membranes are 1200 and 800 μm respectively, and as used polymer was chosen the BTDA-TDI/MDI (P84) co-polyimide. Phenol-functionalized multi-wall carbon nanotubes were chosen as filler materials and their morphological characteristics were investigated by TEM. The membranes were then characterized by FTIR and SANS; T_g variations were evaluated by DSC measurements. The findings provide evidence for uniform dispersion of nanotubes and the existence of small structures formed by the filler addition. Finally, permeance experiments in a series of pure gases (He, H₂, CH₄, N₂, O₂, C₂H₆, CO₂ and C₃H₈) at 25, 60 and 100 °C were carried out. The results revealed that the good multi-wall carbon nanotubes dispersion leads to enhanced gas permeation properties.

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1. Introduction

Polymeric and inorganic membranes constitute a wide research field for applications in separation technology. Due to many advantages of membrane technology in comparison with cryogenic process, a lot of research and demonstration projects have been implemented worldwide during the last decades. These advantages offered by their high stability, efficiency, low energy requirement and ease of operation. Membranes with good thermal and mechanical stability combined with good permeability/selectivity properties are important for industrial processes [1]. To this end the improvement of the thermal and mechanical stability in conjunction with the increasing of the permeability factors is one of the major targets for the membrane research community. Note that the gas separation occupies a central position in the chemical and petrochemical feedstock industry [2]. Some typical examples of membrane gas separations are the following [3]: (i) hydrogen separation, (ii) air separation, (iii) acid gases separation, (iv) water separations, (v) hydrocarbons separation and (vi) helium separation. During the last decades, the development of new type of

membranes is on the top of the research actions because of the large economical interest of all these separations.

In particular, a plurality of new promising membrane materials such as block, even di-block and tri-block, copolymer membranes [3], zeolite membranes [4], carbon molecular sieve membranes [5], AIPO membranes [6], and mixed matrix membranes (MMMs) [7] are reported in the literature. Among all these types of membranes MMMs are traditionally one of the most promising candidates for gas separations, thanks to their ability in the enhancement of the properties of the final structure.

MMMs are composed of homogeneously interpenetrating polymeric and inorganic particles. Generally, the most popular dispersed inorganic particles in polymer matrices are TiO₂ [8,9], ZnO [10], Al₂O₃ [11,12], Au [13], zero-valent iron (ZVI) [14], Pd [15], as well as zeolites [16,17], carbon molecular sieves [18,19], non-porous silica [20], porous silica [21], metal-organic frameworks (MOFs) [22,23] and others. Furthermore nanotubes, especially carbon nanotubes, are one of the high-interest reported nanomaterials because they are also used as filler for composite membrane preparation [24–26]. Carbon nanotubes (CNTs) are a fascinating class of materials thanks to their special properties that can be exploited on numerous applications. More specific, their extremely high aspect ratio, which makes them to molecular-level needles, their electrical conductivity, their mechanical strength and their good thermal properties as well as their wave adsorption

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characteristics establish them promising materials for many applications [27–32]. The interest of using nanoparticles as fillers in membrane structures focuses, in the main, on their beneficial effect on fluxes and fouling resistance [33]. Significant improvement in separation properties compared to neat polymers is expected for the resultant MMMs [34]. Inorganic particles added to a polymer matrix can have the following three effects on the permeability: (i) they can act as molecular sieves altering the permeability, (ii) they can disrupt the polymeric structure increasing the permeability too and (iii) they can act as barriers reducing the permeability [3,35].

Hind et al. [36], in one of the pioneering works in the field, reported in 2004 that nitrogen permeability, when aligned carbon nanotubes incorporate into the polymer matrix, provides a clear indication of the potential of the nanotubes inner cores to act as a feasible channel for their transport. Moreover a plurality of composite membranes obtained mainly with randomly dispersed functionalized/modified carbon nanotubes were reported in the literature in the last 10 years. Specifically in 2007 Cong et al. [25] prepared composite BPPO_{dp} membranes using both pristine single-wall CNTs (SWNTs) and multi-wall CNTs (MWNTs). They concluded that the composite membranes had an increase in CO₂ permeability but a similar CO₂/N₂ selectivity compared to the corresponding pure polymer membrane. In 2009, Weng et al. [37] developed a series of MWCNT/PBNPI nanocomposite advanced membranes with a nominal MWCNT content between 1 and 15 wt% in order to separate H₂ from CH₄. In 2010, Goh et al. [38] prepared matrix polyetherimide (PEI) based membranes by embedding dispersed MWCNTs using surfactants of different charges. The prepared MMMs exhibited permeance improvement of O₂ and N₂ as much as 87.7% and 120% respectively compared to that of neat PEI membrane. Aroon et al. [26] in 2010, fabricated PI/Raw-MWCNTs and PI/chitosan-functionalized MWCNTs (PI/C-f-MWCNTs) mixed matrix membranes by phase inversion method. Gas permeation results showed that addition of 1 wt% (solid base) C-f-WCNTs into casting dope can increase the CO₂ and CH₄ permeabilities by 20.48 and 0.71 Barrer, respectively. Recently, (2011), Ge et al. [39] used MWCNTs, after treatment with sonication in a mixture of H₂SO₄/HNO₃ for 3 h at 60 °C at water bath, as filler materials in polyethersulfone nanocomposite membrane preparation. By this adding the gas permeation fluxes of the derived membranes were increased by ~67%. During the same year, Ge et al. [40] used metal and carboxyl doped MWCNTs as filler materials in PES polymer matrix membranes and they found that the selectivity increases when the added CNTs were modified by Ru, but it remains similar or even decreases when carboxyl and Fe were employed to functionalize CNTs. Furthermore, Sieffert and Staudt [41] reported that they used and characterized commercial, hydroxyl functionalized-MWCNTs prepared in a two-step reaction. Different procedures to prepare homogenous hybrid films by ultrasound dispersion were investigated and appropriate instructions were found.

However, the investigations on MMMs show that these hybrid materials are not simple systems where the effect of the fillers can easily understand. To this end the study of the optimum way where the inorganic particles must be added into the polymer matrices, the physicochemical properties of the inorganic fillers as well as the nanoparticle/polymer interface morphology [42] are individual factors which have to be investigated in order to facilitate the gas permeation properties of these new materials and, finally, to predict the changes of the MMM performance from the age of their design.

In a previous work [43] the gas permeance/selectivity performance of single co-polyimide hollow fiber membranes was reported. Furthermore, in our recent work [44] MWCNTs were prepared, modified and dispersed into co-polyimide based hollow fiber membranes and the permeance coefficients of He, N₂ and O₂ were

studied at 25 °C. In the present study, advanced experimental techniques are utilized for the characterization of the produced nanocomposite membranes together with the polymeric BTDA-TDI/MDI co-polyimide. TEM was employed for observing the morphological characteristics of the fillers. Nanoscale structural characteristics of the composite membranes were revealed by SANS. Further, the thermal properties of the membranes were tested by DSC measurements, whereas FTIR was used for investigating the effect of the filler adding in the character or quantity of the particular bonds. Finally the effect of the filler concentration into the membrane matrix was evaluated by single phase permeance experiments of He, H₂, CH₄, N₂, O₂, C₂H₆, CO₂ and C₃H₈ at 25, 60 and 100 °C respectively.

2. Experimental

One polymeric (S1) and three nanocomposite membranes (C1, C2 and C3) with MWCNT concentrations 1, 2 and 4 wt% respectively were prepared via the wet spinning technique, using a spinning set up, in a way described in our previous works [5,45]. In particular, the functionalized MWCNTs were dispersed in NMP solvent using a sonicator instrument at 50 °C. Afterwards 28.5 wt% of commercial BTDA-TDI/MDI (P84) co-polyimide was added in the solution and mixed mechanically for 8 h isothermally (50 °C). In addition, one more single co-polyimide (without any filler adding), the S1 membrane, was also prepared according the same spinning conditions. The solutions were filtered using a metal filter of 450 mesh and left overnight for outgassing. The extrusion was done using a special spinneret with the following dimensions: needle ID = 0.5 mm, needle OD = 0.7 mm and orifice ID = 1.2 mm. The spinning conditions were constant for all the prepared membranes and described in Table 1.

Previously, MWCNTs were synthesized using a novel catalytic CVD (*Chemical Vapor Deposition*) technique and following the functionalization process certain functional groups, namely carboxyl and phenol groups were introduced on the external surface of the MWCNTs [46,47]. The functionalization procedure towards the –phenol moieties attachment was converted through “wet chemistry” by the addition of p-aminophenol reactants to form sigma bonds with the pz orbitals of the carbon atoms on the outer surface of the nanotube. The TEM images were produced by a JEOL-JEM-2100F Transmission Electron Microscope. SEM pictures obtained with a JEOL-JSM-6390LV and a FE-JEOL-JSM-7401F Field Emission microscopes.

The thermal properties of the samples were tested by differential scanning calorimetry (DSC) in a TA Instruments, Model MDSC 2920. The runs were undertaken using a heating ramp of 2 °C/min, a cooling rate of 5 °C/min with a temperature modulation of ±0.32 °C every 60 s.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a horizontal ATR Trough plate crystal cell (Thermo Electron 6700 ATR diamond) equipped with a Nicolet 6700 FTIR (Thermo Electron Corporation) operating at room temperature. For spectra analysis, the samples were placed on the crystal cell, which was in turn, mounted on the spectrometer. The spectra in the range of 400–4000 cm^{−1} were scanned and the automatic signals were collected. A total of 10 scans were averaged for each sample and the resolution was 4 cm^{−1}. The background spectrum was recorded at room temperature with an empty cell. Before FTIR analysis, all samples were dried at 100 °C in order to remove adsorbed water from the surface.

The small-angle neutron scattering (SANS) measurements were carried out at the PACE spectrometer (LLB, Saclay, France) in a Q-range varying from 0.03 to 2.2 nm^{−1}, corresponding to two sample-detector distances (4.57 m and 0.67 m respectively). All

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