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Preparation and characterization of MWCNT-TEPA/polyurethane nanocomposite membranes for CO_2/CH_4 separation: Experimental and modeling

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ABSTRACT

In the current study, multiwall carbon nanotubes (MWCNTs) were functionalized with Tetraethylene Pentamine (TEPA) and added into polyurethane (PU) polymer matrix to prepare PU-MWCNT-TEPA nanocomposite membranes. The prepared membranes were characterized using FT-IR, XRD and SEM analysis. The analysis results showed that MWCNTs were properly functionalized with TEPA and also uniformly dispersed in polymer matrix. The CO_2 permeability increased by 99.8% at 10 wt.% loading of MWCNTs-TEPA. The nanocomposite membrane's CO_2/CH_4 selectivity was also increased by 9.6%. Impacts of operating pressure and temperature on the membranes' CO_2 permeability and CO_2/CH_4 ideal selectivity were also investigated. Finally, the gaseous penetrants permeabilities through the nanocomposite membranes were predicted using the Maxwell, the KJN, and the modified KJN models by AAREs of 31.4–35.2, 27.8–31.6, and 4.4–5.7%, respectively.

1. Introduction

Traditional processes such as physical adsorption, reactive absorption and solid bed absorption mainly used in sweetening plants and have many advantages. However, they suffer from some problems such as high capital and operational costs and high environmental impacts (Rezakazemi et al., 2014). Then, necessity of more efficient and environmentally-friendly gas purification techniques have led to massive research works to find higher efficient and environmental-friendly separation processes in recent years. Many of these efforts have led into the membrane-based gas separation technologies due to their ease of operation, low energy consumption, and high efficiency. Development and applications of the higher applied polymeric membranes for gas separation require more investigation and improvement in their structure and separation properties (Talakesh et al., 2012).

There are some modifying methods to enhance gas separation properties of membrane such copolymerization(Fang et al., 2016; Nebipasagil et al., 2017), blending (Mozaffari et al., 2017; Yong et al., 2012), making nanocomposites (Isfahani et al., 2016; Zeynali et al., 2018), etc.

In copolymerization, proper comonomer(s) are introduced to make copolymers with desired functional groups controlling their molecular structures and eventually their separation performance (Zhang et al., 2018, 2017a,b). Addition of rigid contortion sites in polyimides dianhydride and/or diamine moieties can enhance their gas separation performance via increasing of the polymer matrix fractional free volume (FFV), i. e. higher permeabilities, and decreasing the polymer chains flexibility, i. e. enhance gas pair selectivities (Ghanem et al., 2008; Zhang et al., 2017b). Zhang et al. (2018) prepared some different crosslinked polyimide membranes such as 6FDA-MPP and 6FDA-PP,

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6FDA-CADA1, 6FDA-CADA2, BTDA-CADA1 and DSDA-CADA1 (Zhang et al., 2017a), using different crosslinking procedures and agents and their separation performances passed over the CO_2/CH_4 upper bound limit Robeson 2008.

Mozaffari et al. (2017) prepared some blended membranes using polyurethane and PEBA and found the blended membranes to have higher gas permeations and selectivities. Also, Yong et al. (2012) prepared some blended membranes using PIM-1/Matrimid blends and found up to 4 time increment in the CO_2 permeabilities while the CO_2/CH_4 permeabilities remained nearly constant up to 30 vol.% of PIM-1. They passed over the O_2/N_2 upper bound limit of Robeson 2008 while approached considerably that for CO_2/CH_4 gas pair (Yong et al., 2012).

Additionally, the other best potential strategies for modification of the polymeric membranes with the enhanced separation performance is incorporation of proper separation performance particles into polymeric matrix to prepare the so-called mixed matrix membrane (MMM) (Jamil et al., 2016; Nasir et al., 2013; Sun et al., 2014). Recently, gas permeation properties of several polymeric and mixed matrix membranes have been studied (Fernández-Barquín et al., 2017; Khdhayyer et al., 2017; Rabiee et al., 2015b). A promising CO_2-philic membrane called semi-interpenetrating networks (SIPN) contain poly(ethylene glycol) dimethyl ether (PEGDME) groups made by one-step UV-induced radical polymerization exhibited high CO_2 permeabilities. This membrane separation performance passed over the Robeson upper bound (Jiang et al., 2017).

Some different polymers used in the MMMs preparation for CO_2/CH_4 separation are reported in Table 1. Polyurethane is one of the most promising rubbery polymers recently used vastly for gas separation applications (Ameri et al., 2015; Sadeghi et al., 2013; Talakesh et al., 2012; Tirouni et al., 2015). Polyurethane contains two important segments: hard segments containing urethane/urea group, and soft segments of polyether/polyester. Good mechanical properties and desirable permeation properties are the main significant properties of this polymer attributed to its functional groups. Due to existence of the alkaline, polar urethane groups and polar ether soft segments, this polymer is one of the candidates for polar and acid gaseous mixtures separation (Talakesh et al., 2012). Sadeghi et al. (2013) prepared some silica containing PU membranes for gas separation application. Permeation of the pure gases of CO_2, CH_4, N_2 and O_2 were studied. They reported that gas permeability through the nanocomposite membranes were reduced as silica particles loaded into the polymer matrix while their CO_2/N_2, CO_2/CH_4, and O_2/N_2 ideal selectivities increased. Similar results were observed by Ameri et al. (2015) as alumina particles (Al_2O_3) incorporated within the PU matrix. The fabricated PU–alumina nanocomposite membranes showed to 42% decrease in the CO_2 gas permeability and 1.55 times increment in the CO_2/CH_4 selectivity.

Different methods such as chemical surface modification or functionalization of the filler particles were also tried to enhance the MMMs' separation performance via providing better membrane structure by incorporating proper functional groups facilitating the desired penetrants preferentially permeation. In this advance, inorganic fillers are usually connected with organic coatings such as carboxyl, hydroxyl and amine groups by the physical or chemical interaction between particles and organic modifiers (Wu et al., 2014; Zhao et al., 2014b). Compatibility of some material can be improved by inserting some functional groups in order to create favorable interactions between the nanoparticle and the polymer matrix chains. For instance, Yang et al. (2017) used in-situ 3D growth of MOFs on the 1D surface of carbon fibers in order to enhance interfacial linker between the fibers and polymer matrix's chains and finally increment in the compatibility between the nanoparticles and the polymer matrix. Addition of the amine functionalized polyhedral oligomeric silsesquioxanes (POSS-NH_2) nanoparticles into the poly ethylene oxide (PEO) matrix caused to increase in the resultant nanocomposite membranes' CO_2 permeability by 2.42 times compared to the neat polymeric membranes while their CO_2/CH_4 selectivities remained nearly constant (Li et al., 2017b). Carbon nanotubes (CNTs) are composed entirely of sp2 bonds, those consisting of one single graphite layer rolled up into a hollow cylinder are single-walled carbon nanotubes (SWCNTs) and those consisting of up to several tens of graphitic shells are MWCNTs (Popov, 2004). CNTs have received great attention since gas transport through them are faster than any other known materials (Chen et al., 2006; Skoulidas et al., 2002). The CNTs have been employed in the several research works for MMMs preparation (Kim et al., 2007, 2006b; Murali et al., 2010; Zhao et al., 2014b, 2017). Zhao et al. (2017) prepared Pebax 1657/functionalized MWCNT nanocomposite membranes for gas separation. They observed an enhancement in the CO_2 permeability by 1.72 times while the membranes' CO_2/CH_4 selectivity remained nearly constant. In another research work carried out by Kim et al. (2007), functionalized SWCNTs were added into the poly sulfone matrix and used for CO_2/CH_4 separation. The MMMs' CO_2 permeability was increased up to 33% at functionalized SWCNT filler particles loading of 10 wt.%, while CO_2/CH_4 selectivity was decreased by 22%. It was reported that the carbon/carbon nanotubes (C/CNTs) hybrid membranes were prepared by pyrolysis of poly(amic acid) (PAA)/MWCNTs precursors revealed higher gas permeabilities than those prepared by incorporation of SWCNTs while their selectivities were remained nearly unchanged. Therefore, they concluded that the gaseous penetrants permeabilities of MWCNTs are higher than those of SWCNTs (Li et al., 2017a; Zhao et al., 2017). Moreover, the CO_2 permeabilities were reported to increase significantly from 321 to 2626 Barrer for SWCNTs and 6661 Barrer for MWCNTs (Li et al., 2017a). Then it was decided to use the MWCNTs as the filler particles of nanocomposite preparation in the current study.

In order to predict gaseous penetrants permeabilities through MMMs, the Maxwell model can be used which was initially developed for prediction of other different properties of composite materials such as thermal and electrical conductivities and mechanical strength (Aroon et al., 2010b; Chiew and Glandt, 1983; Maxwell, 1873) and after that, it was adapted for MMMs' permeabilities prediction (Gheimasi et al., 2013; Gheimasi et al., 2014; Li et al., 2005). This ideal model is applicable for ideal MMMs structure where the matrix polymer chains are intimately connected to the filler particles' surface (Aroon et al., 2010b; Gheimasi et al., 2013; Li et al., 2005). Kang et al. (2011) introduced a new model called KJN (maybe abbreviated from their names of Dun-Yen Kang, Christopher W. Jones and Sankar Nair) for gas permeability prediction through MMMs with the tubular filler particles. The tubular fillers' aspect ratio and orientation in the KJN model are described by parameters of α and angle θ, respectively. These angles with respect to the axis parallel to the bulk phase transport direction varies from 0 to $\pi/2$ radians are in the KJN model and described in Section 3.4.

The Maxwell and the KJN models are ideal. In the ideal models, the MMM's permeability are predicted as functions of their continuous polymer matrices and dispersed filler particles permeabilities and the dispersed phase's volume fraction loading (Aroon et al., 2010b; Gheimasi et al., 2013). On the other hand, in the non-ideal MMMs structures, some undesirable defects occur in the interphase regions of the MMMs structure such as total or partial filler pore blockage in the case of porous filler, polymer chain regasification and/or void formation (detachment of the polymer chains from the filler particles' surface). These structural defects should be introduced to the ideal models via preferentially meaningful proper variable/parameters to enhance their prediction accuracy (Aroon et al., 2010b; Chung et al., 2007; Gheimasi et al., 2013, 2015).

In this study, some nanocomposite membranes were prepared using TEPA functionalized MWCNTs as the filler particles and polyurethane as the continuous phase. The prepared nanocomposite membranes' permeabilities of CO_2 and CH_4 gases were measured at different nanoparticle contents, operating temperatures and pressures. Then the nanocomposite membranes' permeations were modeled by the Maxwell and KJN models which adapted to the nanocomposite structure defects. AARE values of model predictions were calculated using the following equation:

$$AARE_i\,(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{P_i^{Cal.} - P_i^{Exp.}}{P_i^{Exp.}}\right| \tag{1}$$

where $P_i^{Cal.}$ is the predicted i^{th} gas permeability through the nanocomposite membrane, $P_i^{Exp.}$ is the experimentally measured gas