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Enhancement of the gas separation properties of polyurethane membrane by epoxy nanoparticles

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ABSTRACT

In this study, we report highly selective CO_2 polyurethane incorporated with cured epoxy nanoparticles. PU–epoxy composite membranes were prepared via solution casting method. The obtained SEM micrographs confirmed the nano-scale distribution of epoxy particles in the polymer matrix. DSC and FTIR spectra showed different phase separation for the PU composites compared to the pure PU. The effect of epoxy nanoparticles on the gas permeability of CO_2, CH_4, O_2 and N_2 was studied at 25 °C and 10 bar. The selectivity of CO_2/N_2 increased from 25 for the pure PU membrane to 55.5 for the PU–EP10, while the CO_2 permeability was unchanged.

Introduction

Polymeric membrane-based gas separation is gaining a great deal of interest because of its high energy efficient, non-environmental effect, low maintenance costs, a modular process, and a compact system. However, the industrial applications of the polymeric membranes are still limited by the trade of between the gas permeability and selectivity [1–5].

The concept of mixed matrix membrane (MMM) is an effective way to improve the gas separation performance of polymeric membranes. Over the last few years, inorganic particles, e,g. metal oxides, silica [6], zeolite imidazolium framework [7], metal organic frameworks (MOFs) [8] have been utilized to prepare mixed matrix membranes. However, poor compatibility and the density differences between the inorganic and organic phases limit the membrane fabrication process [9]. The lack of good adhesion between carbon molecular sieves (CMS) and polyimide chains at high filler loadings results unselective voids and decreases the selectivity [10].

Some efforts are made to design some functionalized particles in order to improve the interactions with the polymer chains and the solubility of CO_2 in the MMMs [11,12]. For example, the amine modification of UiO66 and MOF-199 is used to enhance the CO_2/CH_4 gas separation performance of the polyimide composite membrane [13]. But, decreasing the thermal stability and using too much solvent limit the commercial applications of these particles. Therefore, the particle synthesis without using organic solvent has been considered in our groups. In our previous publication, MCM-41 mesoporous silica was modified by 3-aminopropyltrimetoxysilane (APTMS) and trimethylchlorosilane (TMCS) by the two different methods with and without using solvents [14]. Moreover, we synthesized silica nanoparticles via hydrolysis of tetraethoxysilane (TEOS) in ethanol, which is environmentally friendly [15]. In another study, the epoxy particles were synthesized by using the emulsion technique based on water in oil water (W/O/W) [16].

The gas separation properties of various MMMs have been studied extensively in our group. The CO_2 and CH_4 gas permeabilities increase with the incorporation of silica in ethylene vinyl acetate and polybenzimidazole membranes [15,17]. However, the adverse results are reported for the PU–silica MMMs, where the gas permeability decreases with the silica contents [18–20]. This behavior is commonly observed for PU MMMs [21–23]. It is believed that the functions of particles in glassy or rubbery polymer membranes are different for gas separation performance [5,24–27].

The limitation of using inorganic fillers within the polymeric membranes induces using organic particles to obtain a good

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interaction between the polymer chains and particles. PIM-1 is used as an organic filler in the polyetherimide-based MMMs [28]. The CO_2 permeability increases at the low concentration (up to 10 wt%) without much compromising gas selectivity. The effect of trimethylsilylglucose (TMSG) particles in the high free volume poly(trimethylsilylpropane) (PTMSG) MMMs is studied. The gas permeability reduction probably relates to the reduced free volume of PTMSG after filling of the pores by TMSG particles [29].

Although many studies on the effects of inorganic particles in the polymeric membranes have been made, there is a lack of research on using organic particles as fillers in the mixed matrix membranes. Here, the nano-sized organic epoxy particles were embedded in the PU matrix to enhance the CO_2 gas separation performance. In our previous publication [16,30], the synthesis and properties of the epoxy nano particles were explained. The particle synthesis process is an environmentally friendly technique as no solvent used and there is no emission of volatile products in the process. Moreover, the cured epoxy particles showed good thermal and dimensional stability, excellent chemical and corrosion resistance and superior mechanical properties [31,32]. The chemical structure and amine curing mechanism of the epoxy resin is depicted in Scheme 1. The gas separation of PU membranes has been studied extensively by our groups [33–35]. The surface of the cured epoxy particles contains a lot of polar OH groups (Scheme 1), which can be useful not only as an active site for CO_2 absorption, but also providing a good interaction with the PU chains [15,36]. Therefore, we investigate the gas separation performance of polyurethane–epoxy nanocomposite membranes at various epoxy contents.

Experimental

Materials and synthesis

Polypropylene glycol, PPG, ($M_w = 2000$), were obtained from Aldrich and dried at 80 °C under vacuum for 24 h to remove any residual water before use. 1,4-Butane diol (BD) chain extender, hexamethylenediisocyanate (HDI), N,N-dimethylformamide (DMF), and dibutyltindilaurate (DBTDL) were purchased from Merck (New Jersey, USA). The CO_2, N_2 and O_2 (purity 99.99) that used for gas permeation tests were purchased from Roham Gas Co., Tehran, Iran and also CH_4 (purity 99.95) was purchased from Air Products Co.

Polyurethane was synthesized by a bulk two-step polymerization method [33,35]. First, PPG was incubated with HDI for 2 h at 90 °C under nitrogen to obtain a macrodiisocyanate prepolymer. The chain extending of polymer occurred by addition of 1,4-butane diol after prepolymerization step at room temperature. The molar ratios of the used components were as follows: PPG:HDI:BDO = 1:3:2. Cured nano-epoxy spheres were produced via transitional phase inversion (TPI) method, as described elsewhere [16,30].

Membrane preparation

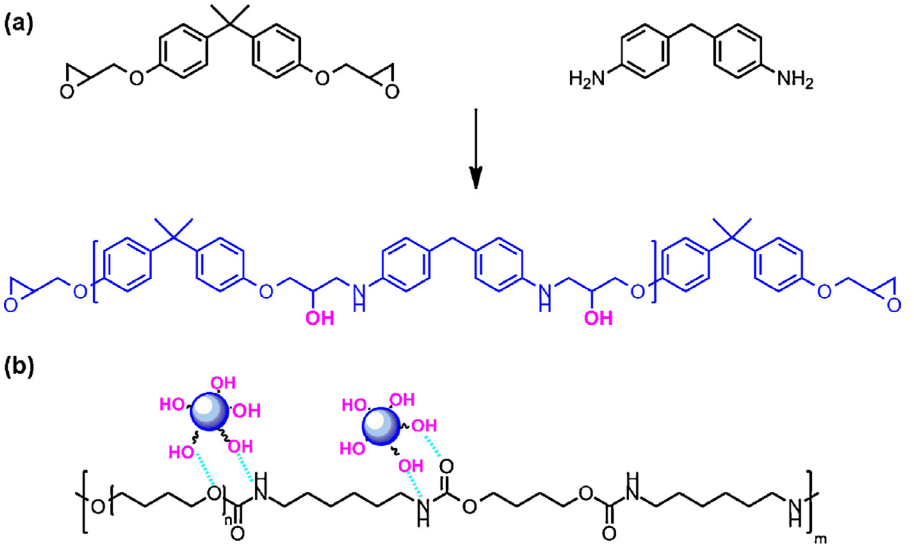
Pure PU and composite membrane were prepared by solution casting method. Epoxy particles were dispersed in DMF by using mixer and ultrasonic equipment and introduced to the PU solution in different loadings of 10, 20, 30 wt%. The membranes were formed by evaporating the solvent at 60 °C overnight. For complete removing the solvent, the prepared membranes were placed in a vacuum oven at 80 °C for 24 h. The thicknesses of prepared membranes were in the range of 70–80 μm. The prepared membranes were designated as PU–EPα, where α indicates the weight percent of epoxy nanoparticles loading.

Gas permeability measurement

The permeability of nitrogen, oxygen, methane and carbon dioxide were determined using constant pressure/variable volume method at 25 °C and 10 bar, which is the plasticization threshold for our membranes. The permeate side was maintained at atmospheric pressure. Each membrane was tested three times for each gas to determine reproducibility, and the averages of these trials were reported. The gas permeability of membranes was evaluated using the following equation:

$$P = \frac{ql}{(p_1 - E_2)A} \tag{1}$$

where P is the permeability expressed in barrer (1 barrer = 10^{-10} $cm^3(STP)cm/cm^2s\,cmHg$), q is the flow rate of the permeate gas passing through the membrane (cm^3/s), l is the membrane thickness (cm), p_1 and p_2 are the absolute pressures of feed side and permeate side, respectively (cmHg), and A is the effective membrane area (cm^2).



Scheme 1. Schematic illustration of the amine curing of the synthesized epoxy particles (a), and the interactions with the PU chains.