



Mixed matrix membranes of polyurethane with nickel oxide nanoparticles for CO₂ gas separation



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ABSTRACT

We developed highly selective polyurethane (PU) membranes with incorporated NiO nanoparticles for gas-phase carbon dioxide separation. PU was synthesized with polytetramethylene glycol and isophoronediiisocyanate, and 1,4-butandiamine/1,4-butandiol as the chain extender (1:3:2 molar ratio). Mixed matrix membranes (MMMs) composed of PU and NiO nanoparticles were fabricated using the solution casting method. Scanning electron microscopy (SEM) confirmed the even distribution of NiO in the PU matrix at the nanoscale. Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) were used to examine the phase separation between the soft and hard domains of PU, and the distribution of NiO nanoparticles in both domains. DSC and X-ray diffraction (XRD) pattern confirmed that the crystalline structures in both soft and hard segments are changed by NiO incorporation. The effects of NiO nanoparticles on the gas permeability, diffusivity, and solubility of pure CO₂, CH₄, O₂, and N₂ gases were studied at various temperatures and feed pressures. A large increase in the CO₂/N₂ permselectivity with a simultaneous reduction in the gas permeability of CH₄, O₂, and N₂ was observed. When the NiO content was low (1 wt%), the CO₂/N₂ permselectivity increased by 79.21%, and the CO₂ permeability increased by 1.57%. Increasing the nanoparticle load to 5 wt% increased the CO₂/N₂ permselectivity by 161.1%, while the CO₂ permeability was decreased by 3.31%.

1. Introduction

The industrial revolution has increased the atmospheric level of carbon dioxide, which is projected to grow further with the expanding global economy. Elevated atmospheric CO₂ level is a major cause of climate change [1] that may disrupt many human activities and natural environments. Consequently, controlling CO₂ emissions is at the forefront of scientific endeavors, with CO₂ capture being one major approach [2,3]. Post-combustion chemical absorption is the conventional method to remove CO₂ and a mature technology [4]. However, the process's large energy consumption and concerns over its environmental impact are huge drawbacks [5]. In recent years, membrane-based gas separation technology has become an interesting alternative, because of its low energy consumption, compact and modular procedure, and reduced environmental emissions [6]. The applications of membranes in CO₂ capture have grown rapidly since the 1980s, after the first industrial membrane-based gas separation plant was established [7].

Some advantages of using polymeric membranes are: low capital cost, low maintenance cost, low energy consumption, easy installation

and commercialization, capability to use at pressure, flexibility, and high product purity [8–12]. The fundamental properties which determine the efficiency of the membranes are permeability and selectivity; therefore, the enhancement of polymeric membrane performance is dependent on improving both permeability (P_f) and selectivity ($\alpha = \frac{P_1}{P_2}$) [13]. Polymers commonly used in gas separation membranes include: polyimides, polysulfones, polyethersulfone, polyurethanes (PU), polyacetylenes, Pebax 1657, and polycarbonates [3,5,13].

Recently, a number of studies have focused on PU membranes, due to their high mechanical properties, thermal stability, and good separation performance [14–19]. PU has a variable polymer microstructure, since it is formed of two phases called the soft and hard segments. The soft segment usually contains polyether or polyester which has high molecular weight, and forms the permeable regions of the gas separation membrane. The hard segment is the low-molecular weight, impermeable region of the membrane that is formed by extending a terminal diisocyanate with diol or diamine. A number of studies have examined the effect of different soft and hard segments, the length of polyol, and the kind of chain extender on gas permeation properties [15,18,20–24].

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Inorganic membranes, made of metals, ceramics or pyrolyzed material, have attracted significant attention for application in gas separation due to their high selectivity and permeability. However, this depends on the process and process conditions; moreover, inorganic membranes are relatively expensive, and it is not cost-effective to use them on an industrial scale.

Different procedures have been applied to overcome the trade-off between permeability and selectivity. Composite membranes containing nanoparticles have attracted a lot of attention, since the nanoparticles are easy to fabricate and inexpensive. Nanocomposite membranes using inorganic nanoparticles, called mixed matrix membranes (MMMs), combine the advantages of organic polymer materials and good gas separation properties of inorganic membranes [25–28]. Inorganic materials considered for this purpose include: silica, TiO₂, Al₂O₃, zeolite, clay, carbon molecular sieves, Fe₃O₄, ZrO₂, MgO, ZnO, and other metal oxides [3,29–37]. It was observed that some metal oxide nanoparticles can interact with polar gas molecules like CO₂ and SO₂ through their surface polar groups. This surface activity can increase both the selectivity and permeability [26,38–41].

Many recent studies have investigated the CO₂ adsorption of metal oxides. In most cases, the absorption of CO₂ is high [42–45]. Vijay et al. [46] prepared Co_{0.6}Zn_{0.4}Fe₂O₃ nanoparticles by a co-precipitation method. Hybrid membranes using these nanoparticles in a polycarbonate matrix have decreased permeability but increased permselectivity. Moghadam et al. [47] investigated the influence of TiO₂ nanoparticles on MMMs based on matrimid 5218. They reported that by adding nanoparticles, the permeability of MMMs increased because of disrupted chain packing and void formation. However, the permselectivity of the membranes decreased at the same time, and a trade-off relationship similar to Robeson's trade-off relationship was observed. Azizi et al. [41] used three types of inorganic nanoparticles (TiO₂, SiO₂, and Al₂O₃) in poly(ether-*block*-amide) matrix. The introduction of these nanoparticles increased both the permeability and selectivity. Ahmadi-zadegan et al. studied the effect of ZnO on polyimide gas separation membranes. Upon adding ZnO, the permeability of CO₂ and the CO₂/N₂ selectivity increased by around 67% and 9%, respectively. The increased permeability is due to increased diffusivity and solubility. With a higher solubility, the permeability of condensable gas increased more than that of non-condensable gases [48]. However, the improvements observed in these studies are still not enough for industrial uses.

This study investigated the effect of nickel oxide (NiO) nanoparticles on the gas separation properties of PU membranes, because creating a stronger interaction between the membrane and specific permeates like CO₂ can increase both the permeability and selectivity. Since CO₂ behaves as a Lewis acid (electron acceptor) [42,49,50], the presence of Lewis bases (electron donor) in the membrane matrix improves the interaction with CO₂ molecules, leading to increased gas permeability and selectivity of the membrane. Byung et al. showed that metal oxides like copper oxide serve as electron donors to CO₂ [49]. The effect of NiO on CO₂ adsorption of activated carbon has been previously studied [51,52]. Jang et al. found that upon loading NiO on activated carbon, the CO₂ adsorption increased [42].

To the best of our knowledge, the effects of NiO nanoparticles on the gas separation properties of polymeric membranes have not been investigated. Therefore, in this study we used NiO nanoparticles to tailor the structure of polyurethane membrane, and examined the interaction between the nanoparticles and gas molecules. The permeabilities of CO₂, CH₄, O₂, and N₂ gases were separately evaluated at various NiO nanoparticle contents, temperatures, and gas pressures. We also compared our results with other studies using MMMs with metal oxide fillers (Fig. 6).

2. Materials and method

2.1. Materials

Polytetramethylene-glycol (PTMG, M_w = 2000 g mol⁻¹) was purchased from Arak Petrochemical Complex (Iran) and dried at 80 °C in a vacuum oven for 48 h to remove residual water. 1,4-Butandiamine (BDA), 1,4-butanediol (BDO), isophorone diisocyanate (IPDI), and N,N-dimethylformamide (DMF) were obtained from Merck Co. The chain extenders (BDO and BDA) were dried under vacuum before use. CO₂, CH₄, O₂, and N₂ gases (purity 99.9%) were purchased from Ardestan Gas Co. NiO nanoparticles were purchased from Sigma-Aldrich.

2.2. Polyurethane synthesis

All PU samples were synthesized via a two-step bulk polymerization procedure [53,54]. A macrodiisocyanate prepolymer was obtained by mixing diisocyanate and PTMG and incubating at 85–90 °C under a nitrogen atmosphere for 2 h. The synthesized prepolymer was chain-extended through the addition of BDO/BDA in 50/50 weight ratio at room temperature. The molar ratios of NCO:OH and NCO: NH₂ were kept at 1:1 to obtain a linear polymer, while that of PTMG:IPDI:BDO-BDA was 1:3:2. The molecular structure of the synthesized PU-urea is depicted in Scheme 1. The presence of BDA leads to urea linkages.

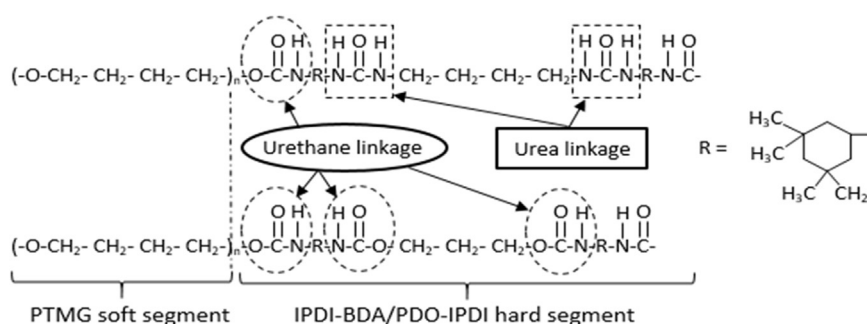
2.3. Preparation of membranes

A homogeneous PU solution was prepared by dissolving 10 g of the synthesized PU in 90 g DMF at 70 °C with the help of a heated stirrer. After filtration, the bubble-free solution was casted in a clean, flat petri dish. We used the Teflon petri dish for convenience. The solution was dried at 60 °C in a convection oven for 48 h. The dried pure PU membrane was kept in a vacuum oven at 60 °C for 24 h to remove residual solvent.

MMMs were prepared by ultra-sonicating NiO nanoparticles in DMF for 10 min, before adding them at various ratios (1, 2.5, 5, or 10 wt%) to the PU dissolved in DMF to avoid agglomeration. The solutions were casted in petri dishes and dried through the same procedure as described above. The volume fraction (ϕ_s) of NiO in the hybrid membrane was calculated based on the following equation:

$$\phi_s = \frac{w_n/\rho_n}{w_{pu}/\rho_{pu} + w_n/\rho_n} \quad (1)$$

Scheme 1. Molecular structure of the synthesized polymer.



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