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Polyvinyl acetate/titanium dioxide nanocomposite membranes for gas separation

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ABSTRACT

Organic–inorganic NCMs were prepared from PVAc and TiO_2 using the solution casting method and compared with pure PVAc membranes. The prepared membranes were characterized by optical microscope, FESEM, XRD, DSC, TGA and single gas permeation. FESEM results show that TiO_2 particles up to 10 wt% are homogenously dispersed and adhered in the PVAc without much aggregation. It was shown by the WAXD results that the crystallinity of PVAc is decreased by the incorporation of TiO_2. The addition of TiO_2 nanoparticles to PVAc has improved the thermal stability of the resulting NCMs as depicted by an increase in the glass transition temperature (T_g) and the TGA results. Single gas permeation of N_2, O_2, CO_2 and H_2 was carried out and the effect of TiO_2 loading, feed pressure and operating temperature on the permeability and selectivity of PVAc and PVAc–TiO_2 NCMs were investigated. It was found that the addition of TiO_2 up to 10 wt% has improved both the permeability and selectivity of the NCMs. The permeability of O_2, CO_2 and H_2 was increased by 95%, 79% and 62% respectively. Selectivity of the gas pairs O_2/N_2, H_2/N_2, CO_2/N_2 was also increased by 38%, 26.5% and 14% respectively. Increasing the feed pressure from 2 bar to 8 bar has no significant effect on the permeability of N_2, O_2 and H_2 resulting in almost unchanged selectivity of the gas pairs O_2/N_2 and H_2/N_2. The permeability of CO_2 has increased with feed pressure leading to increased and decreased selectivity of the gas pairs CO_2/N_2 and H_2/CO_2 respectively. The increase of operating temperature from 30 °C to 50 °C has a positive effect on the permeation of all gases and a corresponding negative effect on the selectivity of the gas pairs O_2/N_2, CO_2/N_2 and H_2/N_2.

1. Introduction

New membrane materials composed of polymer as a continuous phase and inorganic as dispersed phase, are called mixed matrix membrane (MMMs). In MMMs the beneficial aspects of polymer i.e. low cost and flexibility can be combined with the better thermal, mechanical and gas separation properties of inorganic phase to prepare membrane with improved gas separation properties as well as acceptable thermal, chemical and mechanical stability. The use of porous fillers i.e. zeolite [1,2], MOF [3] and ZIF [4] as a dispersed phase has shown to improve the gas separation performance of the polymer in the MMMs. Contrary to the use of porous fillers as dispersed phase in MMMs, a novel membrane design including non-porous nano size particles with polymer called as nanocomposite membrane was proposed by Merkel et al. and He et al. [5–7]. Their application fields have covered microfiltration [8], ultrafiltration [9–12], pervaporation [13] as well as gas separation [14,15]. It has been demonstrated that the inorganic moiety plays an important role in the improvement of the membrane performance since it can enhance the chemical, mechanical and thermal stability of composite membranes, tune the microstructure and improve the gas separation properties.

Many kinds of inorganic-nonporous nanoparticles have been introduced into the polymer matrix to prepare polymer–inorganic NCMs. Titanium dioxide (TiO_2) as a filler has received considerable attention because of its excellent chemical and thermal stability, hydrophilicity and gas separation properties [16,17]. The study conducted by Hu et al. [17] shows that the addition of TiO_2 to poly (amide–imide) in the NCM has shown an increase in the selectivity of the gas pairs CO_2/N_2 and H_2/N_2 and the specific interaction of CO_2 and H_2 with the TiO_2 domain has been considered for this. Therefore TiO_2 was chosen as a suitable dispersed phase in our current work to prepare NCMs. Literature review regarding the effect of inorganic non porous fillers on the membrane permeation shows three types of behavior. In the case of high free volume or poor packing polymers, addition of inorganic fillers disrupt the molecular packing of polymer, increase permeability and keep the

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selectivity unchanged [16,18]. Some of the studies using these high free volume polymers show reverse selectivity and the more condensable gases are preferentially separated from the non-condensable [5,7,15]. The second type of behavior is shown by the use of traditional polymers with inorganic fillers. In this case the membrane permeability may either decrease showing barrier property [17,19], or increase with maintaining selectivity, due the addition of nanogaps [20]. In the third type, some of the studies using traditional polymers with inorganic filler in the NCMs has shown to increase both the permeability and selectivity [21]. These variations in the separation properties may be due to change in the nature of the polymer matrix, filler type used and membrane making methodology.

PVAc is a medium T_g and good film forming polymer. Reported results from literature, show that this polymer has been used as a continuous phase with porous fillers to prepare MMMs. It was found that PVAc has good adhesion with the inorganic fillers and given reasonable separation performance for the gas pairs O_2/N_2 and CO_2/CH_4 [3,22]. Recently we have developed a laboratory methodology and prepared PVAc/zeolite 4A MMMs, where it is shown that the addition of 4A has improved the morphological, thermal and gas separation properties of the MMMs [23]. In the current study the same methodology was used to incorporate non porous filler TiO_2 and prepare PVAc/TiO_2 NCMs. To the best of our search this pair of polymer and filler has never been used in the literature to prepare NCMs. The combination of PVAc and TiO_2 for making NCMs can cause Ti–OH groups on the surface of TiO_2 to react with the alkyl group hydrogen of the PVAc chain, making hydrogen bonding at the interface. In this way PVAc molecules may be anchored to the surface of TiO_2 nanoparticles such that the surface of TiO_2 will be wrapped with the layer of PVAc.

The objective of this research work was to develop PVAc/TiO_2 NCMs. The addition of TiO_2 to PVAc is expected to improve the morphological, thermal and gas separation properties of the NCMs. In the current study pure PVAc and PVAc/TiO_2 NCMs were prepared and characterized by FESEM, XRD, DSC, TGA to find the effect of TiO_2 on the morphological, and thermal properties of the membranes. Finally single gas permeation was carried out to measure and evaluate the separation performance of gas pairs CO_2/N_2, H_2/N_2 and O_2/N_2.

2. Experimental

2.1. Raw materials

PVAc was purchased from Sigma Aldrich with an average M.wt of 100,000 and density 1.18 g/cm^3. It was provided in the bead shape and hydrophobic nature. TiO_2 used in the current study was AEROXIDE hydrophobic fumed TiO_2 P25, having a high specific surface area of 50 ± 15 m^2/g with an average particle size of 21 nm, supplied by Degussa, Germany. Dichloromethane (DCM) was purchased from Sigma Aldrich in spectrophotometer grade $>99.5\%$ pure, having density 1.325 g/cm^3 at 25 °C, M.wt 84.93, boiling point 40 °C and a solubility of 13 g/l in water at 20 °C. The low boiling point of DCM secure that it will need relatively shorter time to evaporate from the system and avoid sedimentation of the inorganic particles in the resulting NCMs.

2.2. Membrane preparation

Polymer–inorganic NCMs can be divided into two types according to their structure: (a) polymer and inorganic phases connected by covalent bonds and (b) solution blending method where the polymer and inorganic phases are connected by van der Waals forces or hydrogen bonds [24]. The solution blending method is a simple way to fabricate polymer–inorganic NCMs. This method is easy to operate and suitable for all kinds of inorganic materials where the concentration of the polymer and inorganic components is easy to control. Fore PVAc membrane, 10 wt% solution of the polymer in DCM was prepared. For NCM-01, the ratio of PVAc and TiO_2 was maintained at 99:1 in a solution containing 90 wt% solvent. The amount of solvent was increased as the amount of TiO_2 is increased and kept at 95 wt% for the NCM-10 and NCM-15. This was done to disperse the increased amount of TiO_2 nanoparticles efficiently within the PVAc. Although membrane with 20 wt % TiO_2 was also prepared successfully, however, it could not be used for permeation test due to its brittleness.

For NCM-01, the solution was sonicated for about 1 min at 60 amplitude without pulsation using direct ultrasonic processor to disperse the TiO_2 particles within the solvent. After that PVAc was added and the flask was put on the roller for overnight mixing. For higher contents of TiO_2, both the polymer and inorganic particles were separately dissolved in the solvent and then mixed together. The time of sonication was also increased such that the dispersion containing 15 wt% TiO_2 was sonicated for 20 min. Both the PVAc–CH_2Cl_2 and TiO_2–CH_2Cl_2 solutions were combined in a scotch flask and put on a magnetic stirrer for the same amount of time it was sonicated. The solution was then put on a roller mixer and left overnight to allow slow mixing of the polymer with the TiO_2 particles. About 6–7 ml solution was casted on a teflon plate and covered with a pin-holed aluminum foil. Inverted glass funnel with tissue paper in its outlet was used to control the fast evaporation of solvent from the surface of solution. After 24 h, dry and defect free membranes were obtained. Finally the membranes were annealed at 5 °C to give additional strength and make it suitable for permeation.

2.3. Membrane characterization

Optical microscope was used to determine the thickness of pure PVAc and PVAc–TiO_2 NCMs in the range from 25 μm to 35 μm. The cross section and surface morphology of the PVAc and PVAc–TiO_2 NCMs were examined using field emission scanning electron microscopy (LV FESEM, Zeiss supra, 55VP). The samples were fractured in liquid nitrogen and coated with gold before FESEM analysis. The wide angle X-ray diffraction of PVAc and PVAc–TiO_2 NCMs were recorded using Cu Kα radiation of wavelength $\lambda = 1.54$ Å with a graphite monochromator produced by Bruker AXS D8 focus advance X-ray diffraction meter (Rigaku, Japan). The X-ray scans were taken in the 2θ range from 4–80° with a scanning speed and step size of 1 °/mm and 0.01° respectively to identify any changes in the crystal structure and intermolecular distances between inter segmental chains. The thermal properties of PVAc and PVAc–TiO_2 NCMs were investigated using TA Q100 differential scanning calorimetry (DSC). The samples were heated from 0 °C to 100 °C under nitrogen atmosphere at a heating rate of 5 °C/min. Thermal stability of PVAc and PVAc–TiO_2 NCMs were evaluated by thermo gravimetric analyzer TGA (TA Q500). The TGA measurements were carried out under nitrogen atmosphere over the temperature range of 25–600 °C at a heating rate of 10 °C/min. Separation properties of PVAc and PVAc–TiO_2 NCMs were calculated from the single gas permeation of N_2, O_2, CO_2 and H_2 by the constant volume method using home-made permeation setup. Details of the permeation setup and membrane cell is given elsewhere [25]. A membrane with known thickness (L) was placed in the membrane cell and the system was evacuated for 24 h by a vacuum pump on both sides through a low pressure chamber denoted as LP with 100 ml capacity and high pressure chamber indicated as HP with a maximum pressure of 15 bar. After that the gas was allowed to pass through the membrane. The extent of gas permeating through the membrane was determined by measuring