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Journal of Membrane Science 310 (2008) 197–207

journal of MEMBRANE SCIENCE

www.elsevier.com/locate/memsci

Transport properties of polymer–aluminophosphate nano-composites prepared by simple mixing

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Received 25 June 2007; received in revised form 5 October 2007; accepted 28 October 2007
Available online 17 November 2007

Abstract

Nano-composite polymer–aluminophosphate membranes do not have molecular sieving properties as previously claimed. The layered microporous aluminophosphate $[Al_3P_4O_{16}]^+ \cdot 3[NH_3CH_2CH_3]^-$ was swollen with a surfactant and incorporated into cellulose acetate, Matrimid 5218©, UDEL P-3500©, PDMS, and a PDMS–6FDA–6FpDA co-polymer using simple mixing in organic solvents. It was anticipated that the addition of layered, microporous aluminophosphate to the polymer matrices would enhance the selectivity of large gas species compared to small gases through a molecular sieving effect. However, the selectivity was not improved using this technique due to insufficient exfoliation of the aluminophosphate and low dispersion of the particles into the respective polymer matrices.

Keywords: Gas separation; Mixed matrix membranes; Nano-composite membranes; Molecular sieving; Aluminophosphates

1. Introduction

It is known that the addition of small amounts of clay to some polymer matrices can reduce the permeability of gas species when compared to the neat polymer. Yano et al. reported the reduction of He, and O_2 permeability by one half with the addition of just 2 wt% of montmorillonite clay to a polyimide [1]. These types of materials are known as polymer clay nanocomposites (PCN). There are several review papers available on this topic, covering many different polymer clay systems [2–6]. A PCN can be formed using several different methods including melt intercalation [7,8], in situ polymerization [9,10], and simple mixing [11,12]. The objective of all of these techniques is to fully exfoliate the clay into the polymer matrix on a molecular level. Once the clay is dispersed at a molecular level, the high aspect ratio of the particles creates a barrier to gas transport through the matrix. The clay platelets produce a more tortuous path for a gas molecule traveling through the film, slowing diffusion for all gas species that permeate through the membrane. The current work will focus on the transport properties that result from dispersing a layered microporous clay-like aluminophosphate into several different polymer matrices using simple mixing in organic solvents.

The layered microporous aluminophosphate used for this work was $[Al_3P_4O_{16}]^{3-} \cdot 3[NH_3CH_2CH_3]^+$ (8MR-AlPO) which was first reported by Gao et al. [13] The crystals of this material contain sheet-like layers composed of aluminum and phosphorous tetrahedra separated by ethyl ammonium ions. The sheets are of comparable thickness and aspect ratio to montmorillonite clay. The difference is that the bonding in the framework structure of the 8MR-AlPO sheets forms a microporous net consisting of 4 × 6 × 8 rings. The largest 8MR has a diameter on the order of 4–5 Å which may be large enough for small kinetic diameter gases such as H_2, He, or CO_2 to pass through. The objective of this work is to investigate the hypothesis that if 8MR-AlPO is exfoliated into a polymer matrix, a small penetrant will pass through the platelets, while a larger gas molecule will take a tortuous path around the platelets resulting in a change in selectivity for the composite material when compared to a pure polymer.

Jeong et al. reported that the addition of 5–10 wt% of the aluminophosphate $[Al_3P_4O_{16}]^{3-} \cdot 3[NH_3CH_2CH_3]^+$ to a hexafluorinated polyimide improved the selectivity of small gases over large gases significantly [14]. The aluminophosphate and hexafluorinated polyimide when combined with simple mixing

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doi:10.1016/j.memsci.2007.10.056

resulted in membranes with dramatic changes in selectivity for some gas pairs. The selectivity of the gas pair He/CH_4 increased by 240% and the selectivity improvement for CO_2/CH_4 was 203% when compared with the neat polymer. These are startling increases. One way to verify these findings is to repeat these experiments using other polymer matrix materials with different transport properties. The matching of gas transport through the exfoliated 8MR-AlPO with that through a given polymer should lead to optimized selectivities [15].

A series of chemically different polymer matrix materials were chosen for comparison. The polymers used in this study were polydimethyl siloxane (PDMS), 20%PDMS–2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride–4,4′-hexafluoroisopropylidene dianiline (20%PDMS–6FDA–6FpDA), UDEL P-3500©, Matrimid 5218©, and cellulose acetate (CA).

2. Experimental

2.1. Materials

The layered aluminophosphate used in this study was $[Al_3P_4O_{16}]^{3-}\cdot 3[NH_3CH_2CH_3]^+$. This compound was synthesized according to well-documented procedures [16]. The surfactant molecules used to modify 8MR-AlPO were cetyltrimethyl ammonium chloride 25 wt% (Aldrich) in water, octadecyldimethyl benzyl ammonium chloride (Pfaltz & Bauer), and 1,12 diaminododecane (Aldrich) and were used as received. The polymer materials used include PDMS RTV615 (GE plastics), Matrimid 5218 (Ciba-Geigy), UDEL P3500 (Solvay Advanced Polymers), cellulose acetate (Eastman Chemicals), and 20%PDMS–6FDA–6FpDA co-polymer synthesized in our laboratory [17]. The reagents for the synthesis of the co-polymer included 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (Clariant Corp.), 4,4′-hexaflouroisopropylidene dianiline (SynQuest Labs Inc.), and aminopropyl terminated PDMS (Gelest Inc.). The structures of the polymers used in this study are shown in Fig. 1. The solvents used to dissolve the polymers were anhydrous tetrahydrofuran, THF, and chloroform.

2.2. Fabrication of polymer aluminophosphate composites

The technique employed to fabricate polymer aluminophosphate composites for this paper was solution intercalation by simple mixing. The concept involves dissolving a polymer in organic solvent followed by the addition of inorganic aluminophosphate to the solution. The objective is to intercalate the polymer chains into the gallery spaces of the aluminophosphate and exfoliate the layers into the polymer matrix.

The basic procedure used to make the polymer 8MR-AlPO solution was as follows. An amount of polymer that was equal to 10–15 wt% solids was dissolved in the THF or chloroform (polysulfone only). The required amount of swollen 8MR-AlPO was mixed in a small amount of the same solvent, stirred then sonicated in a bath (VWR 50HT) for 30 min. The solutions were combined and allowed to mix together at room temperature for at least 24 h. PDMS is a thermoset and therefore not soluble in its crosslinked form. Uncrosslinked PDMS was therefore diluted in THF before the addition of 8MR-AlPO. The THF was driven off before the crosslinking agent was added. The solutions were then cast onto either glass or a Teflon©coated pan. The solutions cast on glass were spread using a casting blade and the solutions cast in Teflon pans were simply poured. Each membrane was then annealed under vacuum in order to remove all of the residual solvent. The temperature was slowly ramped to the glass transition temperature of the polymer and held there for 1 h. The heat was then turned off and the membranes were allowed to cool to room temperature before the vacuum was removed. The

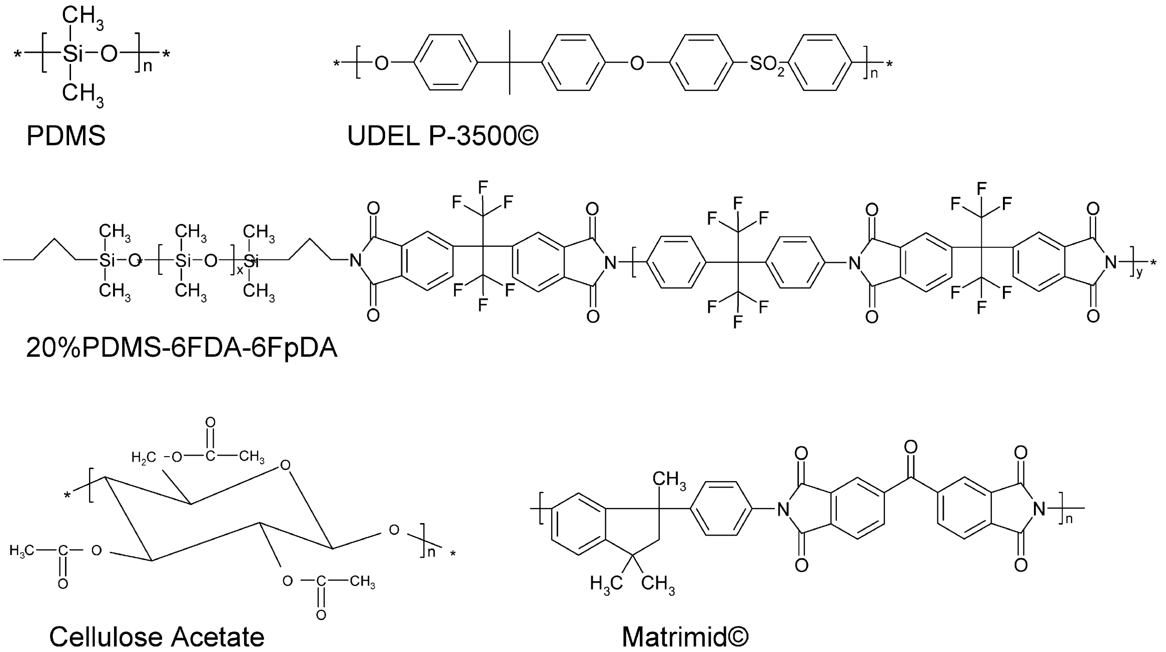

Fig. 1. Structure of polymers used for matrix composites.