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Influence of temperature upon properties of tailor-made PEBAX® MH 1657 nanocomposite membranes for post-combustion CO_2 capture

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ABSTRACT

Tailor-made block copolymer nanocomposite membranes are prepared by incorporation of 40 wt% methoxy poly(ethylene glycol) (PEG) functionalized polyoctahedral oligomeric silsesquioxanes (POSS) nanoparticles in commercial thermoplastic elastomer multiblock copolymer PEBAX® MH 1657. Atomic force microscopy was used to find out the location of the nanoparticles in the block copolymer matrix. Separation of CO_2 from N_2 and H_2 is studied by measurements of single gas transport properties of nanocomposite materials using the time-lag method in the temperature range 30–70 °C. PEG functionalized POSS nanoparticles increase the CO_2 permeability of the nanocomposite membranes without loss of CO_2/N_2 and CO_2/H_2 selectivity. Thermal properties of the nanocomposite membranes are studied by differential scanning calorimetry (DSC) to assess the stability of the nanocomposite membranes upon melting of polyether and polyamide blocks.

1. Introduction

One of the biggest challenges to ensure sustainable industrial growth and to mitigate climate change is to find an economically feasible separation technology for removal of CO_2 from the effluent flue gas streams. Economically, the advantage of membrane gas separation technology is immense. Simple process design and lower energy requirement compared to the conventional gas separation technologies (e.g. liquid adsorption) have paved the way for use of membrane technology in commercial CO_2 removal applications [1]. Large-scale industries, e.g. fossil fuel power plants, oil refineries and steel mills, emit enormous amounts of CO_2. Fossil fuel power plants alone are responsible for approximately 40% of the total CO_2 emission, coal-fired plants being the main contributor [2]. CO_2 selective membranes can offer a cost-effective post-combustion gas stream treatment process to lower the CO_2 emission of existing and future fossil fuel-based power plants. On average, a 600 MW coal-fired power plant generates 500 m^3/s of flue gas. In a typical coal-fired power plant, the flue gas after leaving the boiler is passed through an electrostatic precipitator (to remove particulates), a desulfurizer (to remove SO_2 gas), and then CO_2 can be separated. At this stage the water saturated flue gas is at about 50 °C, nearly atmospheric pressure and has a CO_2 content as low as 10–15% or CO_2 partial pressure of 10–15 kPa [3]. For this particular application the membrane must compensate the low driving force of separation with high CO_2 permeability and moderate selectivity over other gases [4]. Hence, there is an emerging research impetus to increase the permeability of the CO_2 selective polymers at the operating conditions of the power plant stack. Incorporation of nanofillers in the polymer matrix resulting in the formation of nanocomposite or mixed matrix membranes is a facile and efficient way towards this endeavor. Nanocomposite membranes can be prepared by physical blending [5–8] or chemical crosslinking [9,10] with nanosized fillers.

Gas transport through a dense polymeric membrane follows the solution-diffusion mechanism. According to this mechanism, the penetrants (i.e. permeating gas molecules) are adsorbed at the feed side of the membrane, then diffuse across membrane and finally desorb from the permeate side of the membrane. Permeability of a gas is a characteristic parameter for the membrane material, which depends on the solubility and the diffusion coefficient of the penetrant in the polymeric membranes [11,12]. Properties of both the penetrant and the polymer determine the transport of gases through the membrane. Small penetrant size, high polymer chain flexibility or high polymer fractional free volume and small polymer–penetrant interaction lead to enhanced gas diffusivity. On the other hand, strong polymer–penetrant interaction and high penetrant condensability increase

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the solubility [13]. Additionally, in polymer nanocomposite membranes interaction between the surface of the nanofiller with the surrounding polymer chains as well as with the permeating gases contributes to gas transport to a great extent. Hence, one of the biggest concerns in nanocomposite membrane preparation is to decorate the surface of the nanoparticle with a suitable functional group by covalent or non-covalent functionalization. Surface functionality of the nanofillers not only contributes to achieving homogeneous dispersion, but also creates an opportunity to tune the transport of penetrants through the membrane [14,15].

Advances in synthesis and functionalization of nanofillers have opened up a myriad of opportunities for tailoring the properties of traditional polymeric materials. However, in a block copolymer–nanoparticle composite the control of nanostructure and localization of nanoparticle as well as the fundamental understanding of structure–property relationship remains a challenge. The final morphology of the block copolymer nanocomposite is determined by a complex interplay of polymer conformational entropy, translational entropy of the nanoparticle and enthalpic interactions between the block copolymer segment and surface functional group of the nanoparticle. Hence, it is essential to explore new methods and develop a fundamental understanding to exploit this interplay in order to design novel functional materials [16–18].

Commercially available multiblock copolymers of the PEBAX® series consisting of an alternating sequence of flexible polyether and rigid polyamide blocks have already carved out a reputation as an appropriate choice for CO_2 separation membranes. Several studies on the structure and the gas transport properties of this block copolymer series have been reported [19–22]. Researchers have also tried to further explore the gas transport property of PEBAX®-based gas separation membranes by incorporation of numerous fillers [4,15,23–29]. In a previous work, we have reported that PEG functionalized POSS nanoparticle is a suitable nanofiller to improve the commercial viability of block copolymer membranes containing poly(ethylene oxide) segments [30,31]. Moreover, we have also reported PEG functionalized POSS nanoparticle containing an additional functionality can improve CO_2 separation property of the PEBAX® MH 1657 membrane [32]. In this paper we discuss the influence of elevated temperature upon CO_2 separation and stability of the PEBAX® MH 1657 nanocomposite membranes containing 40 wt% nanofiller aiming for post-combustion carbon capture application.

2. Experimental part

2.1. Materials

PEBAX® MH 1657 was purchased from ARKEMA. Glycidyl POSS® and glycidyldimethylsilyl POSS® were purchased from Hybrid Plastics®. Methoxy poly(ethylene glycol) (PEG) (M_n=350 g/mol) was purchased from Sigma-Aldrich®. All the solvents – chloroform, toluene, tetrahydrofuran and ethanol – were purchased from Merck KGaA.

2.2. Membrane preparation

The synthesized PEG modified POSS nanofillers were incorporated in PEBAX® MH 1657 (Arkema) via the solution casting method. The nanofiller content was 40 wt% with respect to the final composition of the nanocomposite. 3 wt% solutions of mixture of polymer and filler were prepared in a mixture of ethanol/water (70/30 wt %) under reflux (80 °C) for 2 h. The obtained homogeneous solution was cooled down to room temperature and poured into Teflon molds. Nanocomposite membranes were obtained by drying the solution at 40 °C for 24 h. The thickness of the membranes was measured using a digital micrometer.

2.3. Characterization

A Veeco MultiMode NanoScope IV atomic force microscope (AFM) operating in TappingMode™ was used to investigate the cross sections of the membranes at room temperature. Cross sections were prepared under cryogenic conditions with a Leica Cryo-Ultramicrotome EM UCT FCS equipped with a diamond knife.

A Zeiss “Merlin” scanning electron microscope (SEM) was applied to analyze the surface and cross section morphologies of the PEBAX®-based membranes at an accelerating voltage of 900 V. With energy selective backscattered (EsB) incolumn detector, the smallest differences in material composition of the membranes could be identified.

A DSC 1 (Star system) from Mettler Toledo was used to study the effect of incorporation of nanofillers upon thermal transitions of PEBAX® MH 1657 in the temperature range from −100 °C to 250 °C at the scan rate of 10 K/min using nitrogen as a purge gas stream (60 mL/min).

Single gas permeability, diffusion and solubility coefficients of N_2, H_2 and CO_2 were determined within the temperature range 30 °C–70 °C via the constant volume, variable pressure (“time-lag”) method. The feed pressure was 1 bar for all the gases. The following equations were used to determine gas permeability (P), diffusion coefficient (D), solubility (S) coefficients and ideal selectivity for pure gases ($\alpha_{A/B}$), respectively

$$P = DS = \frac{V_p l}{ART\Delta t} \ln \frac{p_f - p_{p1}}{p_f - p_{p2}} \tag{1}$$

$$D = \frac{l^2}{6\theta} \tag{2}$$

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A}{D_B}\frac{S_A}{S_B} \tag{3}$$

where V_p is the permeate volume, l is the membrane thickness, A is the membrane area, R is the gas constant, p_f is the feed pressure considered constant in the time range Δt, p_{p1} and p_{p2} are permeate pressures at time moments 1 and 2, Δt is the time difference between two points (1 and 2) on the pressure curve, θ is the time lag, and indexes A and B relate to gases chosen for calculation of permeability, diffusion and solubility selectivities.

3. Results

Glycidyl POSS (Scheme 1a) and glycidyldimethylsilyl POSS (Scheme 1b) are successfully modified with PEG (Scheme 1c) using three different solvent (chloroform, toluene and THF) via the epoxide ring opening reaction in the presence of boron triflouride diethyletharate (Scheme 1d) catalyst at room temperature. A large excess of PEG is used in the reactions to make sure that the reaction proceeds to completion, i.e. there are no unreacted epoxy rings left. Finally, the unreacted PEG is removed by extraction (using dichloromethane and water). The reaction occurs via SN2 mechanism in three of the investigated solvents. The solvent used for functionalization has a pronounced influence upon the final product of the synthesis. For discussion in this manuscript these nanoparticles are given acronyms (listed in Table 1). When toluene is used as the solvent, the reaction (i.e. in PEG-GLY-POSS-Toluene and PEG-GDMS-POSS-Toluene) occurs merely by a nucleophilic attack of PEG and no byproduct is observed. In chloroform, although ca. 80% of the epoxy rings are opened by PEG, some of the epoxy rings are opened by the catalyst