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Improving polysulfone membrane resistance to carbon dioxide induced plasticization during natural gas separation using functionalized carbon nanotubes

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ABSTRACT

Commercial natural gas, generally methane (CH_4), is described as the most efficient energy source with a calorific value per mass of approximate 50.1 MJ/kg. However, raw natural gas is made up of mostly methane and a considerable quantity of other components like C_{2+}, CO_2, water and hydrogen sulphide (H_2S) in varying composition from well to well depending on the geographical location and condition. Membrane technology for gas separation technology has become an acceptable method for CO_2 removal from natural gas. Majority of commercial natural gas separation membrane systems are polymeric due to processing feasibility and low cost. However, conventional polymeric membranes have reached a trade-off threshold between permeability and selectivity, and of great concern is CO_2 induced plasticization due to harsh industrial conditions such as high feed pressure. The addition of carbon nanotubes (CNTs) into polymers appears to offer a unique solution to the deficiencies of conventional polymeric membrane systems.

In this study, carbon nanotubes (CNTs) were produced using a catalyst-assisted chemical vapour deposition method. Ferrocene was used as the catalyst. Effects of carbon sources (acetylene and methane) and production conditions (temperature and type of carrier gas) on the physicochemical property of as-produced CNTs were investigated using field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS), electronic precision balance (EPB) and Raman spectroscopy. The best of as-produced CNTs was purified and functionalized using carboxylation protocol. The surface chemistry, thermal stability, textural property and crystallinity of the functionalized CNTs (FCNTs) were obtained using Fourier transform infrared spectroscopy (FTIR), thermo-gravimetric analysis (TGA), N_2 physisorption at 77 K and X-ray diffraction (XRD), respectively. CNT produced from methane and argon at 900 ^oC displayed the best quality with I_D/I_G ratio of 0.17 while the CNT produced from acetylene and mixture of argon and hydrogen at 1000 ^oC has the highest yield of 1.78 mg/s. FTIR confirms successful functionalization of CNTs. The degree of functionalization obtained from TGA is consistent with that of EPB. N_2 physisorption at 77 K indicates an

increase in pore volume and average pore size of the FCNTs indicating more adsorption sites for the adsorbate. Thereby suggesting that FCNT could be a good filler in membrane synthesis for gas separation.

Dense mixed matrix membranes (MMMs) were synthesized by incorporating functionalized CNTs (FCNTs) at different wt. % (0.2, 0.5, 1.0, and 1.5) into polysulfone (PSF) using evaporation method. The MMMs were characterized using field emission scanning electron microscopy (FESEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), atomic force microscopy (AFM) and texture analysis (TA). Single gas permeation experiment was conducted using a custom-built permeation set-up via constant volume variable pressure technique while mixed gas permeability was measured on a constant pressure variable volume gas permeation apparatus. Surface and cross-section morphology of the MMMs as depicted by FESEM show that the membranes are dense, indicating that the membranes consist of dense structure whose porosity is not observable under an electron microscope. Depth-at-max analysis of AFM images of the synthesized membranes further supports that the pores of the MMMs possess dense structure. TGA indicates improved thermal stability of the MMMs with increasing wt. % loading of FCNTs. DSC results show that the glass transition temperature (T_g) of the MMMs was also improved with the addition of FCNTs. However, the increase in wt. % loading of FCNTs does not significantly increase the T_g of the MMMs. Tensile strength and Young's modulus of the MMM obtained from TA show an increase in these mechanical properties with the addition of FCNTs. Single gas permeation results indicate an increase in CO_2 permeability as the wt. % loading of FCNTs increases up to 1.0 wt. % loading. Mixed gas separation shows similar trend without sacrificing CO_2/CH_4 selectivity.

CO_2 induced plasticization of the membranes was investigated experimentally and by phenomenological modelling. The sorption isotherms showed a typical dual-mode sorption model behaviour for all the types of synthesized membranes with the CO_2 concentration increasing rapidly at low pressures, which indicated a hole-filling of the Langmuir sites. At higher pressure, the rate of increase in the concentration declines due to the saturation of the Langmuir sites, the further

increase in the concentration at higher pressure is because of the penetrant sorption in Henry's law sites. The permeation isotherm of pure PSF indicated plasticization onset at CO_2 pressure of 12 bar. The MMMs showed no sign of plasticization over the pressure range tested (0-20 bar). This indicated an improvement in the CO_2 plasticization resistance of PSF by the addition of FCNTs. The developed model assumed three possible interface interactions in the MMMs; polymer matrix – polymer matrix, CNT – polymer matrix, and aligned CNT – CNT interface interactions. The model also accounted for the plasticization of the membrane. The model equation was solved by using the Levenberg-Marquardt algorithm in the Matlab environment to obtain the plasticization potential and the fraction of the gas held in Langmuir sites that have mobility within the membrane. The model CO_2 permeability is in good agreement with CO_2 permeability obtained experimentally. The PSF plasticization potential obtained is similar to ones reported in the literature. The fraction of the gas held in Langmuir sites that have mobility within the membrane increases with an increase in FCNT wt. % loading which shows high diffusivity through the microvoids with respect to diffusivity through the polymer matrix. This is an indication of an increase in Langmuir sorption sites for the penetrant thereby improving gas permeability.