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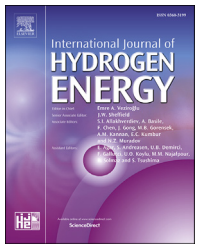

AFM imaging and nanoindentation of polymer of intrinsic microporosity PIM-1

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ABSTRACT

Polymers of intrinsic microporosity (PIMs) have promising gas adsorption properties for potential applications such as incorporation into high-pressure hydrogen storage tanks in an effort to increase the storage capacity or decrease the operating pressure. Such applications require detailed mechanical characterisation and determination of the structure-properties relationships to enable optimisation of the interface between the polymer and the tank. In this study, we show that Atomic Force Microscopy (AFM) nanoindentation can be used to determine the elastic modulus of cast PIM-1 films and that this property is depth-dependent. Average values of elastic modulus obtained experimentally were 1.87 GPa and are compared with elastic tensile modulus and storage tensile modulus obtained in previous studies. In addition, Scanning Electron Microscopy (SEM) and AFM imaging was performed to investigate the surface structure of the cast PIM-1 film, which has been shown to be highly granular.

Introduction

Hydrogen-based energy remains one of the most promising alternatives to carbon-based fuels used in traditional combustion engine vehicles. Hydrogen fuel has many advantages over petroleum as it is free of pollution and greenhouse gas emissions at the point of use. The abundancy of this element indicates that if a method to efficiently obtain hydrogen from its compounds is developed, a vast source of energy will be available. There are other issues that have to be solved in order to facilitate the deployment of hydrogen fuelled cars, such as fuel cell life time and efficiency, safety issues, and the need for an infrastructure to deliver the fuel, but a key challenge is the storage of hydrogen [1]. Hydrogen, as a result of its good energy density per unit mass but poor energy density per unit volume, requires either high pressurisation in 70 MPa tanks or liquefaction at 20 K. Both methods have their disadvantages; high pressure tanks raise safety concerns due to a high risk of leakage of the very small sized molecules through

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the tank wall, and liquefaction requires high energy input to cool the hydrogen to its condensation temperature and to maintain it in this state [2].

Storing hydrogen in solid materials, made of microporous structures, has recently drawn the attention of researchers due to the potential of obtaining very high densities of hydrogen within the pores, much higher than is feasible in high pressure or liquid form. This densification can be obtained thanks to physisorption which is a mechanism of adsorbing gas molecules on the surface of a material with a weak bonding. Many materials have been investigated in terms of their maximum hydrogen uptake [3–9] to determine if they might constitute a feasible alternative material for use in pressurized hydrogen tanks which is currently one of the main methods to store hydrogen for light duty vehicles. Potential materials properties of interest include rapid and completely reversible hydrogen sorption, efficient adsorption at relatively high temperatures and low pressures, thermal stability, and good mechanical properties [10,11]. These requirements are currently being met by microporous polymers which, due to their light weight and solution processability, are competitive candidates in this field. In this study, we have focused on the polymer of intrinsic microporosity PIM-1 which has shown good adsorptive capabilities, and rapid and completely reversible adsorption of hydrogen [12–17]. It has been previously investigated as a material for gas separation membranes [18,19] and its maximum hydrogen uptake has shown to be sufficiently promising (1.44 wt% per mass H_2 in 77 K, 1 MPa) [17] to investigate its potential as a hydrogen tank liner to enhance hydrogen storage capacity or decrease the operating pressure.

For potential applications in gas separation membranes, hydrogen storage media and tank liners, the determination of the mechanical properties of this material is necessary. The main properties of relevance include the ultimate stress, strain, and modulus of elasticity, which have been investigated in detail in previous studies [13,15,20–22]. Considering the specific application of the material as a hydrogen tank liner, additional properties should be determined. For example, as the tank may be filled at cryogenic temperatures, the determination of thermal stability and temperature dependent properties have been performed [20]. In addition, in order to ensure an appropriate mechanical interface between the tank wall and PIM-1 liner film, an analysis of film surface topography at the micro scale is required. The determination of the mechanical properties at a micro scale would also add to the understanding, optimisation and failure model of the tank-film interface. For solution-processable polymers that are formed by casting into films, only limited characterisation methods are available, such as a macro scale tensile test. In order to analyse the elastic properties of the material with a force applied perpendicularly to its surface, we have used a relatively new method, AFM nanoindentation, which can be employed to characterise materials with small volumes, such as films [23] or nanofibres [24,25]. Previously, only traditional indentation experiments using a Berkovich tip were reported, where average Young's modulus reached 1.876 GPa with a 1 μm indentation [21] and 2.8 GPa at 300 nm indentation [21,26]. Both techniques can determine material properties at a nanometric resolution, however AFM nanoindentation is considered more accurate on a smaller scale due to the lower tip radius (in range of nanometres instead of microns) and reduced indentation depth; thereby eliminating the influence of adhesion and plastic deformation on the measurement. This improvement is associated with the fact that in AFM the 'approach curve' is used to calculate the Young's modulus, whereby a 'withdrawal curve' is used in the case of traditional nanoindentation. AFM approach is particularly beneficial in testing low stiffness materials such as polymers [27]. A tensile modulus obtained in the above study [21] was in the range 1.2–1.7 GPa. A tensile storage modulus measured with dynamic mechanical thermal analysis of approximately 1 GPa was previously reported [13,20], as well as average tensile Young's modulus 1.26 GPa [20].

In this paper, we present the results of an AFM nanoindentation analysis that has been performed to determine the elastic moduli of the PIM-1 film at the micro scale at different indentation depths on the surface of the material. Additionally, we have performed AFM imaging to determine surface topography. The topography analysis was supported with analysis of the microstructure using scanning electron microscopy (SEM). To the best of our knowledge, this paper reports the first attempt to characterise PIM-1 films using an AFM nanoindentation technique.

Experimental

PIM-1 was prepared according to the original procedure published by Budd et al. [13]. A mixture of 3,3,3′,3'-tetramethyl-1,1″-spirobisindane, 2,3,5,6-tetrafluoroterephthalonitrile and potassium carbonate in anhydrous dimethylformamide was heated to 65 °C for three days. PIM-1 was isolated by filtration, washed with water and purified by repeated reprecipitations of chloroform solutions in methanol. The BET surface area of the material, obtained by analysis of an N_2 isotherm measured at 77 K (~750 $m^2\ g^{-1}$) and the molar mass distribution are in good agreement with the values found in the literature [14]. Self-standing films were cast from a 2 wt% solution of PIM-1 in chloroform poured into a large glass Petri dish and left to evaporate for at least 24 h inside a desiccator. This resulted in a bright yellow, transparent and flexible film, as presented in Fig. 1. After curing for an additional 8 h in a vacuum at 80 °C to remove residual solvent vapour, the film was cut into samples and characterised by AFM and SEM. The film thickness was on average 40 μm, as measured with an Absolute Mitutoyo Micrometer Screw Gauge with a measurement force adjustment.

SEM imaging of top and bottom surface of the film was performed using a JEOL JSM6480LV instrument. AFM imaging, roughness and mechanical properties were determined using an AFM JPK NanoWizard II system with ElectricMulti 75-G silicon probe with a resonant frequency of 75 ± 15 kHz and a force constant in range of 1–7 N m^{-1}. The elastic modulus of the samples was calculated after fitting to the Hertz-Sneddon model [28,29] for spherical contact using the following equation:

$$F = \frac{E}{1-\upsilon^2}\left[\frac{a^2+R^2}{2}\ln\frac{R+a}{R-a} - aR\right],\quad \delta = \frac{a}{2}\ln\frac{R+a}{R-a},$$

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