AFM Imaging and Nanoindentation of the 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 container. 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 1.45 GPa and are compared with elastic tensile modulus and storage tensile modulus obtained in previous studies. In addition, Scanning Electron Microscopy and AFM imaging was performed to investigate the surface structure of the PIM-1 film, which has shown to be highly granular.

Keywords:

polymer of intrinsic microporosity, PIM-1, hydrogen storage, mechanical characterisation, AFM nanoindentation

1. 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 –252°C. 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 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 % per mass H_2 in 77 K, 10 bar) [17] to investigate its potential as a hydrogen tank lines to enhance hydrogen storage capacity or decrease the operating pressure.

For potential applications in gas separation membranes, hydrogen storage medium and tank liner, the determination of the mechanical properties of this material is necessary. The main properties of relevance include the ultimate stress, stain, and modulus of elasticity, which have been investigated in detail in a 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 has 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, which 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 ± 0.13 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.

2. 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 hours inside a desiccator. This resulted in a bright yellow, transparent and flexible film, as presented in Fig. 1. After curing for an additional 8 hours 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.

(a) (b)

Fig. 1 Bright yellow transparent PIM-1 film cast in a Petri dish over University of Bath logo shortly after evaporation (a), PIM-1 film after removing from Petri dish (b).

SEM imaging of top and bottom surface of the film was performed using a JEOL JSM6480LV instrumnent. 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:

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

where *F* is the measured indentation force, *E* is Young's modulus of a sample, *v* is Poisson's ratio of a sample (assumed to be typical for polymers as 0.3), *α* is the half cone angle at the apex of pyramid indenter (10°), *δ* is the tip-sample separation and *R* is a radius of the spherical indenter. For small indentations (up to 5 nm), a sphere at the tip apex with radius equal to 10 nm was assumed. In order to obtain values of elastic moduli corresponding to different indentation depths, the Young's modulus was fitted to a Hertzian model within different ranges of the tip-sample separation curve. Indentations were performed 64 times within one square sample area 2.5 μm wide. The same experiment was performed multiple times to ensure repeatability.

3. Results and Discussion

SEM imaging was performed at different areas of the same sample and on the upper and lower surface of the cast film to ensure that the observed structures were typical for the PIM-1 films prepared as described in Section 2. In all cases, a microstructure similar to that shown in Fig. 2(a) was observed to be a dominant pattern, and was consistently present across the surface. An AFM image of the vertical cantilever deflection confirmed the granular-like structure of the film surface (Fig. 2(b)).

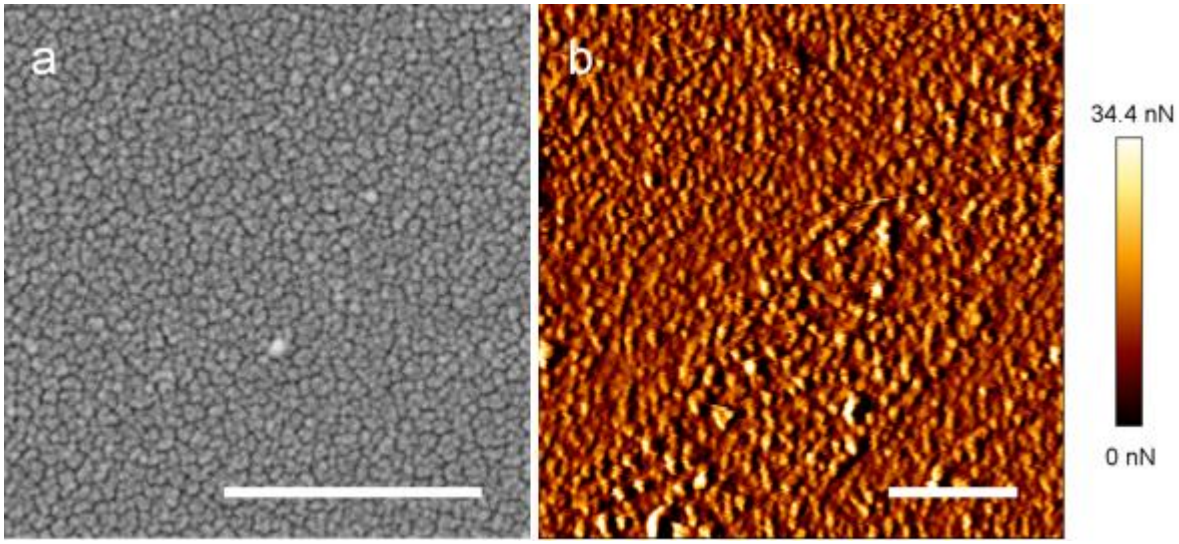

Fig. 2 SEM image (a) and AFM vertical deflection image (b) of PIM-1 film microstructure (bottom surface). Scale bar: 2 µm.

The average Young's modulus was measured to be 1870 MPa and it was observed that the modulus was dependent on the indentation depth. Modulus values obtained from curve fitting within different force-indentation ranges, and therefore different nanoindentation depths, are given in Table 1. Multiple indentations were performed to ensure that results are repeatable, and exhibit low standard deviations from the average (Table 1). The highest stiffness (2649 MPa) was obtained at smallest indentations and was observed to decrease with increasing depth to a value of 1487 MPa at a 5 nm tip immersion; see Fig. 3. This behaviour suggests that mechanical properties differ on various depths of film in the vicinity of the surface which may be due to a surface layer of the polymer film forming during evaporation of the solution. Relaxation of polymer chains may result in the formation of a stiffer outer layer, whereas at a deeper location within the film, the polymer remains more elastic. A strong influence of evaporation process on the microstructure of the polymer, manifesting itself with the appearance of macro pores within the film structure has been previously shown [20], which suggests that the mechanical properties can vary with depth.

The average Young's modulus was slightly higher than the tensile Young's modulus, and then the tensile storage modulus reported in a previous study [20] (1.87 GPa compared to 1.26 GPa and 0.97 GPa respectively), and then the storage modulus reported by Budd et *al.* [13] (1 GPa). Standard indentation experiments using a Berkovich tip performed by Song et al. showed comparable values at a depth of 1 µm; 1.88 GPa [21], yet, values obtained with smaller indentations were significantly higher 2.8 GPa [21, 26]. However, the tensile modulus from conventional mechanical testing was also higher which suggests slightly different film properties in general. This might in turn be caused by higher molar mass of the polymer used in the study (M_n = 58 000 g mol^{-1} in this study compared to 70 000 and 80 000 – 100 000 g mol^{-1} for the material used in previous works [21, 26]).

The observed difference in stiffness with depth suggests that cast films have two depth regions with different elasticities; an outer surface with a higher stiffness providing mechanical robustness to the film, and a lower stiffness interior. The more compliant interior can be beneficial in the case of providing access paths for pressurised hydrogen to penetrate inside deeper pores and channels could deform within their elastic limit to enable efficient packing of hydrogen. Understanding the inhomogeneous structure and elastic properties also enables further material treatment in order to obtain desirable properties, i.e. a layered materials with thin plies and surface layers will result in stiffer structures, whereas membranes

with a thicker elastic inside could undergo surface treatment to remove the stiffer outer layers and create more open pores for more efficient adsorption and faster equilibration. On the other hand, a stiffer bottom layer would provide lower mismatch between the elastic properties of both the liner and tank. The roughness, especially at the microscale, could have an important influence on enhancing adhesion between the tank surface and the polymer film, enabling efficient bonding of the two materials during the curing process.

Table 1 Young's moduli values on different depths of the polymer determined by AFM nanoindentation

Indentation depth [nm]	E [MPa]	Stand. Dev. [MPa]
1	2649	73
2	1962	49
3	1694	47
4	1551	56
5	1487	69

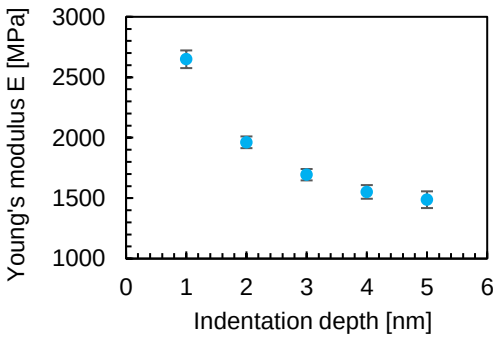

Fig. 3 Dependency of Young's modulus with AFM nanoindentation depth

4. Conclusions

We have employed atomic force microscopy (AFM) nanoindentation to determine the Young's modulus of PIM-1 films for the first time. The obtained results are in good agreement with previously reported tensile modulus and storage tensile modulus. Despite the fact that they describe elasticity of the material, these moduli reflect different properties of the material and therefore the moduli obtained with static tensile test, dynamic tensile experiments and indentations cannot be directly compared. However, we have shown that these parameters of elasticity have values close to each other which indicates that AFM nanoindentation method can be successfully applied to characterise PIM-1 film properties.

AFM and SEM imaging was performed to examine the microstructure of the PIM-1 film surface and its surface roughness was determined. We have also shown that elastic properties vary with depth of indentation which indicate that stiffness of the polymer surface is higher than the bulk. We attribute this to the evaporation mechanism and relaxation of polymer chains on the surface. Further analysis of the mechanical properties in cross-section will confirm this hypothesis, and the understanding of the mechanics of film surface will enable the development of additional functionalities of PIM-1 film for hydrogen storage, for example by employing further material treatment or optimising the film casting procedure. Processing the outer layers can enhance hydrogen adsorption and develop materials with depth-gradient of properties. For example, we can develop highly adsorptive structures with a partially impermeable surface giving the liner the potential to reduce hydrogen leakage through tank walls, whereas improved surface properties and roughness confer good resistance to higher pressures exerted on the liner.

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