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Force spectroscopy determination of Young's modulus in mixed matrix membranes

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HIGHLIGHTS

- Self-standing [BMIM][BF$_4$]/Pebax®1657 membranes were successfully prepared.
- AFM force spectroscopy determines mechanical properties of membranes.
- Good quantitative agreement between tensile tests and force spectroscopy.
- Nano-scale and bulk properties can be analysed, depending on the tip size.
- A silicon environment reduces capillary forces and improves data quality.

ARTICLE INFO

ABSTRACT

This paper presents Atomic Force Microscopy (AFM) as a powerful alternative to the more commonly used tensile tests for the analysis of the mechanical properties of polymeric membranes. The Young's modulus measurements by the traditional tensile tests were compared with AFM operated in Force Spectroscopy mode. AFM measurements were carried out with nanometric and micrometric tips on dense membranes of neat Pebax®1657 and on mixed matrix membranes of Pebax®1657 with different concentrations of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF$_4$]. The use of a nanometric AFM tip enables the determination of the local Young's modulus of the individual domains of the microphase-separated block-copolymer, while a larger tip gives average values of the bulk polymer. We found excellent correlation between the data obtained with common tensile tests and those obtained in compression by AFM with the micrometric tip, with important additional information on morphological features, when using the nanometric tip. This offers good perspectives for the analysis of samples where traditional tensile tests cannot be used, for instance composite membranes or particularly small samples.

1. Introduction

The development of novel materials with superior gas transport properties is needed for the exploitation of polymer gas separation membrane technology in new markets or for the replacement of traditional technologies [1]. Alongside the synthesis of completely new materials, an interesting method to improve the gas separation performance of a material is the preparation of mixed matrix membranes (MMMs), i.e. the incorporation of a filler in the polymer matrix [2,3]. The main idea is to combine the good processability and mechanical stability of the polymer, with the superior gas transport properties of suitable fillers, including ionic liquids (ILs) [4–6]. ILs possess thermal

and chemical stability, low vapor pressure and a tunable nature [7]. Their exceptional properties offer interesting perspectives in the field of CO_2 capture, storage and utilization. Mass transport in ILs is usually much faster than in polymeric materials, thus allowing higher fluxes through the membrane [8]. High performance membranes must couple superior gas transport properties to mechanical and chemical stability at the working conditions. Jansen et al. [9] have demonstrated that the mechanical properties of IL containing membranes may be correlated with their transport properties. The analysis of the mechanical properties can be useful for their practical applicability in industrial modules, because in many processes the membranes are subjected to high pressures. Traditionally these properties are investigated by tensile tests

or rheological characterization [10]. However, these techniques require often quite large sample sizes, which are not always available for novel experimental materials. When only small membrane samples are available, Atomic Force Microscopy (AFM) may allow the quantitative and qualitative investigation of the mechanical properties on different scales [11–14], besides being a tool for imaging surface topography [15].

In this work, the mechanical properties of the rubbery Pebax®1657, with different amounts of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]) are investigated. Pebax®1657 is an elastomeric multiblock copolymer, with a molecular structure consisting of amorphous rubbery polyether blocks and semi-crystalline polyamide blocks. This polymer is already used for CO_2 removal from light gases [16] and here we propose further modification by the incorporation of ionic liquids. The choice of the particular IL, [BMIM][BF$_4$], is dictated by the results of previous works, which show that ILs containing fluoroalkyl chains improve the CO_2 solubility [17,18]. The proposed Pebax®/IL membranes present a complex multiphase system with different local mechanical properties.

The aim of this paper is to develop AFM tools, which have been consolidated for pure polymers [19], as a valid alternative for analysis of the mechanical properties by tensile tests of much more complex systems such as the present mixed matrix membranes. Mechanical properties measured on three different scales are discussed. Measurements on micro- or macro scale provide information on the bulk properties; AFM analysis on nano-scale provides additional information on the local morphology. A good match between the mechanical properties measured by the traditional tensile tests and by AFM force spectroscopy on micro scale is found, ensuring the reliability of the latter method for the characterization small scale membrane samples. We anticipate that after appropriate optimization, similar studies may also be performed to analyse the mechanical properties of thin film composite membranes [19], where traditional tensile tests would fail due to the presence of the support layer.

2. Experimental part

2.1. Materials

Ethanol (99.5%) and polydimethylsiloxane oil with a density of 0.95 kg L^{-1} were purchased from VWR. Pebax®1657 multi-block copolymer of poly(ethylene oxide) (PEO) and poly[imino(1-oxohexamethylene)] (PA6) in molar ratio 60/40 was kindly provided by Arkema as pellets (Fig. 1). The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]) was supplied by Sigma-Aldrich (Fig. 1). All products were used without any further treatment. The gases used in the permeation tests (nitrogen, oxygen, methane, helium, hydrogen and carbon dioxide, all with purity of 99.99 + %) were supplied by Sapio.
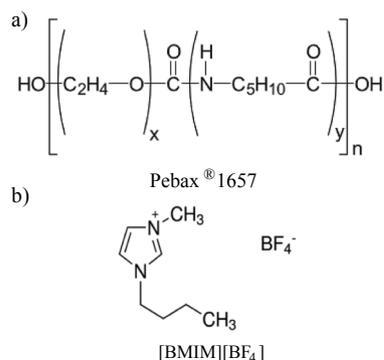
Fig. 1. Structures of the polymer (a) and the ionic liquid (b) used in this work.

2.2. Membrane preparation

The polymer solution (8 wt%) was prepared by swelling the Pebax pellets in a mixture of ethanol/water (70/30 wt%) under stirring for 24 h, after which the solution was left for 2 h at 80 °C under reflux and vigorous stirring. The ionic liquid was added to the hot polymeric solution in different amounts (0–40 wt% on the basis of the final membrane weight after solvent evaporation). The resulting solution was stirred until it became homogeneous and then it was poured into metal casting rings on a glass plate. Slow evaporation of the solvent at room temperature yielded translucent self-standing dense membranes.

2.3. [BMIM][BF$_4$] absorption in Pebax®1657

Membrane samples of pure Pebax®1657 with a diameter of 47 mm were immersed in an excess of [BMIM][BF$_4$] to analyse the spontaneous IL absorption. The experiments were carried out at temperatures of 25 °C, 35 °C, 45 °C, 55 °C, 65 °C and 80 °C. The absorption of ionic liquid was determined by monitoring the weight and volume change of the samples as a function of the time and temperature. For all temperatures, the samples were soaked for sufficiently long time in the IL to reach steady state sorption (generally up to 60 h).

2.4. Gas permeation analysis

Single gas permeation tests were performed as described elsewhere [20] on a fixed volume/pressure increase instrument, constructed by Elektro & Elektronik Service Reuter. Tests on all membranes were carried out at 25 °C and at a feed pressure of 1 bar. The effective membrane area was 11.3 cm^2 and the gases were tested in the order H$_2$, He, O$_2$, N$_2$, CH$_4$, and CO_2. Permeabilities (P) were reported in Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}), and the diffusion coefficient (D) was determined with the time-lag method according to the equation:

$$D = \frac{l^2}{6\Theta} \tag{1}$$

where Θ is the so-called diffusion time-lag and l is the membrane thickness. The gas solubility coefficient (S) is calculated assuming the validity of the solution-diffusion model as the ratio of the permeability over the diffusion coefficient:

$$S = \frac{P}{D} \tag{2}$$

2.5. Scanning electron microscopy

The morphology of the membrane surface was studied by scanning electron microscopy (SEM, Phenom ProX Desktop model) at room temperature, applying an acceleration voltage of the primary electron beam of 10 kV. SEM images were acquired in backscatter electron imaging mode. The samples were sputter-coated with gold to eliminate charging effects and to optimize the sample resolution.

2.6. AFM morphology and phase image

AFM analysis was performed at room temperature in air on a Multimode 8 AFM system with a Nanoscope V controller (Bruker) providing a phase image, while simultaneously imaging the topography. The measurements on membranes of Pebax®1657 were acquired with probes with a conical tip with and a nominal end-radius of 10 nm at a resonance frequency of 320 kHz.

2.7. Force spectroscopy

Measurements were performed at room temperature in air and in