Surface and bulk porosity mapping of polymer membranes using infrared spectroscopy

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ABSTRACT

The porosity is a key characteristic parameter and significantly influences the behavior of a membrane in a given application. This work demonstrates the use of infrared (IR) spectroscopy for mapping the porosity of polymer membranes. Conventional transmission IR spectroscopy is employed to assess the bulk porosity across the entire thickness of a polyethersulfone (PES) membrane, while attenuated total reflection IR (ATR-IR) provides information about the porosity of a thin layer at the membrane surface. The results indicate that the bulk porosity of the studied membrane is rather homogeneous while the surface porosity is characterized by systematic local deviations from its mean value up to about 30%. IR spectroscopy turns out to be a suitable and straightforward method to characterize the porosity distribution of membranes.

1. Introduction

Polymer membranes are gaining an ever increasing interest in the engineering and science disciplines [1,2]. They have been traditionally used for size exclusion applications such as micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF), and reverse osmosis (RO). Membrane bioreactors (MBR) are now widely used for municipal and industrial waste water treatment [3,4]. Membranes are also used as support matrices for immobilization in the fields of biosensors and enzyme based bioreactors [5–7]. Moreover, affinity and ion-exchange chromatography with functionalized membranes is increasingly applied in the pharmaceutical and biotechnology industry [8–10]. However, due to the large number of available materials and preparation procedures, the characterization of membrane properties is becoming more and more important in order to predict the membrane performance in a given application. Needless to say, that such characterization should involve both bulk and surface properties including the chemical as well as pore structure at various scales. In addition, it should be fast, require no special sample preparation, be non-destructive, and be user-friendly.

The surface of a membrane is particularly interesting as it represents the direct interface with the fluid system to be treated;

hence, knowledge of the surface chemical composition and porosity is essential. In the past, a number of analytical methods have been employed to characterize the surface of membranes. A good overview was provided in the book of Xu et al. [11]. The chemical composition is normally probed by techniques such as attenuated total reflection infrared (ATR-IR) spectroscopy [12,13], X-ray photoelectron spectroscopy (XPS) [14,15], mass spectrometry (MS) [16,17], and energy dispersive X-ray (EDX) spectroscopy [18,19]. For analyzing the surface morphology it is common to use microscopic methods including confocal laser scanning microscopy [20,21], scanning electron microscopy (SEM) [22,23], and atomic force microscopy (AFM) [24,25]. All those microscopic techniques provide very good spatial resolution in the order of micrometers or even better. However, this may sometimes be a disadvantage: micrometer resolution will facilitate accurate characterization of a small sample area (in the order of mm × mm) but it may be not practicable to screen a full membrane at cm or dm scale; hence large scale abnormalities may not be picked up.

In order to overcome this problem, we propose the use of ATR-IR and transmission IR spectroscopy for determining the surface and bulk porosity of polymer membranes, respectively. It typically provides a spatial resolution of about a millimeter. This means it is not suitable for analyzing nano- or microscale structures but it can provide measurements over a larger sample area. As aforesaid, ATR-IR is a common tool for studying the surface chemistry of polymer membranes, for example to characterize protein fouling on standard and functionalized membranes [12,26,27]. In the present work, we make use of the fact that the measured absorbance is a function of

the local porosity: simplistically speaking, the lower the absorbance the higher the porosity. Consequently, ATR-IR and transmission IR spectroscopy can be employed for mapping the porosity of an entire membrane in a straightforward manner. In order to prove the concept, we study a polyethersulfone (PES) membrane commonly employed in ultra- and micro-filtration processes as well as chromatography applications. The next section describes the experimental procedure and presents an approach for avoiding mechanical damage to the membrane. This is followed by a theoretical assessment of the signal–porosity relationship to allow quantitative information to be extracted from the experimental data. Subsequently, results from the PES membrane in terms of porosity maps are presented and discussed. The final section concludes.

2. Experimental

The experiments were carried out on a Bruker Vertex 70 instrument equipped with a Platinum ATR accessory. The internal reflection element (IRE) was a single-reflection diamond crystal. IR-spectra were recorded with $2\,cm^{-1}$ resolution and 16 scans were averaged in order to obtain good signal to noise ratio. The ATR measurement area was a circular spot of approximately 1.5 mm diameter. The measurement spot was stepwise moved across the membrane to obtain a two-dimensional map of spectral information. The membrane studied was taken from a Mustang Q XT5 anion-exchange membrane chromatography capsule purchased from Pall Inc. (East Hills, NY, USA). It is a modified hydrophilic polyethersulfone (PES) membrane whose surface is coated with an irreversibly cross-linked polymer containing pendant Q groups. In the XT5 capsule, 15 layers of flat membrane sheets are stacked with a total bed height of 2.20 mm and a frontal area of $22.06\,cm^2$. One membrane sheet of 0.15 mm thickness and 6 cm diameter was investigated in this study.

The membrane was pressed onto the ATR crystal in order to have sufficient contact with the surface and allow interaction with the evanescent IR field. Initially, the metal stamp of the instrument was used for this purpose as illustrated in Fig. 1a. However, this lead to irreversible mechanical damage of the membrane as indicated by the arrows in the enlarged image of Fig. 1c. This could not only be observed with the naked eye, but also was evident in the spectra as discussed below. To overcome this problem, a rubber bung was placed in between the stamp and the membrane (see Fig. 1b), which helped to distribute the mechanical force to a larger area.

The spectra obtained either with the stamp only or with the rubber bung are displayed in Fig. 2a. Those recorded with the stamp only show a 50% higher absorbance. This can be attributed to the fact that the force is sufficiently high to mechanically compress the porous material and increase the polymer density at the crystal surface. The marks and the change in absorbance are not the only signs of the irreversible damage. Fig. 2b displays normalized spectra of the peak at $554\,cm^{-1}$, which can be assigned to an aromatic out-of-plane CH bending mode [28]. It is clear that the spectral shape as well as the peak position change significantly when the metal stamp is used. A red-shift of about $1\,cm^{-1}$ is observed, which indicates a weakening of the CH bonds, which in turn can be interpreted as strengthened intermolecular interactions at this location [29,30]. Such interactions can be facilitated when the porous material is mechanically compressed: the walls at opposite sides of a pore can touch each other and form, e.g. hydrogen bonds. With the rubber bung in place such effects were not observed and the measurement was fully reproducible.

For the transmission IR measurements, the ATR accessory was removed and the membrane was mounted on a translation stage which allowed the measurement position to be varied systematically. A 1.5-mm pinhole was inserted into the IR beam in order to obtain a spatial resolution similar to the ATR experiment. The instrument settings were identical.

3. Signal–porosity relationship

In order to convert the measured absorbance values to a porosity map, the relationships between the signal and the desired property must be understood. Owing to the different absorption path lengths, the transmission and attenuated total reflection cases must be considered individually. Both cases are based on the Beer–Lambert relation

$$A = -\lg T = \varepsilon(\lambda)cl_{eff} \tag{1}$$

where A is the absorbance, T is the transmission, ε is the molar absorptivity as a function of wavelength λ, c is the concentration of the absorber, and l_{eff} is the effective absorption path length. For the following considerations we assume that the light scattering contribution to the extinction is negligible, which is justified at the long wavelengths in the mid-infrared as scattering phenomena normally scale with λ^{-4}.
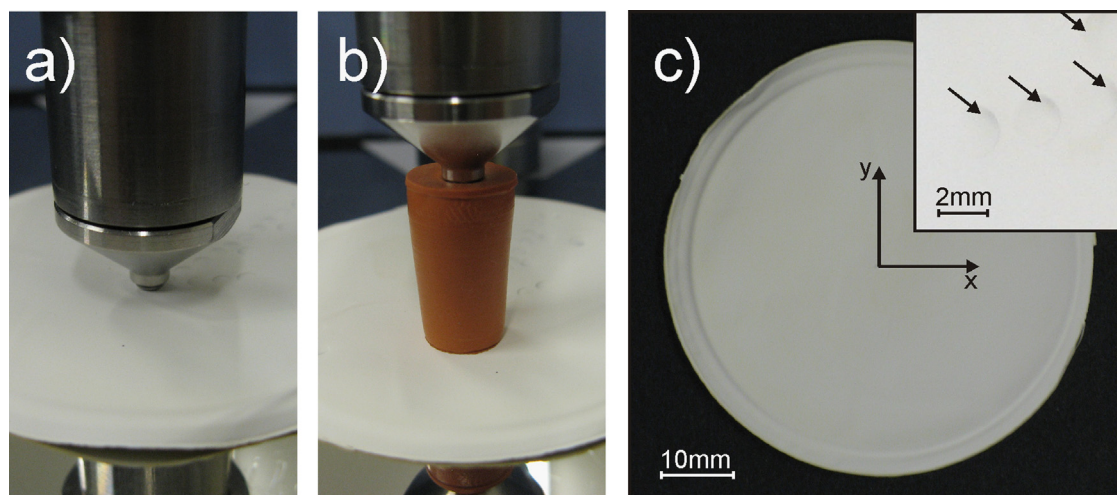

Fig. 1. Photographs of (a) the membrane pressed onto the ATR crystal with the metal stamp, (b) the membrane pressed onto the ATR crystal with the rubber bung, (c) the full membrane with the coordinate system indicated. The enlarged inset in (c) shows the marks indicating local mechanical damage due to the treatment with the stamp.