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In-situ non-invasive imaging of liquid-immersed thin film composite membranes

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ABSTRACT

We present a non-invasive method to directly image liquid-immersed thin film composite membranes. The approach allows accessing information not only on the lateral distribution of the coating thickness, including variations in its swelling and density, but also on the distribution of substrate porosity, roughness, accessibility of pores to liquid, and even the degree of pore intrusion related to the thin layer deposition process. The method can be particularly helpful in the fields of functional coatings or membranes to allow laterally-resolved studies under realistic application conditions thereby opening completely new research avenues. The approach is demonstrated in a study of two polymers of intrinsic microporosity, PIM-1 and PIM-6FDA-OH, coated on polyacrylonitrile support and immersed in water. Variations of the skin morphology using different coating methods (floating, spin-coating and dip-coating) are evaluated with the help of the presented method. Surfaces of at least tens of cm^2 can be potentially analyzed.

1. Introduction

Direct imaging of lateral surfaces is pertinent to many fundamental- and application-oriented studies. The control of thickness and density distributions on planar substrates is crucial, for instance, in the fields of coatings, catalysis, biosensors, micro-nano fabrication, microfluidics or membrane technology. Among numerous available imaging methods the light-based techniques, such as Brewster angle microscopy (BAM) [1], microinterferometry [2], total internal reflection ellipsometry [3], imaging spectropolarimetry [4], or (spectroscopic) ellipsometry imaging [5,6] have the advantage of being relatively easily implementable, inexpensive, fast, non-contact and non-destructive. These characteristics are key when considering possibilities of in-situ analysis of coatings or membranes immersed in a fluid.

The possibility to image thin films on porous substrates in the presence of a liquid medium would be of large benefit for membrane applications. Industrial membranes are used to efficiently separate mixtures on size-scales ranging from several mm down to single molecules. For the separations on a molecular level often layered composite configurations are used, where a thin, dense layer is deposited on a porous, highly mechanically stable and permeable substrate. During membrane operation various factors play important roles, including the behavior of both the support and the skin layer in terms of swelling, stability or stimuli responsiveness, as well as a possible deposition of other components on the membrane surface (e.g. fouling). When a membrane is removed from its operating environment, for instance to perform surface analysis, its structure may change irreversibly thus complicating drawing meaningful conclusions about the in-situ state. Moreover, in reverse osmosis (RO), organic solvent nanofiltration (OSN) or gas separation (GS) only the very interaction of the membrane with the separated mixture gives rise to its proper operation as membrane transport properties adapt to the liquid feed and permeate compositions. Until now a suitable non-invasive method for investigations of operating membranes was lacking.

One of the most powerful of the optical techniques is spectroscopic ellipsometry [7], where a change in the light polarization state reflected from a thin film is used to gain information on the sample structure, including the thicknesses and refractive indices of multilayers. Because ellipsometry is non-destructive, as opposed to e.g. scanning electron microscopy, the technique can be used to study thin films on dense or porous substrates in-situ in a presence of the separating medium. In-situ ellipsometry requires the use of a dedicated measurement chamber with optical windows to feed the probing light in and out while maintaining the desired measurement environment (high pressure, liquid, desired pH etc.) [8]. Ellipsometry has been used to study swelling and aging phenomena in thin films of glassy polymers designed for gas separation

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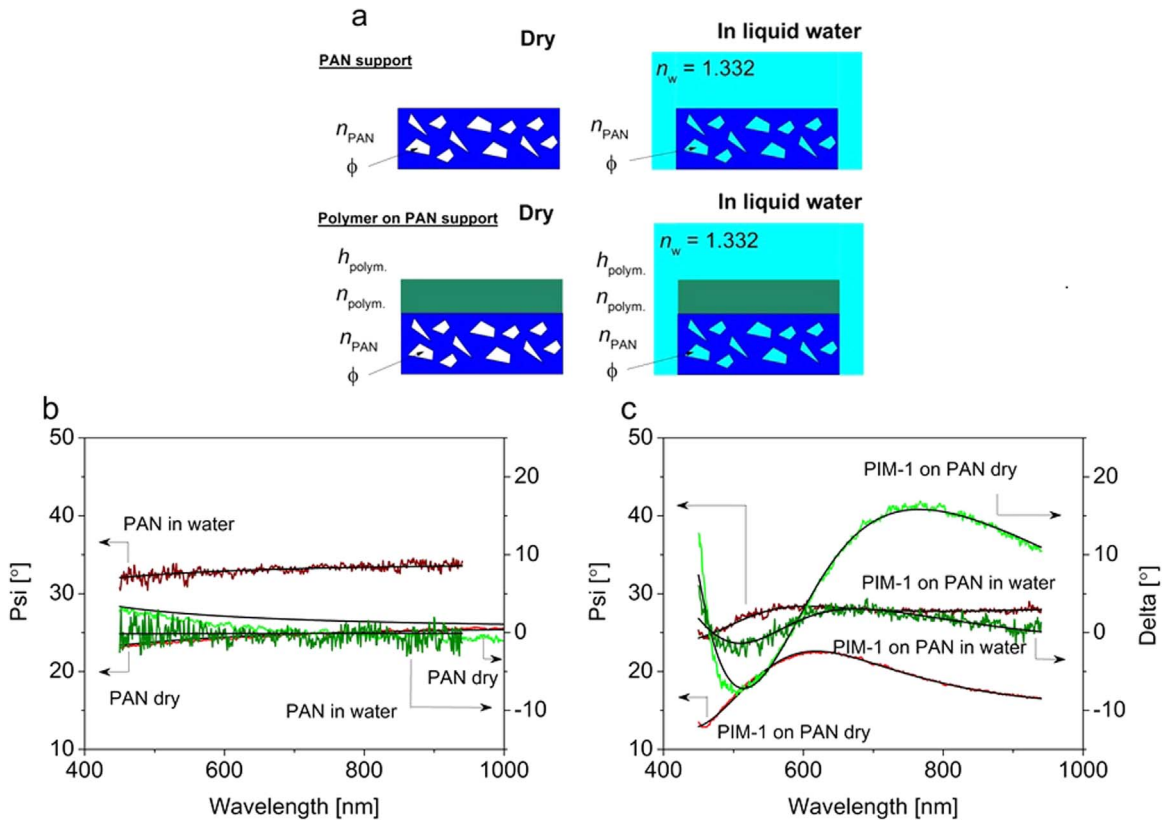

Fig. 1. Scheme of the optical models used to image membranes together with model fit parameters (a) Psi and delta spectra (red and green lines) together with model fits (black lines) for bare dry and water-immersed porous PAN support (b) Psi and delta spectra (red and green lines) together with model fits (black lines) for a dry and water-immersed 200 nm PIM-1 coated on top of the porous PAN support (c). The data in (c) shows oscillations in the Psi and Delta spectra as a result of polarized light interference caused by a film presence on top of PAN support. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

applications [9,10], study diffusion kinetics of organic solvents in thin polymer layers [11], investigate the response of swollen layers under hydrostatic pressures in the context of the solution-diffusion or pore flow models [8], or pH-responsiveness of ultra-thin RO skins [12].

While ellipsometry imaging on dense substrates, e.g. silicon wafers, glass slides or metals, has been under accelerating development roughly since the mid 1990-s, it remained challenging to apply the technique on porous substrates in-situ. The main difficulties are the reduced reflected light intensity, surface scattering and light depolarization originating from the roughness of porous materials, as well as typically rather poor optical contrast between the thin film and the porous substrate. Overcoming these challenges at least in some cases would open a range of entirely new possibilities in studying the processes of swelling [8], fouling [13], surface modification [14,15], stimuli-responsiveness [16] or stability of various membrane systems.

In this work we present a novel method based on spectroscopic ellipsometry to directly image interface structure of composite membranes in-situ in a liquid environment. The sample membrane consists of a dense polymeric glassy film made of either one of two polymers of intrinsic microporosity (PIMs), PIM-1 or PIM-6FDA-OH, deposited on a well defined, relatively smooth porous polymer support (polyacrylnitrile, PAN). The used PIMs belong to a promising class of new membrane materials with permeabilities and selectivities much above those of the state of the art polymers. The presented approach is, however, not limited to PIMs and will be largely analogous in case of other composite membranes.

2. Results and discussion

Polyacrylonitrile (PAN)-based polymeric supports are frequently used in membrane technology because they show very limited swelling and high stability in most common solvents. PAN can also be easily prepared as a relatively smooth and highly porous substrate, which aids subsequent deposition of separating dense layers. PIM-1 and PIM-6FDA-OH belong to a very promising class of polymers of intrinsic microporosity (PIMs) where an exceptionally rigid polymer backbone hinders chain packing and creates excess free volume fractions often above 25%. As a result very high permeabilities and good selectivities are observed when PIMs are used as a membrane to separate mixtures. PIM-1 has been under intense research in such applications as gas separations [17,18], solvent filtration [19] and even battery technology [20,21]. PIM-6FDA-OH [22] combines features of PIMs (microporosity) with those of functional polyimides (higher polarity and affinity to water), and has been developed for natural gas processing. The approach presented in this paper is valid for other types of substrates and coatings as well, for instance, for membranes used in RO or NF, bio-sensors, barrier layers, as well as ceramics [23]. The necessary conditions include limited surface roughness, with size-scale much below light wavelength to limit scattering and depolarization effects, and sufficient optical contrast at the fluid/thin film and thin film/substrate interfaces.

In spectroscopic ellipsometry the reflection coefficients (r_p for in-plane, r_s for out-of-plane of incidence, respectively) are measured and converted to two characteristic angles, psi and delta by:

$$\rho = \frac{r_p}{r_s} = tan(\Psi)\cdot e^{i\Delta} \quad (1)$$

To extract useful sample properties, such as film thickness or refractive index, optical modeling is necessary. For thin films deposited on substrates the optical models usually consist of a layer(s) representing the film(s) and a bulk layer representing the support. Each of these layers is assigned a set of fit parameters related with, e.g. refractive index, extinction coefficient or thickness (for films). In this process psi and delta