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Atomic force microscopy of nanofiltration membranes: Effect of imaging mode and environment

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ABSTRACT

The atomic force microscope (AFM) has become a useful tool for studying the morphology of membrane surfaces as well as their fouling characteristics. One principle advantage of the AFM over other high resolution imaging techniques is the ability to make observations in both ambient air and liquid environments. Diverse imaging modes also exist, each with their own advantages and disadvantages. In this study two different imaging modes in both air and water are compared when examining two different nanofiltration membranes, to compare the strengths and weakness of different methods of obtaining surface topography when applied to nanofiltration membrane characterization. When imaging the more hydrophobic of the two membranes using tapping mode in a water environment features consistent with the existence of surface adhered nanobubbles were observed. Such features have implications for the fouling of membranes by hydrophobic materials, as well as effects on the ability to image hydrophobic membrane surfaces under such conditions.

1. Introduction

As an imaging technique AFM is capable of resolving features from a few micrometers down to the sub-nanometre scale [1–3] for both conducting and non-conducting surfaces, does not require vacuum to function, and is capable of visualising samples under ambient conditions as well as in liquids. This is of great use to researchers interested in studying membranes and other surfaces, which are routinely exposed to aqueous solutions, as it means that they may be studied in their operational environment.

Contact mode is often the mode of choice when imaging a hard and flat surface due to its simplicity and relatively high speed of operation. However, the high forces with which the probe interacts with the sample can cause a deformation of the sample leading to an increase in contact area between the probe and the surface, reducing the resolution. Lateral forces can occur when the probe traverses steep edges on the sample, which may cause damage to the probe or the sample, or also result from adhesive or frictional forces between the probe and sample leading to a decrease in the resolution due to stick-slip movement of the probe tip over the surface.

Where a soft, and therefore easily deformable and easily damaged, sample is to be imaged, dynamic modes of imaging, such as intermittent contact or noncontact modes, are usually preferable. In order to overcome the limitations of contact mode imaging as mentioned above, the intermittent contact, or tapping, mode of imaging was developed [4–6]. During tapping mode the cantilever is allowed to oscillate at a value close to its resonant frequency bringing the sharp tip into intermittent contact with the surface. In this manner lateral forces, as the probe is scanned across the surface, may be greatly reduced in comparison to the contact mode.

1.1. AFM of nanofiltration membrane surfaces

Over the past decade and a half the AFM has been increasingly used to study membrane surfaces both in air and in a variety of liquid environments [7–14] due to the ability to measure surface roughness, pore size and pore size distribution, as well as measurement of interaction forces between membrane surfaces and foulant particles. The first reported measurements specifically of nanofiltration membranes reported in the literature were made by Bowen et al. in 1995 [10,15] examining their appearance in air. Much of the early work in the characterization of nanofiltration membranes using AFM techniques were comprehensively reviewed previously by Hilal et al. [16], with studies concentrating on measuring surface roughness, pore diameters and the pore size distribution.

Boussu et al. [17,18] compared tapping and non-contact modes when used to study nanofiltration membranes. They found that the two modes gave different roughness values, but ranked the membranes in the same order of roughness, with tapping mode showing

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a greater difference in roughness between each membrane than was seen with non-contact mode. In addition an increase in the root mean squared (RMS) roughness with increasing scan area was noted. The authors attributed this to the dependency of this measure of roughness on the spatial wavelength of the scanned area and also possibly due to the formation of a fractal structure on the membrane surface when polymers become assembled as nodules.

Great care must be taken when identifying pores and assigning pore sizes. Firstly it must be remembered that the AFM can only give the sizes of the openings of the pores, and does not give any information about their sizes in the interior of the membranes, which is a possible reason for any discrepancies in values obtained from other methods studying flow through the membrane. Also features observed at high resolution are actually a convolution between the geometry of the probe tip and the actual surface. This may lead to broadening of protrusions on the surface and also a possible reduction in the observed diameter of pores [19]. The ability to observe pores of size lower than the probe tip radius of curvature as seen with nanofiltration membranes has been attributed to possible imaging by the serendipitous presence of small asperities on the probe tip surface [19,20].

The primary aim of this work is to study the effect of mode (contact and tapping) and imaging environment (air and high purity water) when using atomic force microscopy to assess the surface characteristics of water purification membranes. To the authors' knowledge there are currently no studies comparing tapping mode and contact mode imaging of nanofiltration membranes. AFM measurements will be complimented by using the membrane transport method to assess pore size and pore size distribution and contact angle measurements to assess the hydrophobicity of membranes studied. For this work two different membranes were chosen. Firstly a membrane was fabricated utilizing the phase inversion method with solutions containing polyethersulfone (PES) 20% and poly(vinyl pyrrolidone) (PVP) 20% by weight. The second membrane used in this study is a commercially available nanofiltration membrane, NF270 (Dow).

1.2. Membrane formation

The phase inversion method is an important technique for the preparation of polymeric membranes [21,22]. This method has been used for the preparation of asymmetric membranes since Loeb and Sourirajan successfully developed cellulose acetate membranes for seawater desalination in the late 1950s [23]. During preparation of asymmetric membrane the prepared polymer solution precipitates after immersion in a nonsolvent bath, where this nonsolvent diffuses into the polymer solution film [21].

The mechanism of asymmetric membrane formation by the phase inversion method has been investigated intensively by previous authors [22,24–29]. Different parameters potentially affect the performance and morphology of fabricated membranes including the concentration of polymers in the casting solution [29], presence and concentrations of additives as well as the type of solvent utilized [30], as well as the temperature of the polymer solution and coagulation bath [31].

Polyethersulfone (PES) is a material commonly used for the production of filtration membranes for a number of reasons [32–34]: (i) flexibility in membrane fabrication in a wide variety of configurations and modules; (ii) PES has an excellent resistance to chemical attack; and (iii) excellent thermal stability and mechanical properties. Despite these advantages PES is a relatively hydrophobic material and is consequently susceptible to fouling by hydrophobic chemicals and particulates in the feed stock. As a result, poly(vinyl pyrrolidone) is commonly added to the polymer solution to enhance the hydrophilicity of PES with the intention of reducing membrane fouling [33,34]. However, it is also worth noting that in some cases a hydrophobic membrane may be preferable where selectivity in the preferable retention of polar substances is required [35].

2. Theoretical

2.1. Pore size and pore size distribution calculation by membrane solute transport method

Pore size and pore size distribution are two of the major parameters used to characterize filtration membranes. Based on the type of membrane, one of several different methods may be used [36]. These methods can be classified into two types: (1) physical methods to determine the pore size and pore size distribution of a membrane and (2) methods based on permeation and rejection performance using reference molecules and particles [37,38]. These methods include: microscopy based techniques including AFM and SEM; bubble-point methods; mercury porosimetry; gas adsorption-base methods; thermoporometry; permporometry; liquid displacement; permeability method and the solute transport method [37,39–43].

In this study in order to characterize the membrane pores and their distribution, the solute transport method was used. This method correlates the membrane pores and their distribution with solute size and corresponding solute rejection percentage.

Cooper and Van Derveer [44] developed a method for characterizing the transport properties of UF membranes, where a solution of a polydisperse polymer was employed. The solute separation is calculated using the following equation:

$$f = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (1)$$

where C_p and C_f are the solute concentrations in the permeate and in the feed solution, respectively. The effect of concentration polarization on separation is not considered in this equation [45].

In this study, polyethylene glycol (PEG) was used as the solute to find the pore size and pore size distribution. These were characterized using the Einstein–Stokes diameter of PEG solutes from their molecular weights using the following relationship [45,46].

$$a_d = 33.46 \times 10^{-10} M^{0.557} \qquad (2)$$

where a_d is the Einstein–Stokes diameter in cm and M is the molecular weight of the corresponding molecule in g mol^{-1} (Da). In this method the solute separation (%) of the membrane was plotted versus the solute diameter (ds) as a log-normal chart. From this plot, providing a straight line is obtained, the mean pore size (μ_s) can be calculated as ds corresponding to $f = 50\%$ and geometric standard deviation (σ_g) can be determined from the ratio of ds at $f = 84.13\%$ and at 50%. The mean pore size and the geometric standard deviation of the membrane can be considered to have the same value as the mean solute size and solute geometric standard deviation [44,45,47].

The pore size distribution of the membrane can be expressed by the probability density function as shown in the following equation [46]:

$$\frac{df(dp)}{d(dp)} = \frac{1}{d_p \ \ln \sigma_p (2\pi)^{1/2}} \exp\left(-\frac{(\ln d_p - \mu_p)^2}{2(\ln \sigma_p)^2}\right) \qquad (3)$$

where d_p is the pore size, σ_p the geometric standard deviation and μ_p is the geometric mean.

2.2. AFM roughness measurements

Numerous roughness parameters may be obtained from surface topographies obtained by AFM typically by using the instrument