A comparison of vertical scanning interferometry (VSI) and atomic force microscopy (AFM) for characterizing membrane surface topography

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Abstract

In this paper, vertical scanning interferometry (VSI) and atomic force microscopy (AFM) were used to characterize the topography of several nanofiltration and reverse osmosis membrane surfaces. Comparing roughness results from the two different characterization techniques revealed unique results for the various membrane surfaces. Roughness values tended to be higher from the interferometry measurements compared to those from AFM measurements for the same membranes. This was attributed to the inability of the AFM to capture dramatic changes in surface height of several microns or more. Based on interferometric measurements surface roughness was also found to increase with increasing scan-size up to a scan-size of 250,000\(\mu\text{m}^2\) after which it remained relatively constant. Because such large scan-sizes are too large to be captured through AFM measurements interferometry appears to provide a more comprehensive characterization of membrane surface roughness.

Keywords: Interferometric method; AFM; Roughness; Scan area; Membrane surface topography

1. Introduction

There currently exists a variety of analytical tools for characterizing the morphology of polymeric and ceramic membrane surfaces [1–4]. Some of the more popular surface characterization techniques for membranes include scanning electron microscopy (SEM) and atomic force microscopy (AFM). Each of these tools is capable of providing atomic level quantitative analyses of the morphological characteristics of membrane surfaces. For instance, using these tools it is possible to characterize membrane properties like surface roughness [5–8], porosity and pore size distribution [9–11], and deposit layer thickness [12]. Such characterization is important given findings demonstrating the critical role of these characteristics in determining membrane performance [6,7,13].

Of the surface characterization techniques that are available to membrane scientists, AFM has been used due to the ease of sample preparation and its ability to characterize membrane surfaces in both wet and dry environments [2,5,7,9–11,14–16].

An atomic force microscope operates using a combination of principles from the scanning tunneling microscope and the stylus profilometer [17,18]. Here, a sharp tip, with a radius of around 50–100 nm, is scanned over a surface with feedback mechanisms that enable piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. Tips are typically made from silicon nitride and extend down from the end of a flexible cantilever. Surface morphology and/or surface interactions are measured based on the vertical deflection of the cantilever. The resolution of the AFM is determined by the sharpness of the tip and typically approaches the atomic scale. Thus, AFM may be used to provide high-resolution information regarding membrane surface morphology in addition to other characteristics. Nevertheless, despite the many advantages of AFM and its success in characterizing membrane surfaces a number of limitations do exist.

One of the principle drawbacks of the AFM is the relatively small area that can be scanned at any given time. For instance, the maximum scan area for most AFMs is approximately 100 \(\mu\text{m}^2\).
This limitation is principally due to the operational set up of the AFM and the size of the single cantilever used to produce the AFM image. Such a limited scan-size makes it difficult to determine how representative the measured image may be of the surface at large. For instance, Boussu et al. [9] found that membrane surface roughness increased with increasing scan-size, suggesting that roughness statistics derived from relatively small scan areas may be misleading. Another issue pertains to the distortion of surfaces features as a result of tip convolution. Additionally, it is difficult to characterize surfaces where the changes in height are dramatic (Δ > 5 μm) in which contact may be lost between the tips and sample, on the tip may become damaged. Further drawbacks of the AFM include the time required to obtain an image and the operation of the instrument, which are both rather intensive.

Optical interferometry is a rather new technique that may be used to characterize membrane surfaces with regard to surface morphology and structure [19]. Optical interferometry is a type of microscopy where nanometer level characteristics of a sample surface may be characterized through the interpretation of light reflected from a surface. With optical interferometry it is possible to obtain scan-sizes of up to a square millimeter with a vertical resolution of approximately 2 nm. The larger scan-size made possible with optical interferometry, allows for a more comprehensive analysis of surface roughness and is drastic improvement of the small scan-sizes (typically 100 μm²) that are possible with an AFM. In this respect, the impact of scan-size on calculated roughness statistics may be determined, providing new insight and perspective into the interpretation of values derived from much smaller scan-sizes, as is the case for AFM generated values.

In this paper, roughness statistics generated by AFM measurements are compared to those determined using optical interferometry for several nanofiltration and reverse osmosis membranes. The impact of scan-size on the calculated roughness statistics is used to evaluate the ability of AFM to fully characterize membrane surface roughness as a function of length scale. The role of optical interferometry as a characterization technique for membrane surface is compared with that of AFM.

2. Experimental

2.1. Membranes

This study examined three commercially available nanofiltration (NF) and reverse osmosis (RO) membranes; GE Osmonics HL (Minnetonka, MN), the DOW Film Tec NF70 (Minneapolis, MN) nanofiltration membranes, and the Hydranautics LFC-1 (Oceanside, CA) reverse osmosis membrane. These membranes were selected as they represent a range of surface morphologies as determined in previous investigations [13, 20, 21]. Each membrane was supplied as dry flat sheets and was stored accordingly until used.

2.2. AFM analysis

All AFM experiments were carried out using a Park Scientific Instruments (Sunnyvale, CA) Autoprobe CP atomic force microscope. Measurements were performed on dry membrane samples under ambient atmospheric conditions. Silicon cantilevers with integrated pyramidal tips (Model #: MPP-11100, VEECO Instruments Inc., Fremont, CA) were used to image membrane surface topography. The membrane surfaces were imaged in tapping mode. At least five separate scans, each covering an area of 100 μm², were acquired on each membrane to...
determine mean roughness values and their associated standard deviations. Roughness is reported as average roughness ($R_a$), root mean square roughness ($R_q$), and surface area difference (SAD).

2.3. Interferometric analysis

Optical interferometry measurements were carried out using a MicroXam vertical scanning interferometer (ADE-phase Shift Technology, Tucson, AZ). The basic operating principles of the interferometer are illustrated in Fig. 1 [19,22]. Here white light is emitted by a conventional light source and is split into two beams by beam splitter housed inside the Mirau double beam interferometer objective. The reference beam is directed to a mirror located in the objective, which serves as the reference surface. Conversely, the sample-beam travels directly to the sample surface. A high precision ceramic piezo (ZSCAN DSP) allows 7\,\mu\text{m} of vertical relief to be imaged per second. As a consequence, the actual interferogram shows only a small range of fringes that moves across the sample surface during the scan process. Up to 100\,\mu\text{m} of relief can be scanned in this manner. The interferograms are digitized with a CCD camera and converted into a topographic map with MAPVUE software (ADE-Phase Shift Technologies, Tucson, AZ) [19].

The interferometer was operated on a vibration-dampening table to reduce noise and optimize image quality. Measurements were performed on at least 10 different locations on each sample membrane surface. Additionally, at each location 10 different scan-sizes were evaluated, ranging in size from 64\,\mu\text{m}^2 to 0.5\,\text{mm}^2 (Fig. 2). Results are reported for each membrane as average roughness ($R_a$), root mean square roughness ($R_q$), and surface area difference (SAD). All interferometric measurements were carried out on dry membrane samples.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$R_q$ (nm)</th>
<th>$R_a$ (nm)</th>
<th>SAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>21.2 ± 23.85</td>
<td>14.8 ± 17.14</td>
<td>3.1 ± 3.97</td>
</tr>
<tr>
<td>LFC1</td>
<td>105.3 ± 12.95</td>
<td>84.7 ± 10.39</td>
<td>61.4 ± 24.27</td>
</tr>
<tr>
<td>NF70</td>
<td>64.6 ± 3.59</td>
<td>51.0 ± 2.99</td>
<td>29.4 ± 8.40</td>
</tr>
</tbody>
</table>

The scan-size was 100\,\mu\text{m}^2 for the AFM and 64\,\mu\text{m}^2 and 0.5\,\text{mm}^2 for interferometric measurements. All membranes were imaged dry and in air.

3. Results and discussion

Mean roughness statistics determined using AFM and interferometric analysis are reported for each membrane in Table 1. For the AFM measurements, the roughness parameters were determined for a scan area of 100\,\mu\text{m}^2, while those reported for the interferometric measurements were determined for the 64\,\mu\text{m}^2 and maximum allowable scan-size for that instrument, 0.5\,\text{mm}^2, respectively. According to the AFM measurements the LFC1 membrane has the roughest surface followed by that for the NF70 and HL membranes, respectively. However, according to the interferometric analysis the NF70 membrane surface was the roughest followed by the LFC1 and HL membrane surfaces, respectively. Topographic renderings of the three membrane surfaces determined from the AFM and interferometric
measurements are shown in Figs. 3 and 4, respectively. The interferometric method gave very different images at a larger scale when compared with the AFM images at a smaller scale.

The roughness results for these two methods can be compared at roughly similar scales using the 100 \( \mu \text{m}^2 \) scan-size for the AFM and 64 \( \mu \text{m}^2 \) for the interferometric method. At similar scales these two methods yielded different results (Table 1). Root mean square (\( R_q \)) roughness values were 21.2, 105.3, and 64.6 nm for HL, LFC1, and NF70 membranes, respectively, at a scan-size of 100 \( \mu \text{m}^2 \) for AFM. However, interferometric measurements gave the roughness values as 107, 43, and 75 nm for HL, LFC1, and NF70 membranes, respectively, at a scan-size of 64 \( \mu \text{m}^2 \). The biggest disparity in the roughness statistics determined from the two methods was for the HL and LFC1 membranes. The LFC1 membrane was characterized as having the smoothest surface by the interferometric measurements, while the AFM measurements indicated it was the roughest.
surface at similar scan-sizes. However, the HL membrane was characterized as the roughest surface by the interferometric measurements, while the AFM measurements indicated it was the smoothest surface at the same scan-size. For the LFC1 membrane the standard deviation in the roughness statistics was high for the interferometric measurements, particularly when compared to that calculated for the AFM generated values (Table 1). This may account for the disparity in the two sets of results in which the LFC1 was determined to be rough according to the AFM measurements and smoother via interferometry analysis. In fact, for all of the membranes the standard deviation was substantially higher for the interferometric measurements at the smaller scan-size of 64 µm$^2$ compared to those determined by the AFM at 100 µm$^2$ (Table 1). Thus, for the interferometric measurements the roughness statistics generated at smaller scan-sizes were highly variable and may in fact represent minimum scan-size that is appropriate to obtain statistically accurate measurements. For the LFC1 membrane then, the difference in the AFM and interferometric results may be due to the difference in scan-size used by the two techniques.

For the HL membrane the disparity in the two sets of results may be explained by the appearance of sharp peaks ($h \sim 4$ µm) in the interferometric scans of the HL membrane surface (Fig. 4).

Notably, these peak-like features appeared in both the interferometric and AFM images of the HL membrane surface (Figs. 3 and 4), thus confirming that they are actually present on the surface and not merely instrument noise. However, in the AFM scans these peaks on average approached a height of approximately 0.1 µm. The discrepancy in the height of these features as determined by the different techniques may be attributed to the operating principles of the AFM. In tapping mode AFM the tip that is scanned across the membrane surface oscillates at a set distance above the membrane surface. If a feature were to be higher than the height of this separation distance than the AFM would not be able to accurately determine its height and would either skip around the feature or lose contact with the surface at which point it would no longer produce an image of the surface. If the former scenario were to occur...
then the AFM may erroneously interpret the signal or change in cantilever oscillation as a smaller feature. Therefore, for membrane surfaces with substantially large features (up to 100 μm) the interferometric method appears to be a more robust characterization technique compared with AFM.

The ability of the interferometer to examine relatively large scan area provides a basis from which the impact of scan-size on the magnitude of surface roughness may be examined. The roughness statistics for each membrane ($R_a$ and $R_q$) as determined from the interferometric measurements were plotted as a function of scan-size in a normal and log–log format and are reported in Figs. 5 and 6, respectively. For each membrane, both $R_a$ and $R_q$ increased with increasing scan-size in a logarithmic fashion. Initially, roughness increased linearly with scan-size until a scan-size of approximately 60,000 μm$^2$ was reached. After this point, the slope of the curve was much lower and the increase in roughness with increasing scan-size was much lower. The onset of this plateau occurred at a scan-size of approximately 250,000 μm$^2$ for both $R_a$ and $R_q$ for each of the three membranes. As each membrane had a similar inflection point at approximately 250,000 μm$^2$ it would seem that this value is statistical and not physical in origin. In other words, this scan-size appears to represent the necessary sample size for which to obtain statistically sufficient results. However, this point requires further examination using surfaces with controlled surface structures. The data reported in Fig. 5 may then be divided into two regions, one where roughness increases with scan-size (Region 1) and two where the change in roughness with scan-size is much less substantial (Region 2). The impact of scan-size on the magnitude of the measured roughness statistics is further illustrated in the height profiles for the HL membrane (Fig. 7). At the larger scan-sizes the HL membrane surface appears to be rougher ($R_a = 873$ nm) compared to that at the smaller scan-size ($R_a = 318$ nm). This is further illustrated in the height profiles and surface renderings for the larger and smaller scan areas shown in Fig. 7a and b, respectively.

The data shown in Fig. 6 was fit using a power law ($y = ax^b$) and the associated constants $a$ and $b$ were calculated and are reported in Table 2 for the different membranes. For each membrane the relationship between either $R_a$ or $R_q$ and scan-size was well described ($R^2 > 0.93$) by the power law. While the $a$ values increased, the $b$ values decreased with scan-size (from Region 1 to 2), indicating that roughness is independent of scan-size.

![Image](image.png)

**Table 2**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Region</th>
<th>$R_a$</th>
<th>$R_q$</th>
<th>$a$</th>
<th>$b$</th>
<th>$R^2$</th>
<th>$a$</th>
<th>$b$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>1</td>
<td>33.33</td>
<td>0.25</td>
<td>0.98</td>
<td>39.22</td>
<td>0.26</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>121.97</td>
<td>0.13</td>
<td>0.93</td>
<td>155.98</td>
<td>0.13</td>
<td>0.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF70</td>
<td>1</td>
<td>12.04</td>
<td>0.43</td>
<td>0.97</td>
<td>13.72</td>
<td>0.46</td>
<td>0.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>115.84</td>
<td>0.19</td>
<td>0.99</td>
<td>211.87</td>
<td>0.16</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LFC1</td>
<td>1</td>
<td>5.34</td>
<td>0.46</td>
<td>0.99</td>
<td>5.79</td>
<td>0.51</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>74.41</td>
<td>0.18</td>
<td>0.99</td>
<td>174.49</td>
<td>0.14</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Regions 1 and 2 correspond to the two separate regions of linearity shown in Fig. 5.
once it has exceeded 250,000 μm², as roughness is more constant as the \( b \) value approaches zero (Scan area \( \rightarrow \infty \), \( R_q \) or \( R_a \) \( \rightarrow \) constant).

The effect of scan-size on AFM generated roughness statistics for a variety of membranes was previously studied by Boussu et al. [9]. These authors examined the variability of membrane surface roughness with scan-sizes ranging from 1 to 100 μm² using both tapping and non-contact modes for AFM imaging. Notably, these scan-sizes fall within Region 1 of our interferometric analysis, as shown in Fig. 6. Thus, it would be expected that roughness would increase rather linearly with increasing scan-size as was indeed found by the authors of that study and as illustrated in Fig. 8, which shows the \( R_q \) as a function of scan-size determined by Boussu et al. [9]. Additionally, the data taken from Boussu et al. [9] was fit using a power law and the associated constant values (\( a \) and \( b \)) from the fit are reported in Table 3.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Region</th>
<th>Tapping mode (( R_q ))</th>
<th>Non-contact mode (( R_q ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( a )</td>
<td>( b )</td>
</tr>
<tr>
<td>HL</td>
<td>1</td>
<td>5.05</td>
<td>0.18</td>
</tr>
<tr>
<td>Desal 5 DL</td>
<td>1</td>
<td>9.33</td>
<td>0.12</td>
</tr>
<tr>
<td>NTR7450</td>
<td>1</td>
<td>0.79</td>
<td>0.33</td>
</tr>
<tr>
<td>NF-PES-10</td>
<td>1</td>
<td>1.14</td>
<td>0.25</td>
</tr>
<tr>
<td>N30F</td>
<td>1</td>
<td>1.55</td>
<td>0.29</td>
</tr>
<tr>
<td>UTC20</td>
<td>1</td>
<td>2.81</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The HL membrane was the only membrane that was used in both our interferometric and Boussu et al. [9]’s AFM analysis. While the \( a \) constants determined from the power law fit for the HL membrane data were different in each case for interferometric method (\( a = 39.22 \)) (Table 2) and AFM in Region 1 (\( a = 3.33 \) for non-contact mode and \( a = 5.05 \) for tapping mode) (Table 3),
similar results were obtained for b constants for interferometric method (b = 0.26) (Table 2) and AFM in Region 1 (b = 0.24 for non-contact mode and b = 0.18 for tapping mode) (Table 3). The different results between the a values could be due to the different scan-sizes. Additionally, the a and b values determined from the power law fits to the Bousou et al. [9] data followed the same trend as that observed for the interferometric measurements (Fig. 9). Here, the magnitude of a tended to increase with increasing surface roughness while b decreased with increasing roughness, indicating that roughness was increasing with scan-size. A plateau was not reached in this case as the scan-sizes were well below the critical size (250,000 m²). A plateau was not reached in this case as the scan-sizes were well below the critical size (250,000 m²) that was determined in the current investigation.

4. Conclusions

Membrane surface roughness increases with increasing scan-size until a critical scan-size is reached. This critical scan-size appears to be similar for all the polymeric membrane surfaces studied here. Because this value is significantly larger than that which can be obtained with an AFM suggests that AFM derived roughness statistics provide an incomplete assessment of membrane morphology. Conversely, interferometry allows for rapid and accurate characterization of membrane roughness, at substantially larger scan-sizes. Finally, for a complete evaluation of membrane surface roughness scan-sizes of at least 250,000 m² should be used.

References