# Surface Morphology of Nafion 117 Membrane by Tapping Mode Atomic Force Microscope

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**ABSTRACT:** Surface morphology of Nafion 117 membrane was studied by tapping mode atomic force microscopy. Three different samples were analyzed and correspond respectively to dry membrane and wet membrane equilibrated either with water or with tributylphosphate. These studies show the supermolecular structure of the membrane, which is made of nodules or spherical grains of a mean diameter of 11 nm, and are surrounded by interstitial regions of a mean thickness of 50 Å. Roughness analysis of the samples shows the influence of the swelling properties of the membrane on its surface morphology. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 503–508, 1998

**Key words:** membrane; atomic force microscopy; swelling

## INTRODUCTION

Ion exchange membranes play a vital role in numerous areas of life sciences and technological engineering,[1] including batteries,[2,3] fuel cells,[4] electrochemical sensors and electrochemical reactors.[5–8] The perfluorinated sulphonic acid cation exchange Nafion® membrane, manufactured by E.I. du Pont de Nemours and Co. in 1972, shows unusual and very interesting properties that justify the great deal of research still performed on such a polymeric film. Nafion membrane shows a good chemical stability when it is immersed in the required electrolyte solution[9,10] and it has a remarkable mechanical strength, a good thermal stability,[11,12] and a high electrical conductivity.[13–16] Moreover, this membrane shows a high selectivity to the desired ionic species,[17–20] even in a high-salt concentration environment. Various studies were performed to devise sophisticated models linking macroscopic transport rates to the molecular level structure of the solute, solvent, and membrane.[21] The molecular level structure of Nafion focuses on the cluster network model proposed by Gierke,[22] who described the membrane as a series of clusters or inverted micelles, interconnected by narrow pores.

In order to model their ionic diffusional results, Yeager and Steck[23] proposed to describe the Nafion structure as three regions, as shown in Figure 1. Region A consists of fluorocarbon backbone material, some of which is in a microcrystalline form.[24] The interfacial region B is seen as a large fractional void volume, which contains sidechain material, a small amount of water, and some free sulfonate exchange sites. Region C contains ion clusters, in which exist the sulfonate exchange sites, counterions, and sorbed water.

In this article, the perfluorosulphonated ionomer (PFSI) membrane studied was Nafion 117, with the following chemical formula:

$$-(CF_2CF_2)_n-\underset{\underset{|}{CF_2}}{\underset{|}{C}}FO(CF_2-\underset{CF_3}{\underset{|}{C}}FO)_mCF_2CF_2SO_3^-H^+$$

where $n = 6.5$ and $m = 1$, with an equivalent weight of 1100 g meq$^{-1}$.

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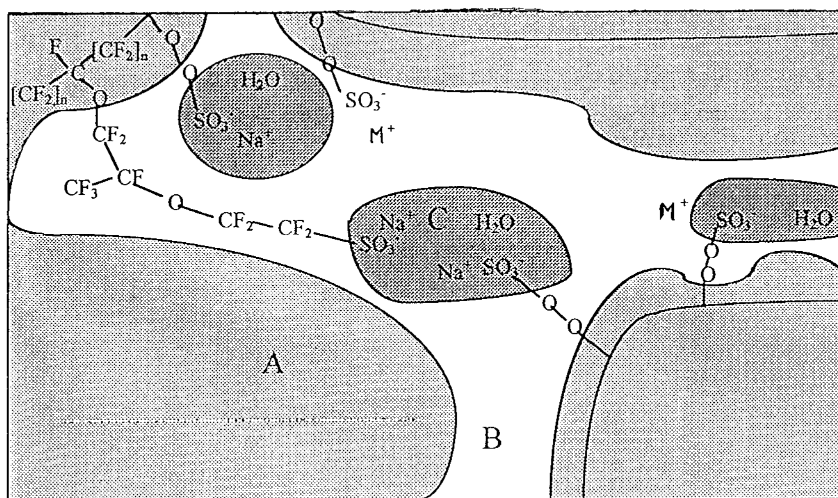


**Figure 1** Three regions structural model for Nafion.[23]

We focused on the structural properties of this membrane because of its good physical and chemical properties and for its wide industrial applications.[1] We have investigated the structural analysis of the membrane surface by using atomic force microscopy (AFM). This high-resolution technique is newly developed to study the morphology of the surface of thin films. In the study of membranes, it has been especially used for the study of the morphology of biological membranes.[25–30] However, few articles have appeared in the literature for the study of the structural properties of synthetic membranes by AFM.[31–33] In the present article, we report the surface morphology of Nafion 117 membrane by tapping mode atomic force microscope (TM AFM). Three samples have been analyzed when the membrane was dry and equilibrated either with water or tributylphosphate (TBP) in order to determine the influence of the swelling properties of the membrane on the structural investigation.

## EXPERIMENTAL

Before any measurement, a pretreatment of the membrane was carried out in order to expel impurities. The membranes samples were immersed successively in aqueous hydrochloric acid, (Prolabo, 35%) 1 mol dm$^{-3}$ for 24 h, and washed in deionized water for 24 h. This cycle was repeated one more time before boiling the samples for 1 h in deionized water.

Three samples of the Nafion membrane have been studied. The sample denoted M1 was dried under vacuum at 80°C. The sample M2 was first dried, and, before the AFM measurement, a drop of deionized water was put on the membrane. The AFM apparatus was kept under a box in Plexiglass and several petri dishes filled with water were placed around the AFM apparatus in order to have a constant rate of humidity. Nothing was changed during the measurement. The sample M3 was first dried, and, before the measurement, a drop of TBP (Prolabo) was put on the membrane, and the same precautions were observed.

Small squares of an approximately 1-cm$^2$ area were cut from each prepared membrane and stuck with reversible Scotch tape on metal disks. The images of the surfaces were obtained using TM AFM on a Nanoscope III from Digital Instruments.[34] We used a Si–n tip whose curvature radius is in the range of 5–10 nm. The spring constant of the tip is in the range of 30–92 N m$^{-1}$, and the resonance frequency range is 305–440 kHz.

The tapping mode is a new technique developed by Digital Instruments for operating the AFM. The lateral resolution is quite comparable for the contact and noncontact AFM. Moreover, the pressure force applied to the sample in TM AFM is much lower than in the contact AFM. The applied pressure is lower by a factor of ten; therefore, the sample is less perturbated by the tip.

The membrane surfaces were compared by means of roughness parameters, such as the mean roughness $R_a$, the root mean square (rms) of the $Z$ data $R_q$, the maximum height $R_{\max}$, and the surface area difference $SAD$. The mean roughness is the mean value relative to the center plane,

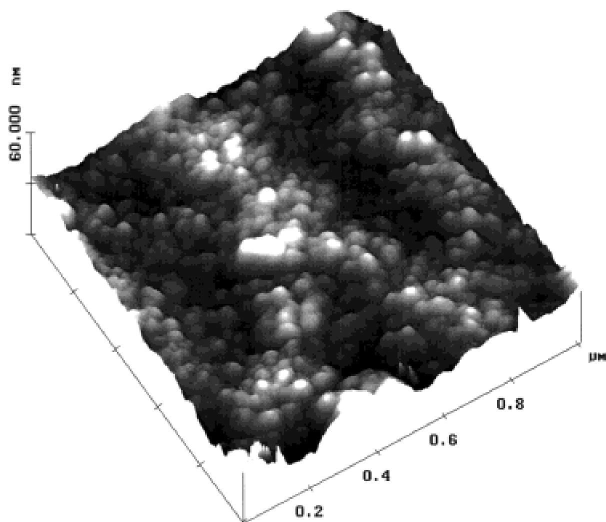


**Figure 2** Surface plot of the image by TM AFM of the M1 sample.

which is parallel to the mean plane; the volumes enclosed by the image surface above and below the center plane are equal.[35] $R_a$ is defined as

$$R_a = \frac{1}{L_x L_y} \int_0^{Ly} \int_0^{Lx} |f(x, y)| \, dxdy$$

where $f(x, y)$ is the surface equation relative to the center plane, and $L_x$ and $L_y$ are the dimensions of the sample under study. $R_{\max}$ is the height difference between the highest and lowest points on the surface relative to the mean plane. $R_q$ is the standard deviation of the $Z$ values within the given area, and is calculated as

$$R_q = \left( \sum_i (Z_i - Z_{\text{avg}})^2 / N \right)^{1/2}$$

where $Z_{\text{avg}}$ is the average of the $Z$ values, $Z_i$, the current $Z$ value; and $N$, the number of points. The surface area difference $SAD$, in percentage, is defined as

$$SAD = \left[ \frac{\text{Surface area}}{\text{Projected area}} - 1 \right] \times 100$$

where the surface area is the three-dimensional surface obtained by the sum of the triangles formed by three adjacent points, and the projected area is the two-dimensional surface produced by projecting the surface onto the threshold plane. The rugosity factor $\Gamma$ is related to $SAD$ by the following relation:

$$\Gamma = 1 + SAD$$

## RESULTS AND DISCUSSION

Figures 2 and 3 show the representative three-dimensional images of the M1 sample in the following two different scan sizes: $1 \times 1$ $\mu$m $\times$ 30 nm and $50 \times 50 \times 3$ nm, respectively. The light areas correspond to the maximal heights in the $Z$ direction, and the dark areas are related to the minimal heights. Figure 2 shows supernodular aggregates, which is characteristic of the supermolecular structure of ionomeric materials.[36] This superstructure is constituted of spherical domains having an average diameter of 45 nm. At a lower scan size (Fig. 3), the structure is conserved and presents spherical grains with an average diameter of 11 nm. The section analysis of this microstructure (Fig. 4) shows that the interstitial regions have a mean thickness of 49 Å, which may correspond to the pore (or cluster) size in Nafion membranes.[12] However, it could be also assumed that the interstitial regions are not free of matter but rather that they are the region of lower polymer density.[33] As we can see, between the two triangles on Figure 4, there is no hole.

Figure 5 shows the three-dimensional image of the M2 sample in the scan size ($1 \times 1$ $\mu$m $\times$ 30 nm). It is seen that the supernodular structure is

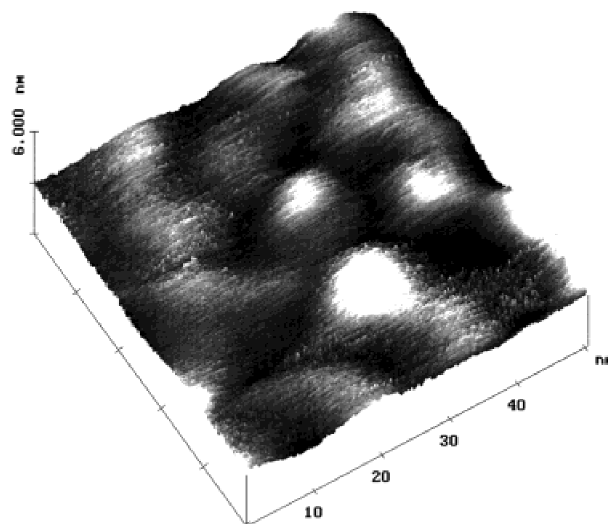


**Figure 3** Surface plot of the image by TM AFM of the M1 sample for a lower scan size.

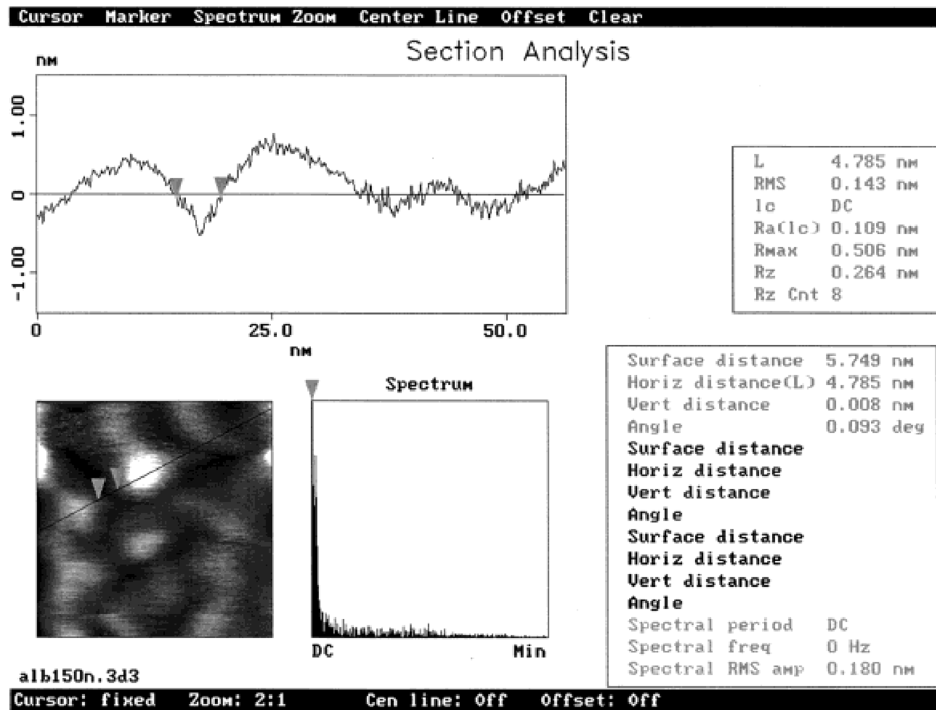


**Figure 4** Section analysis of the TM AFM image of the M1 sample.

always conserved with larger interstitial regions and a lower roughness (1.7 nm instead of 3.1 nm). It is known that for the Nafion 117 membrane, the volume increase with water is about 40%,[37] which may imply a distribution density of the spherical grains less important than for the M1 dry sample.

Figure 6 shows the three-dimensional image of the M3 sample in the scan size ($1 \times 1\ \mu m \times 150$ nm), when the membrane is equilibrated with TBP. A real change of the membrane structure with a nonuniform distribution of the grains and wide and deep rifts ($R_a$ = 9.9 nm) can be seen. It is known that the volume increase of the

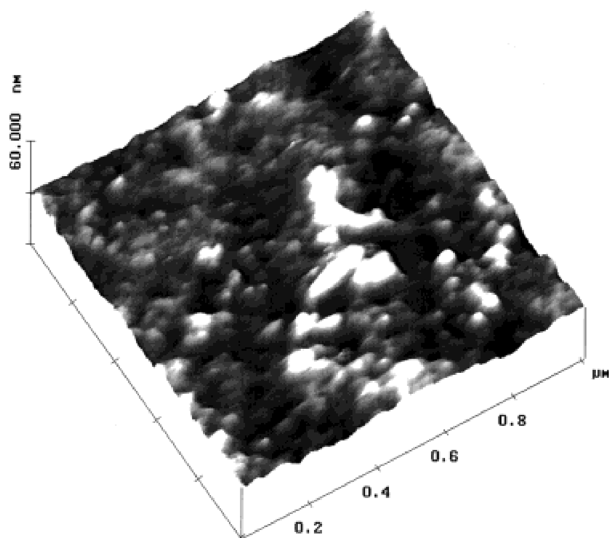


**Figure 5** Surface plot of the image by TM AFM of the M2 sample.

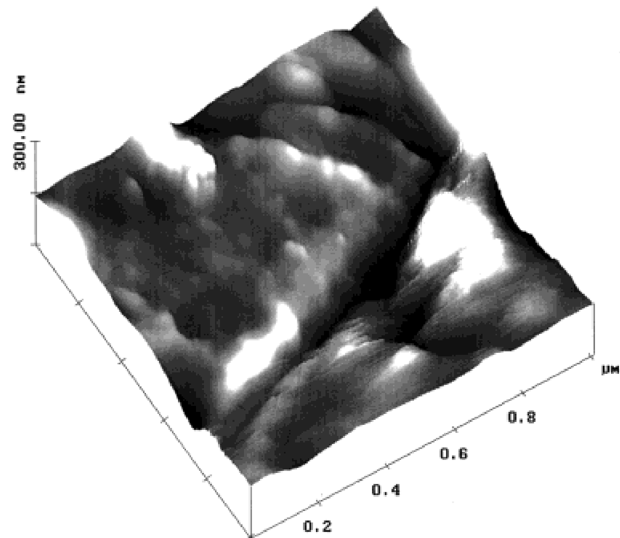


**Figure 6** Surface plot of the image by TM AFM of the M3 sample.

**Table I Roughness Parameters for Membrane Surfaces of the Three Samples**

| Sample | $R_a$ (nm) | $R_{max}$ (nm) | $R_q$ (nm) | *SAD* (%) | Γ |
|---|---|---|---|---|---|
| M1 | 3.1 | 29.5 | 3.9 | 1.8 | 1.02 |
| M2 | 1.7 | 18.4 | 2.2 | 1.2 | 1.01 |
| M3 | 9.9 | 134.9 | 13.7 | 28.9 | 1.29 |

membrane upon absorption of TBP is quite important (≈ 360%),[37] which can justify such a difference, which is characteristic of a change in the polar sites hydration of the membrane.

The analysis of the roughness parameters of the three different samples (Table I) shows that the surface membrane is quite rough, especially for the M3 sample. We must add that these roughness parameters depend on the curvature and size of the TM AFM tip, as well as on the treatment of the captured surface data (plane-fitting, flattening, and filtering), and they should not be considered as absolute roughness values. However, it can be noticed that the membrane swelling upon absorption of TBP is also observed in the *Z* direction.

## CONCLUSION

TM AFM is a new technique, which can be adapted to the study of the morphology of synthetic membranes. We present here the first results, which could be studied further in order to describe more precisely the pore or cluster network in Nafion membranes. However, TM AFM presents a limited resolution (≈ 1 nm) for such materials, and it would be interesting to use techniques as contact AFM or STM, which present a higher resolution.

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