Effect of Roughness as Determined by Atomic Force Microscopy on the Wetting Properties of PTFE Thin Films*

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The influence of film roughness on the wetting properties of vacuum-deposited polytetrafluroethylene (PTFE) thin films has been investigated using atomic force microscopy (AFM) and contact angle goniometry. Surface roughness has been characterized by atomic force microscopy in terms of RMS roughness (R_q) and fractal dimensions. A contact angle correlation with surface roughness, as determined by AFM, is evident from these results, which are discussed on the basis of wetting theory. The results also confirm that the high water contact angles (as high as 150°) recently observed at the surface of a new water repulsive coating material (mixture of PTFE and binder) are because of surface roughness. Such measurements clarify the effect of nanometer-size surface asperities on the wetting properties of hydrophobic coatings.

INTRODUCTION

It is well known that wetting of a surface by a liquid is affected by the roughness of the surface (1–14). This property has been exploited in the development of new water repulsive materials by Nippon Telegraph and Telephone Corporation (NTT) for a variety of applications (15). For example, this new water repulsive material (mixture of PTFE and binder) can be used for communication antenna materials at high elevations to minimize snow accumulation and maintain high quality reception. Contact angles as high as 150° have been observed at the surface of this water repulsive material. These high contact angles are believed to be due to the presence of the hydrophobic PTFE particles as well as the surface roughness of this new composite coating. Early studies have showed that surface roughness decreases the spreading of a non-wetting liquid on low energy solids (1–4). Similar work with high energy substrates and liquids indicates that roughness strongly influences the wetting characteristics of the surface (5–8).

Atomic Force Microscopy

The atomic force microscopy (AFM), invented by Binning, Quate, and Gerber (16), has become an important tool for imaging surfaces (17). In AFM, a sharp tip at the end of a cantilever is scanned over a surface. While scanning, surface features deflect the tip and thus the cantilever. By measuring the deflection of the cantilever, a topographic image of the surface can be obtained. With sufficient sensitivity in the spring deflection sensor, the tip can reveal surface profiles with subnanometer resolution. Therefore, the effect of microroughness on the wetting properties of the PTFE surface has been examined by using atomic force microscopy (AFM) to characterize the surface roughness.

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Theoretical Models for Rough Surfaces

The first theoretical model describing the contact angle for a liquid drop at a rough solid surface was proposed by Wenzel (1) in 1936. He modified the Young's equation as follows:

$$\cos\theta_a = r\cos\theta \tag{1}$$

where $\cos\theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv}$; γ_{lv}, γ_{sv}, γ_{sl} are the interfacial tensions at the liquid-vapor, solid-vapor, and the solid-liquid interfaces, respectively, θ is the equilibrium contact angle, r is the surface roughness ratio ($r = a/A = (da/dA) \geq 1$), θ_a is the apparent contact angle, a is the actual area of surface, and A is the apparent area, or geometrical area of the surface. A thermodynamic derivation of Wenzel's equation was presented by Good (18).

This treatment implicitly assumes that the surface features of the substrate are insignificant compared to the drop dimensions and that their geometry is of no consequence if it does not affect the surface area.

Cassie and Baxter (3) modified the Young's equation to describe the contact angle at a porous surface as follows.

$$f_1(\gamma_{sv} - \gamma_{sl}) - f_2\gamma_{lv} = \gamma_{lv}\cos\theta_a \tag{2}$$

Equation 2 is commonly expressed in the literature as

$$\cos\theta_a = f_1\cos\theta - f_2 \tag{3}$$

where f_1 and f_2 are fractions of solid-liquid and liquid-air interfaces at the porous surface.

Although, Cassie and Baxter originally proposed this model to describe wetting phenomena at porous surfaces, it can also be used for rough hydrophobic surfaces when liquid does not penetrate the surface structure. The advantage of this model over the Wenzel's approach is that it describes real systems more accurately. However, in Cassie and Baxter's model, it is difficult to accurately determine the parameters f_1 and f_2 for randomly roughened surfaces.

In an another attempt to describe the influence of surface roughness on the substrate wetting properties, Shuttleworth and Bailey (9) considered

$$\theta_a = \theta + \alpha \tag{4}$$

where α is the maximum slope of the surface feature at the liquid periphery as indicated in *Fig. 1*. Consideration of the minimization of the surface energy of the drop shown in *Fig. 1* led to the conclusion that α will be positive for an advancing angle and will be negative for a receding angle. Accordingly, the apparent contact angle, θ_a, changes depending on the shape of surface asperities as described by α.

More detailed theoretical analyses by Dettre and Johnson (10), Huh and Mason (11), and Eick and Good (12) have produced models that incorporate both the Wenzel, and the Shuttleworth and Bailey treatments.

Research Objective

In this contribution, the wetting properties of PTFE films of different surface roughness, produced by vacuum deposition, were studied. Atomic force microscopy and contact angle goniometry techniques have been used to measure the surface roughness and wetting properties respectively of the PTFE thin films.

EXPERIMENTAL

Materials

Silicon nitride cantilevers (193 μm length, 0.6 μm thickness, and 36 μm width) were purchased from Digital Instruments Inc. and used for imaging the surfaces. PTFE powder with an average particle diameter

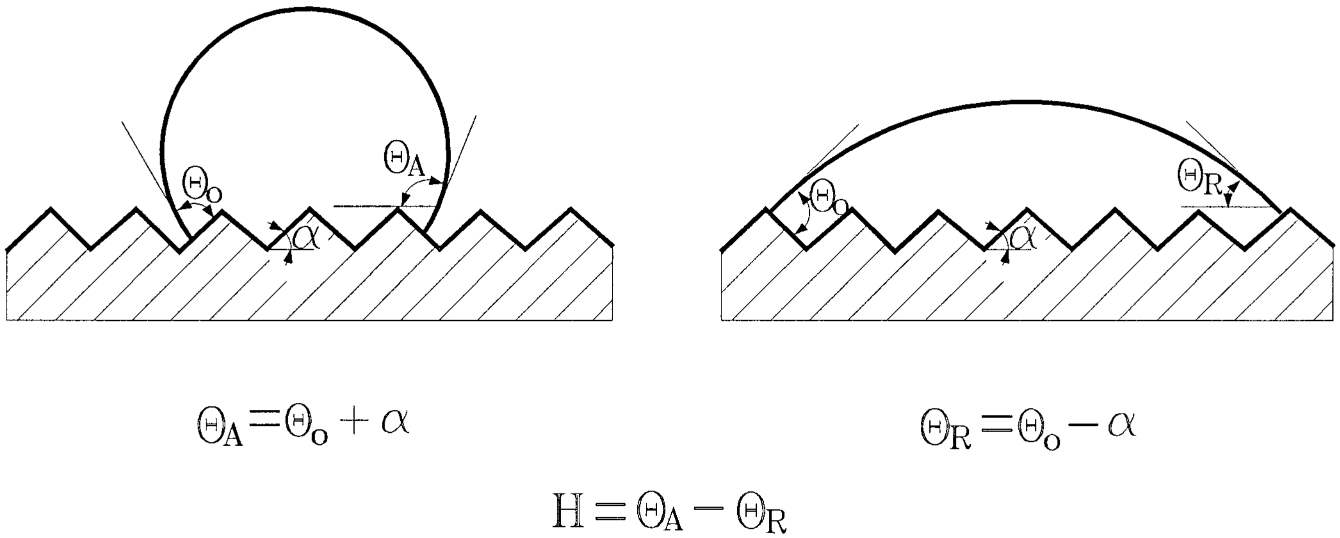


Fig. 1. Schematic of contact angles for a water drop at a rough surface. θ_A is the advancing contact angle, θ_R is the receding contact angle, θ_o is the equilibrium contact angle, α is the maximum slope of the surface feature at the liquid periphery, and H is the contact angle hysteresis.

of 3.9 μm, melting point of 315°C, and a molecular weight of 8500 was supplied by NTT and used as received.

Vacuum Deposition of PTFE

PTFE was vacuum deposited on glass plates by the following procedure. A glass plate was thoroughly washed and cleaned by water, acetone, and plasma treatment. The cleaned glass plate was then placed above a copper boat filled with PTFE powder in a vacuum chamber at 10^{-5} Torr. Then the copper boat filled with PTFE powder was heated by an electron beam at a temperature of 315°C for 2 min to deposit a PTFE thin film on the glass plate.

RMS Roughness Measurements by AFM

In the present study a Nanoscope E (Digital Instruments Inc.) AFM was used in the constant deflection mode (19) and microfabricated silicon nitride cantilevers were used for imaging in air with a 5 μm scanner.

The surface topographical images of the PTFE thin films obtained by AFM were treated by using the image processing software, version 3.1 (Digital Instruments Inc.). RMS roughness (R_q) of the PTFE surface, defined as the standard deviation of the elevation, z values, within the given area, is calculated from (20)

$$R_q = \sqrt{\sum (z_i - z_{\mathrm{ave}})^2 / N} \tag{5}$$

where z_{ave} is the average of the z values within the given area, z_i is the z value for a given point, and N is the number of points within the given area. Images of the PTFE thin film were obtained at five different locations and the average RMS roughness was determined for a particular PTFE thin film based on these images from five different locations.

Fractal Analysis

The surface roughness of the PTFE thin film was also characterized by using fractal analysis. In this analysis, a three-dimensional array of cubes are superimposed on the three-dimensional image so that the cubes completely encompass the image. The size of the cubes is varied and the number of cubes intersected by the image is recorded for each cube size. For a given cube size, rougher samples intersect more cells than smooth samples. The fractal dimension, defined as the slope of the line obtained by plotting the log of cell size vs. the log of the cell count, increases with the surface roughness of the PTFE sample. This fractal dimension varies from a minimum of 2, for a flat sample, to a maximum of 3, for an extremely rough sample (21, 22). To make direct comparisons between two surfaces with this method, AFM images were obtained at identical scan sizes and the fractal z ratio for all measurements was set at one.

Contact Angle Measurements

The sessile drop technique was used for contact angle measurements with a NRL goniometer (Rame-Hart, Inc.). The PTFE film was placed in a rectangular glass chamber and a water drop was introduced onto the substrate through a microsyringe. The needle was maintained in contact with the drop. Special care was taken in these measurements to avoid vibrations of the needle and to avoid distortion of the drop shape by the needle. The three phase contact line of the water drop was made to advance or recede by adding or withdrawing a small volume of water. The advancing and receding contact angles were measured for water drops with 3 to 4 mm drop base diameter at room temperature (22 to 23°C).

RESULTS AND DISCUSSION

The wettability of two PTFE surfaces with varying roughness as determined by AFM, was studied to examine the influence of surface roughness on the wetting characteristics of the water repulsive coating. The two surfaces were prepared by vacuum deposition of a PTFE thin film on a glass plate and then carefully peeling the film from the plate. The PTFE surface in contact with the glass plate was denoted as surface *A* and the other surface, which was not in contact with the glass plate was denoted as surface *B*.

AFM images of the two surfaces are presented in *Fig. 2* and the corresponding roughness values measured using the described software, are shown in *Table 1*. It can be noticed from *Fig. 2* that surface *A* is clearly much rougher than the surface *B* as indicated by the RMS roughness values presented in *Table 1*. The measured RMS roughness values for surfaces *A* and *B* are 83.6 nm and 8.3 nm, respectively. The topographical images of the PTFE surface were obtained at five different locations and the average RMS roughness values were determined as shown in *Table 1*. *Figure 2* presents one image obtained at a particular location. The surface roughness values presented in *Table 1* were characterized by the statistical parameter R_q, defined by *Eq 5*.

In addition to the RMS roughness measurements, the surface of PTFE thin films was also characterized by fractal analysis. These results are presented in *Fig. 3*. The fractal dimensions calculated for the two PTFE surfaces *A* (rough surface) and *B* (smooth surface) are 2.2 and 2, respectively (see *Fig. 3*). The fractal analysis results (briefly described in the experimental section) clearly indicate that there is a marked difference in the roughness of these two surfaces and that surface *A* is much rougher than surface *B*. For example, the fractal dimension of 2.2 measured for the PTFE surface *A* is sufficient to significantly alter the wetting behavior of surface *A* as will be clear from contact angle results presented in the following section. Similar fractal results were reported by Hazlett (22) for a polytetrafluoroethylene surface and it was argued that a fractal dimension of 2.14 could shift the water contact angle from 108° to 180° (perfect non-wetting behavior) at this surface.

After the surface roughness characterization of the PTFE surfaces *A* and *B* by image processing and frac-

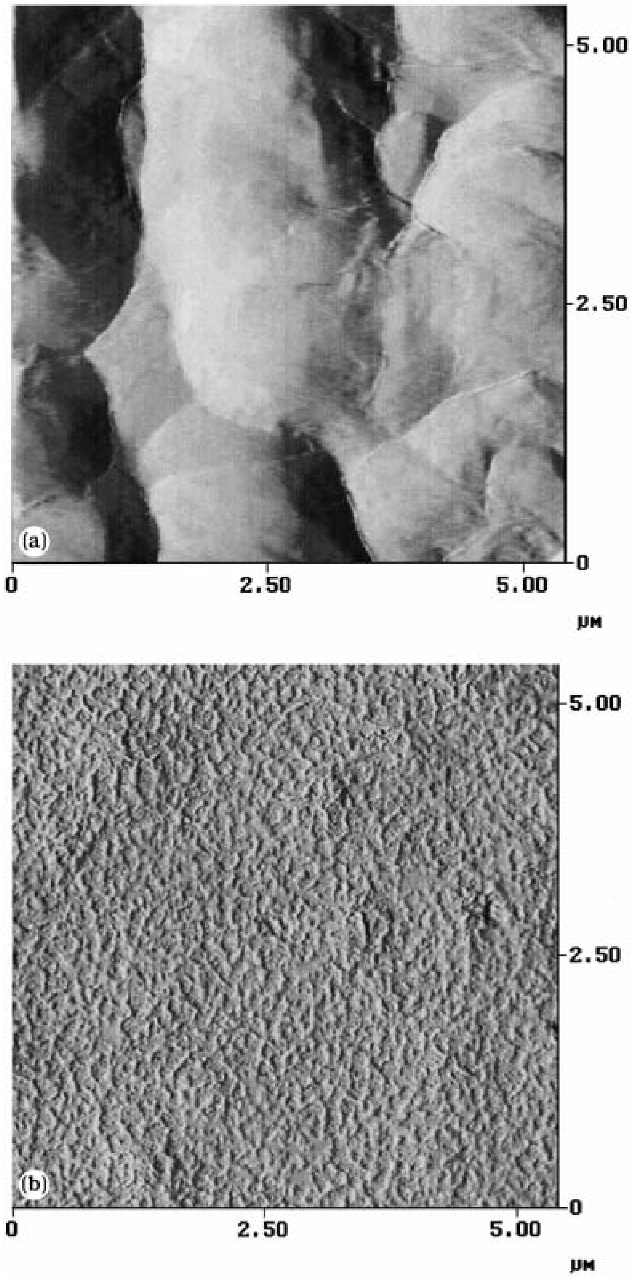


Fig. 2. AFM images of PTFE thin films, a: Surface A, b: Surface B.

Table 1. RMS Roughness Values of PTFE Surfaces *A* and *B* as Determined by Atomic Force Microscopy.

Sample	RMS Roughness (nm)
PTFE Surface A	
1	87.0
2	75.9
3	94.7
4	101.4
5	58.9
Average	83.6
PTFE Surface *B*	
1	8.3
2	8.4
3	8.6
4	8.0
5	8.1
Average	8.3

tal analysis, wetting studies by contact angle measurements were carried out using the sessile drop technique as described in the experimental section. Both the advancing and the receding contact angles were measured for PTFE surfaces *A* and *B* at different locations. These results are presented in *Table 2.* These data show that the advancing angles measured at surface *A* (146°) were larger than those measured at surface *B* (94°). Also, it is interesting to note that the difference between the advancing and the receding contact angles for PTFE surface *A* was much larger than that observed for PTFE surface *B*. These contact angle results clearly indicate that an increase in surface roughness results in a decrease in the wettability of a PTFE surface.

The results from this work show that surface roughness influences the wetting of the solids even at extremely low R_q values. Busscher *et al.* (23) and Hitchcock *et al.* (24) reported similar effects of roughness on the wettability of polymers and solid ceramics. In these works, surface roughness was created by polishing and abrasion and measured by profilometry. Busscher *et al.* measured the effect of surface roughness (created by polishing and abrasion and measured by profilometry) on the wetting behavior of at least 12 different commercial polymers and concluded that the surface roughness values (measured as stylus surface roughness) < 0.1 μm do not influence the wettability of the substrate. However, the results from the present work show that even extremely low surface roughness values (in the nanometer range) are important and influence the wetting behavior of the PTFE.

The model developed by Shuttleworth and Bailey (9) was considered to explain the effect of the observed roughness on the wettability of PTFE surfaces. This model was briefly described before by *Eq 4* and *Fig. 1*. Section analysis was performed on the AFM images as shown *Fig. 4* by using the image processing software. From this analysis the maximum slope of the surface feature, α, at the liquid periphery was determined (see *Fig. 1*). According to this model, the apparent contact angle, θ_a, can be calculated by knowing the equilibrium contact angle, θ, and by measuring the parameter α, which is related to the surface roughness (*Eq 4*). The parameter α, as measured from the sectional features of the PTFE surface *A*, is 50° ± 5°. This angle was measured at different locations and the average value was calculated. The equilibrium contact angle (θ) at a PTFE surface as reported in the literature is around 95° (23). By substituting these values in *Eq 4*, the apparent contact angle, θ_a, is calculated as 145°. From contact angle measurements, it was ob-

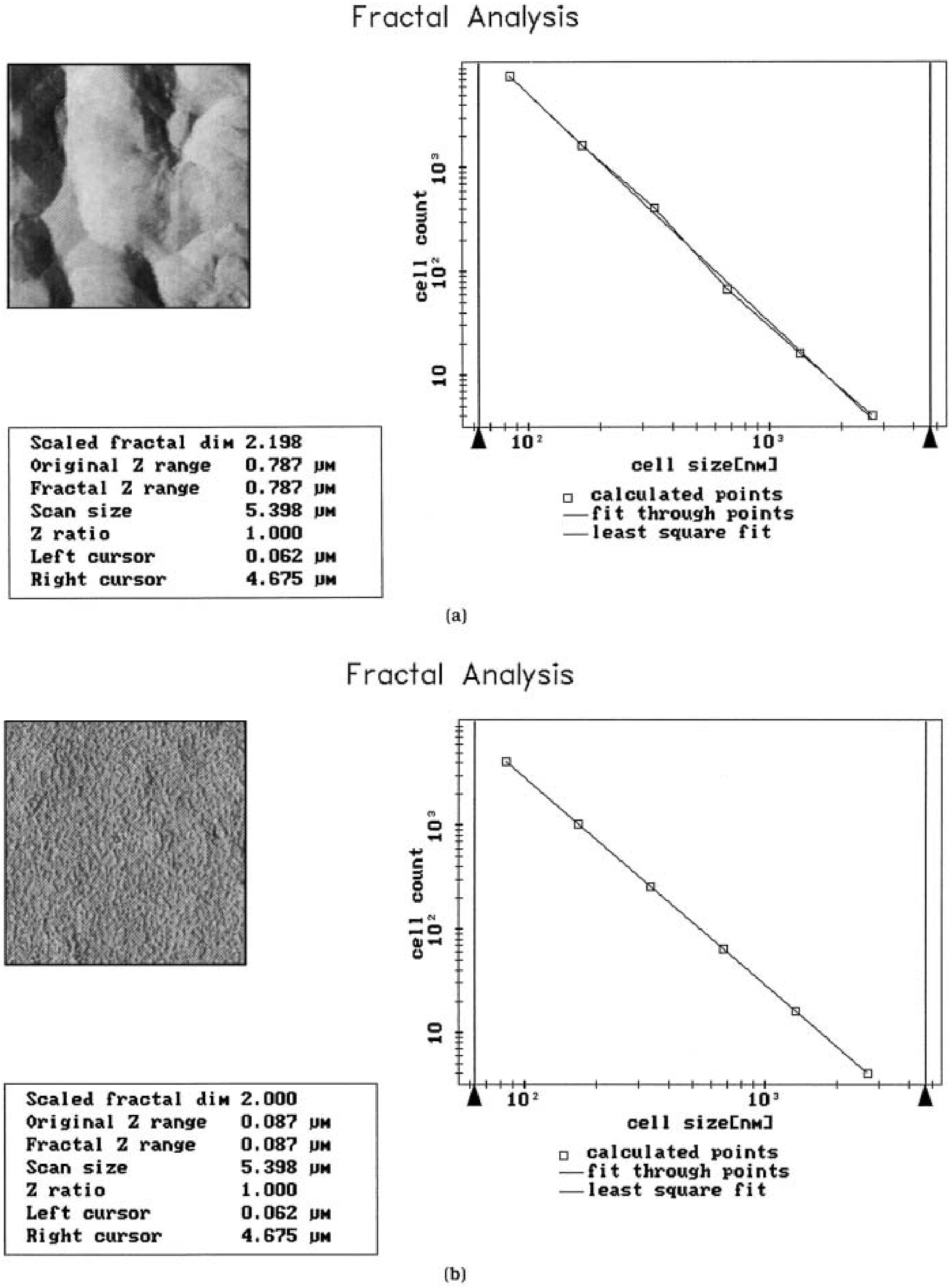


Fig. 3. Fractal analysis of PTFE thin films, a: Surface A, b: Surface B.

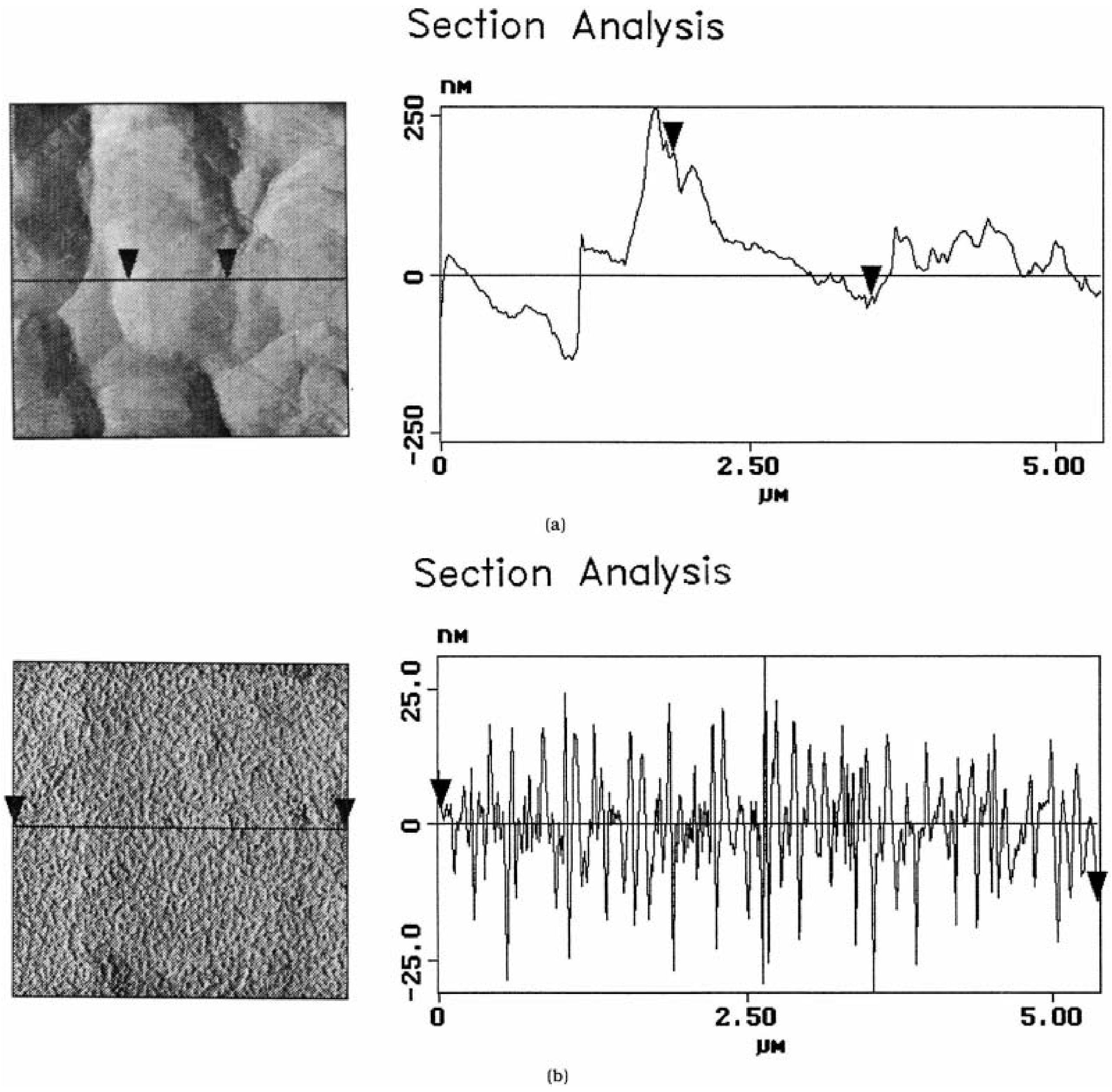
served that the advancing water contact angle at PTFE surface *A* was ~146°. Thus it can be argued that the model proposed by Shuttleworth and Bailey explains the effect of surface roughness on the wetting behavior of the PTFE thin films used in this work. However, for the receding contact angle was not estimated with such accuracy. According to the above theoretical approach, the receding contact angle for PTFE surface *A* is ~45° but the measured value is 60°. In the case of surface *B*, the roughness

Table 2. Contact Angle Data for PTFE Surfaces *A* and *B*.

Sample	Contact Angle (degrees)		Sample	Contact Angle (degrees)	
A	**Advancing**	**Receding**	***B***	**Advancing**	**Receding**
	140	63		99	46
	144	59		92	39
	149	55		93	43
	148	60		92	43
	141	62		91	41
	145	62		94	46
	146	60		93	43
	149	61		95	42
	148	63		94	41
	147	57		92	45
Average	146	60	Average	94	43

asperities were too small to allow any penetration of water into the open space (space between asperities). Consequently, we believe that the above approach using *Eq 4* can not be used in the analysis of such surfaces. In this regard, further work must be done to develop new theoretical models to describe the wetting characteristics of rough surfaces with nanometer size asperities and porosity.

Finally, these results suggest that production of PTFE surfaces with designed surface roughness can be useful to control the wetting of PTFE thin films, such as the water repulsive material developed by NTT, Japan. It is expected that the wetting of this new material can be altered substantially merely by chang-



(a)

(b)

Fig. 4. Section analysis of the PTFE thin films, a: Surface A, b: Surface B.

ing the surface roughness features, rather than by changing its composition.

CONCLUSIONS

It has been demonstrated that nanometer size surface roughness strongly influences the wetting behavior of water at the surface of PTFE thin films. AFM is especially recommended for the analysis of such polymer surfaces with nanometer size irregularities. It was found that variation in surface roughness influences the wetting characteristics of the PTFE thin films even at low surface roughness values ($R_q \simeq 80$ nm). The substrate roughness as characterized by fractal analysis (fractal dimension = 2.2) was found to increase the water contact angle significantly, thereby decreasing the wettability of the PTFE thin film. The preparation/production of surfaces with specifically designed surface roughness features should be useful in the development of more efficient water repulsive materials.

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