J. Cosmet. Sci., 54, 579–588 (November/December 2003)

Effects of conditioners on surface hardness of hair fibers: An investigation using atomic force microscopy

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Accepted for publication July 29, 2003.

Synopsis

Conditioners are known to have a prophylactic effect on hair damage caused by cosmetic chemical treatments or mechanical grooming procedures (1). They are known to impart softness and smoothness to hair by moisturizing the fiber (2). Since the amount of conditioners deposited on the fiber is very small in quantity, it is conceivable that mainly the surface is moisturized. This is especially true of polymeric conditioners, which deposit preferentially on the surface of the fiber, rather than penetrate into the cortex. Therefore, this study strictly investigates whether cationic polymeric conditioners impart softness to the surface cuticle cell as a result of their hydrophilicity, with no regard to its applicability to cosmetic effects. Such softening can be detected by indentation of the surface and can be quantified by measuring the depth of the indent in real time.

Atomic force microscopy (AFM), equipped with nano-indentation capability, is ideally suited for this purpose. In this work it was used to determine changes in the microhardness (micromechanical properties) of the hair fiber surface as a result of fiber/conditioner/moisture interactions. In a preliminary study, we observed that the scale faces of hair treated with Polyquaternium 10 (PQ-10) conditioner gave deeper indents, while scale edges yielded shallower ones in comparison to cuticle cells of untreated hair. This suggests that the conditioner softens the scale face and hardens the scale edges. However, because of significant amounts of conditioner residues left on the scale face, this conclusion was rather ambiguous.

Therefore, the study was repeated in which multiple indentations were made on the surface cuticle cells of a larger number of the *same* hair fibers before and after multiple applications of the conditioner. This reduces errors due to fiber-to-fiber variation in pre-existing microhardness differences in surface cuticle cells. Also, the larger number of fibers investigated in the current work allowed for a statistical outcome. This latter study has led to a rather definite conclusion that the scale face is indeed softened by polymeric conditioners such as Polyquaternium-10 (PQ-10). These studies will ultimately help in the development of conditioners with suitable moisturizing and softening effect on hair.

INTRODUCTION

Conditioners are applied to hair fibers to protect them from abrasion/ablation during everyday grooming (1), to improve general manageability, combability, and luster, and to reduce static charging (flyaway). In this study we strictly want to show whether a cationic conditioning compound present on the fiber surface imparts softness to the surface cuticle cell as a result of its hydrophilicity, with no regard to its applicability to cosmetic properties. Most often, the active component of the conditioning formulation is a polymeric (such as PQ-10) or monomeric (such as cetyl trimethyl ammonium bromide CETAB) cationic quaternary compound, which has great affinity to the negatively charged hair fiber surface (pH = 3.67, isoelectric point) at pH values close to neutral. These conditioners adsorb strongly by electrovalent interaction with sulfonic acid groups on the hair fiber surface. Acid/base interaction between the conditioner and the keratin fiber can lead to different degrees of interaction. We hypothesize that penetration of at least the low-molecular-weight components of the cationic conditioning compounds into the intercuticular regions leads to plasticization of the cuticular sheath, which, in turn, may lead to its softening. On the other hand, in the case of conditioning compounds dominated by hydrocarbon structures, the conditioner/keratin interaction may also occur by hydrophobic bonding between the hydrocarbon chains, which may reduce the moisturization and lead to hardening of the protein–conditioner complex (3) (as observed in our studies involving synthetic fibers).

Using AFM, work of this nature has been done at TRI on synthetic fibers, providing useful information on the effect of topical finishes on the hardness of fibers (3). We extended this study to hair fibers. Atomic force microscopy (AFM) techniques have become quite unique for high-resolution examination of various materials on a nanometer scale, including keratin fibers. AFM provides information not only on the topography, but also on the adhesive, attractive, repulsive, viscoelastic, and micromechanical (microhardness) properties of the fibers. Although some work has been done using AFM to study the topography of untreated and conditioner-treated hair, no attempt has been made to study the hardness of the hair surface. In this work, we have used AFM to study the hardness of the hair fiber surface, which has been modified by the deposition of a cationic conditioning compound.

EXPERIMENTAL

MATERIALS

Hair fibers. Root sections of individual hair fibers were from 14-inch-long, dark brown European hair from DeMeo. To avoid problems stemming from fiber-to-fiber variation, great care was taken that the study was carried out on adjacent regions of the *same* hair fiber root sections before and after multiple applications of a conditioner.

Conditioner. The conditioner employed was Polyquaternium-10 (PQ-10).

TREATMENTS/PROCEDURES

1. *Pretreatment/cleaning.* An appropriate number of untreated hair fibers with diameters of ~90 μm were selected. The fibers were cleaned while under constant stirring for *ca.* 30 minutes at 40°C in a surfactant solution (12.5% Texapon ASV 50, pH = 5.0). The cleaned fibers were air-dried overnight under controlled conditions (22°C, 45% RH).

2. *Nano-indents before conditioner applications.* Six nano-indents were carefully placed onto flat and "clean" regions of surface cuticle cells of seven hair fibers, totaling 42 nano-indentations. AFM tests were carried out on these fibers under controlled conditions (22°C, 45% RH).

3. *Conditioner treatment.* The cleaned and "indented" hair fibers were moistened and exposed to a total of ten 2-minute treatments with 0.5% of Polyquaternium-10 (infinite bath), each time rinsed for 1 minute in running DI water (gal/min) at 40°C, and dried with a hair dryer at moderate temperature.

4. *Nano-indents after ten conditioner applications of the same hair fibers.* A total of 42 nano-indentations were placed again onto the 10× conditioner treated, "clean-appearing," flat regions of surface cuticle cells of the adjacent regions of the same hair fibers, which had been indented prior to the conditioner treatment (not onto the same scale face indented prior to the conditioner applications).

AFM techniques used

Fiber surface properties were obtained on a nanometer scale with a NanoScope® MultiMode™ scanning probe microscope from Digital Instruments, equipped with nano-indentation capabilities (3–6). Specific AFM scanning techniques used to characterize conditioner-induced changes in the surface properties of hair fibers were:

1. Height, phase contrast, and amplitude signals: These techniques characterize topography/morphology, surface adhesion, and viscoelasticity, and can be used to measure microroughness and total surface area.
2. Topographical 3-D height profile (in the "tapping mode"): This measures topography by "tapping" the fiber surface with an oscillating diamond probe tip.
3. Nano-indenting: This measures the microhardness of the fiber surface by indenting the surface with a diamond probe tip mounted on a metal-foil cantilever. The surface indent is imaged, recorded, and measured in real time. A schematic of the technique is shown in Figure 1, which shows the various positions of the indenter and the corresponding force curve giving the force at each position of the indenter.

Nano-indentation is a relatively new technique, which has been adapted by the AFM protocol to determine or compare the microhardness of surfaces of materials (3–6). In this study, nano-indentation measures the microhardness by indenting the hair fibers (*preferably the same hair fibers*) before and after treatment with a conditioner.

In this study, the indents were made on the scale faces with a defined maximum force of 30.1 μN and separated from each other by several micrometers. The cantilever constant of the indenter was 405 N/m. The maximum surface indentation depth was approximately 60 nm. Profile analysis measured the depth of the images of the indents, which were saved in real time.

4. Profile scanning analysis: (also called "cross section analysis"): This measures the depth of the saved images of the indentations (which were recorded in real time) after the experiment. From these images, features related to the relaxation behavior of the material can be derived.

RESULTS AND DISCUSSION

PRELIMINARY STUDY

In the preliminary study, untreated and conditioner-treated hair fibers were indented on the scale faces and the scale edges. Compared to untreated fibers, indents were deeper on the scale faces and shallower at the scale edges of conditioner-treated hair fibers. The

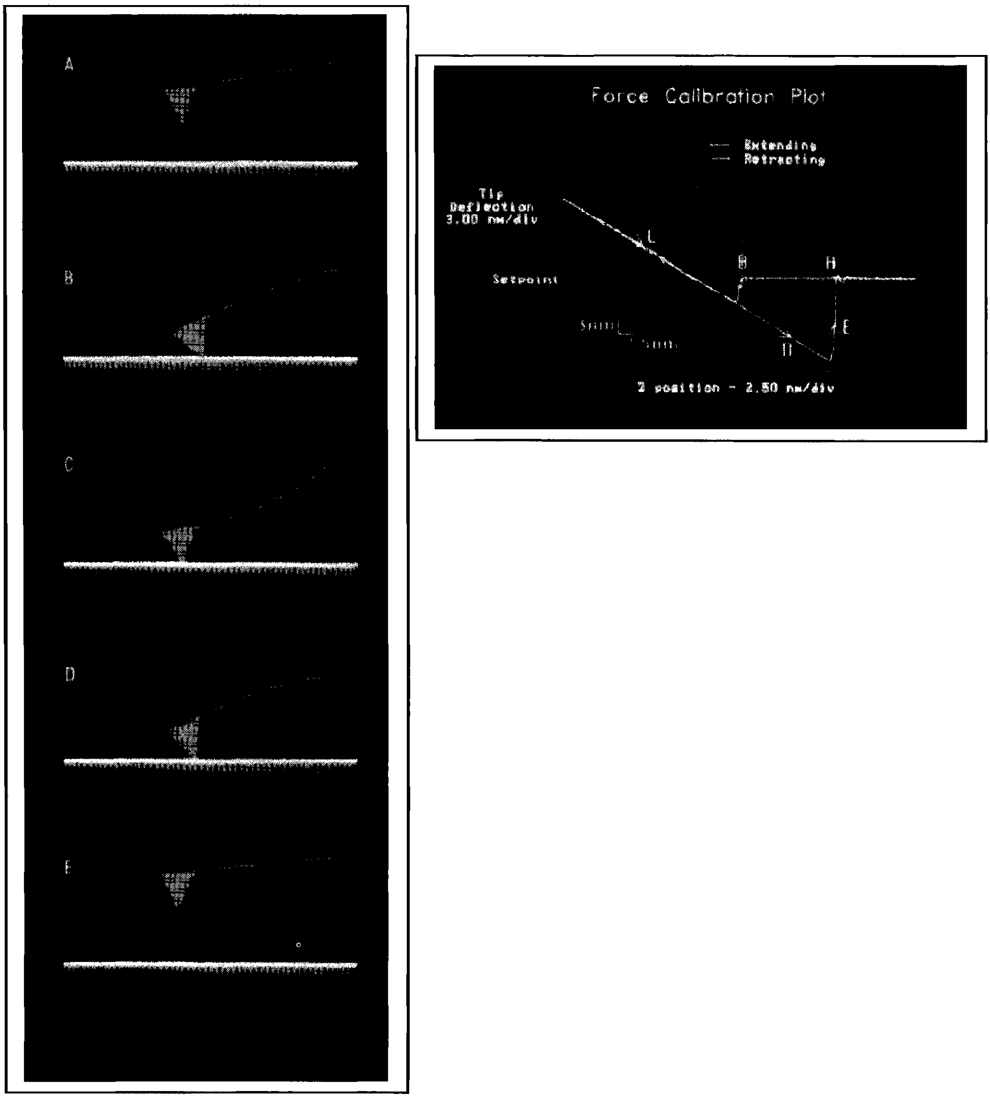


Figure 1. "AFM force measurement" of cantilever-sample interaction (left) shown schematically at several points along the force curve (right), including: (A) approach, (B) jump to contact, (C) contact and indentation, (D) adhesion, and (E) pull-off or separation. (From Digital Instruments Brochure.)

outcome of this study suggested that conditioners may have a softening effect on the surface of the harder scale faces and a hardening effect on the originally softer scale edges. Although these results can be explained on the basis of interactions and polymer properties, the fact that the work was carried out on different hair fibers before and after conditioner application, disregarding differences in pre-existing variations in hardness, questioned the reliability of the data. The presence of significant amounts of conditioner residues further confounded the outcome of this study.

DETAILED STUDY

In this in-depth study, multiple indentations were made on the scale faces of a considerably larger number of the *same* single hair fibers (root sections) before and after multiple applications of the conditioner, to be able to statistically verify the results of the earlier feasibility study. An attempt was made to rinse the fibers thoroughly to remove conditioner deposits from the surface. Observations in the microscope confirmed that a "clean" cuticle surface was obtained and indents were made in close quarters on adjacent scale faces of the *same hair fibers before and after application of the cationic conditioning compound.* The results were analyzed by appropriate procedures to highlight the effects of the conditioner on fiber mechanical property.

HEIGHT/AMPLITUDE IMAGES AND 3-D HEIGHT IMAGES BEFORE/AFTER NANO-INDENTATION

Figures 2a and 2b are typical examples of height and amplitude images of the real-time nano-indentations made on the scale faces of the same untreated and conditioner-treated hair fibers (obtained in the tapping mode), respectively. As can be seen in these figures, the indents were carefully placed on relatively "flat" areas to eliminate problems with the curvature of the hair fiber.

A magnified version of indents shown in the height and amplitude images in Figures 2a and 2b is displayed in "real time" 3-D height images in Figure 3. The images of these indents were recorded in "real time" for subsequent profile scanning analysis to measure the indentation depth. "Real time" acquisition of the images of the indents is important to avoid errors in depth measurements due to partial recovery of the material. Differences in indentation depth between the untreated and conditioner-treated cuticle surface can be attributed to the effect of the conditioner on the hardness of the "scale face."

PROFILE SCANNING ANALYSIS OF THE REAL-TIME IMAGES OF THE INDENTATIONS

It is very difficult to make quantitative statements about changes in the microhardness of the scale faces of the fiber based on the 3-D images alone. Therefore, "profile scanning analysis" is used to interpret the data by measuring the vertical depth of the saved "real time" images of the indentations. Recording the indents in "real-time" is an important aspect, since it stores an image of the actual indent prior to recovery of the deformed substrate. Typical examples of the profile scans across three sequential indents are shown in Figures 4a and 4b along with the corresponding "real-time" height images of the untreated and conditioner-treated hair fibers.

Evaluation of the indentation data. Evaluation of the nano-indentation depths made on flat, "clean" regions of the scale surface (devoid of detectable conditioner deposits) clearly shows a definite decrease in microhardness after multiple conditioner treatments. We feel that this softening effect of the scale faces is strictly due to the hydrophilicity of the polymer present on the keratin surface. Its applicability to cosmetic effects was not the goal of this study. The change in surface hardness is indicated by the scatter plot in Figure 5, showing 42 paired sets of depths of nano-indentations made on the same hair fibers before and after conditioner treatments.

The mean values and standard deviation of the indentation depths show statistically significant differences (at 95% confidence level) between 49.4 nm ± 5.6 for the unconditioned hair and 61.9 nm ± 8.8 for the conditioned hair. The result of the t-test yields

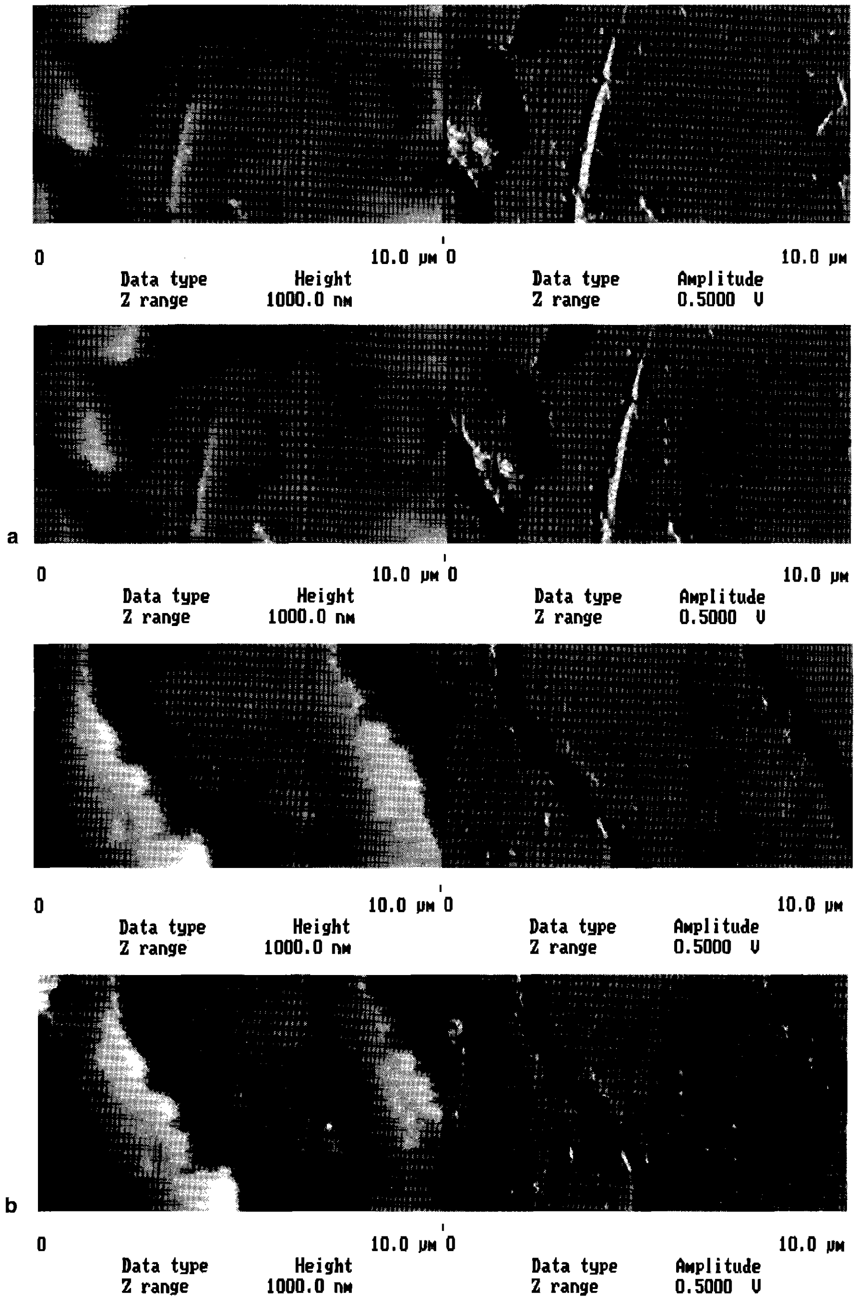


Figure 2. a: Height and amplitude images before (top) and after (bottom) sequential nano-indents on the surface cuticles of the same untreated hair fiber. b: Height and amplitude images before (top) and after (bottom) sequential indents on the surface cuticles of the same conditioner-treated hair fiber.

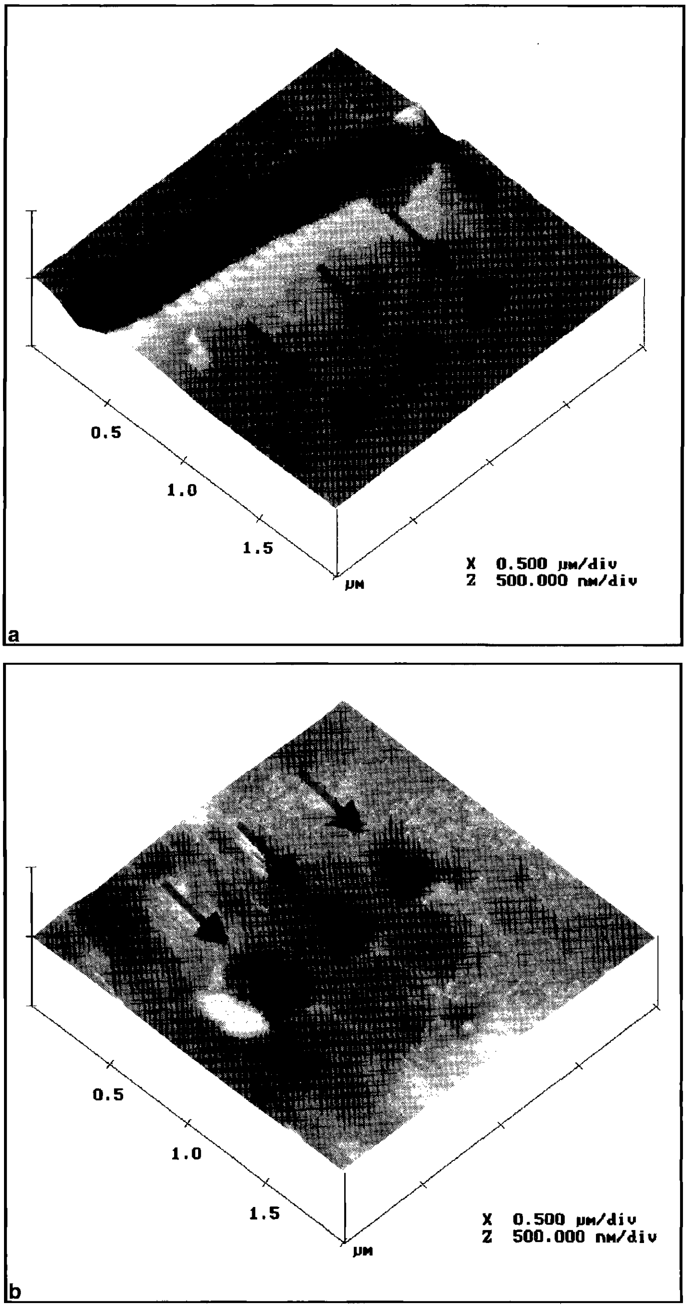
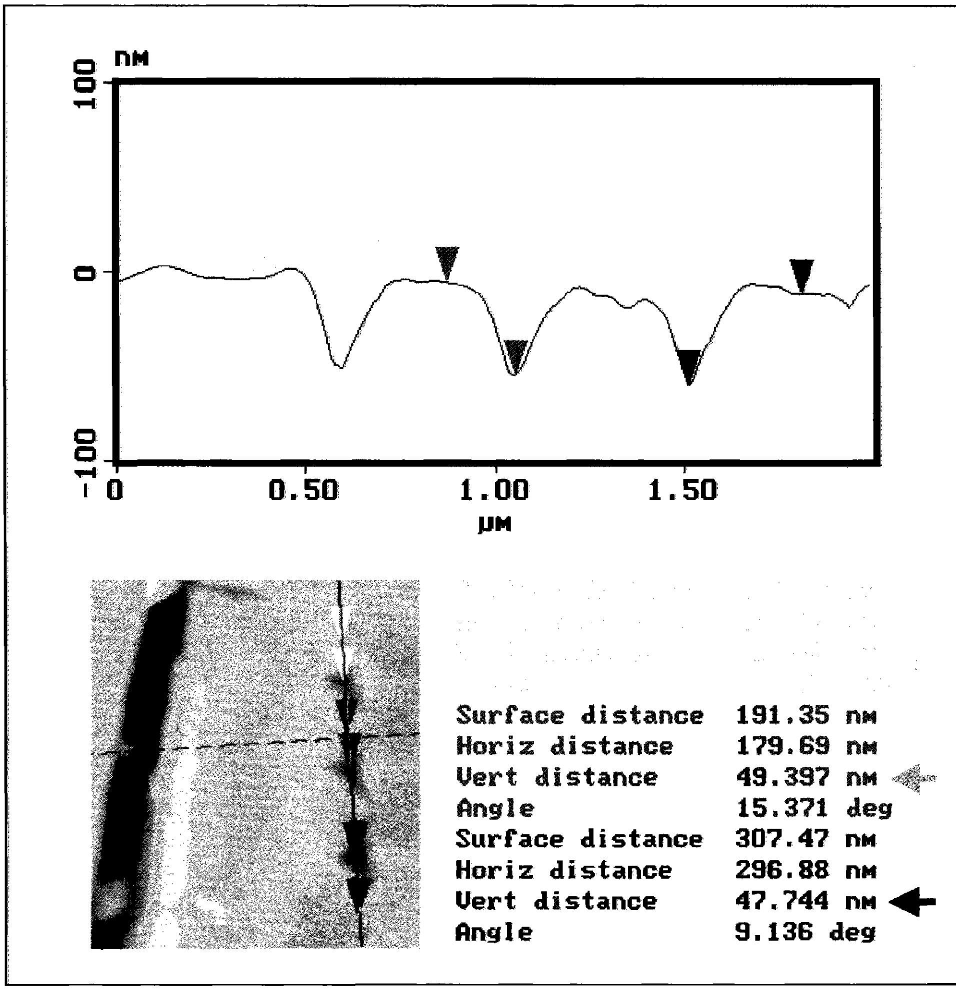


Figure 3. "Real-time" 3-D height images of nano-indents on the "scale faces" of the same hair fiber (a) before and (b) after conditioner-treatment. (3-D height images: scan size = 2 µm; scan rate = 1.001 Hz; number of samples = 256; data scale = 500 nm.)



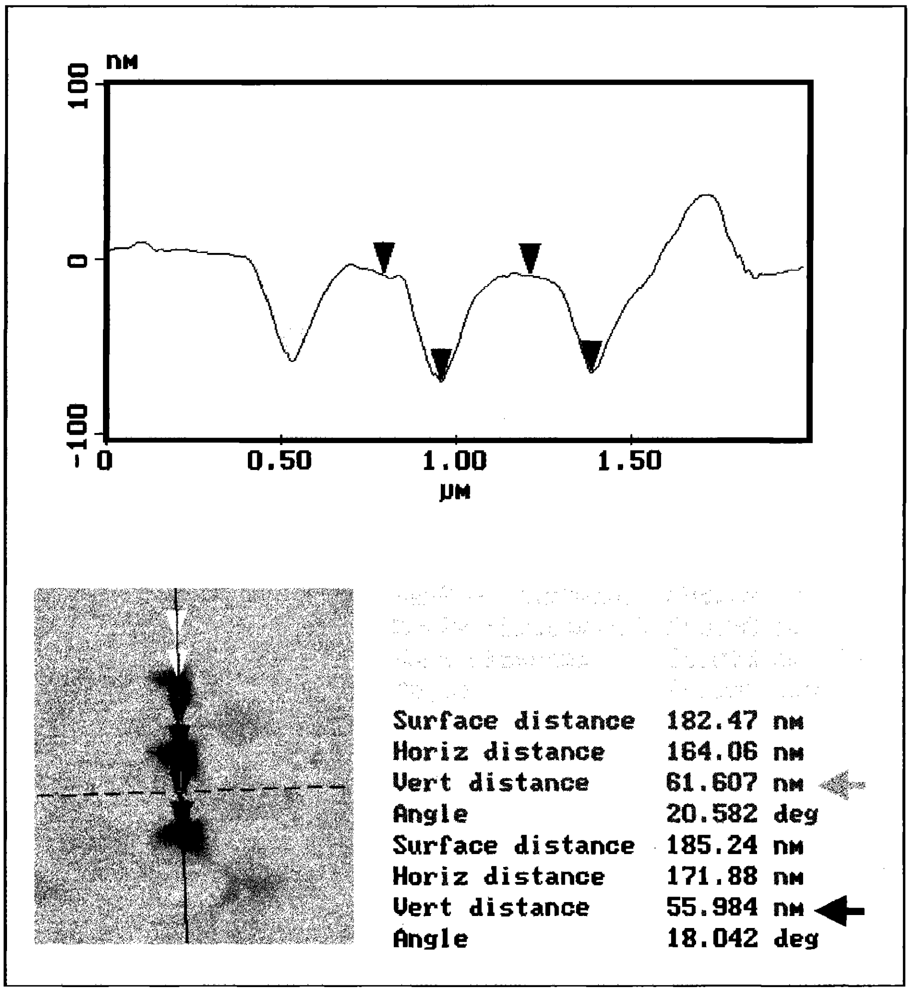
a

Figure 4. a: Profile scan with the corresponding "real-time" height images of nano-indents on the "scale faces" of the untreated hair fiber. b (facing page): Profile scan with the corresponding "real-time" height images of nano-indents on the "scale faces" of the conditioner-treated hair fiber.

4.2×10^{-9}, which indicates that these are two independent measurement rows at 99.99% probability.

CONCLUSIONS

These investigations show that AFM measurements with the nano-indentation technique are capable of distinguishing between the hardness of the scale faces of untreated and conditioner-treated hair fibers. This technique is useful in establishing conditioner-induced modifications in micromechanical properties (hardening or softening) of the hair fiber surface. Multiple indentations were made on the surface cuticle cells of a larger number of the *same hair fibers before and after multiple applications of the conditioner.* Making measurements on the same hair fibers before and after multiple conditioner treatments



b

Figure 4. Continued.

eliminates errors due to fiber-to-fiber variation in pre-existing differences in microhardness and receptivity to conditioner deposition. The larger number of fibers investigated allows statistical comparison of the data and improves the reliability of the conclusion. This study suggests that cationic hydrophilic polymeric conditioning compounds, such as PQ-10, have a softening effect on the surface of the scale faces because of their water-retaining capabilities.

ACKNOWLEDGMENTS

The work was carried out in context with TRI's "Analysis and Quantification of Hair Damage" project and was financially supported by a group of TRI corporate participants from the international hair care industry.

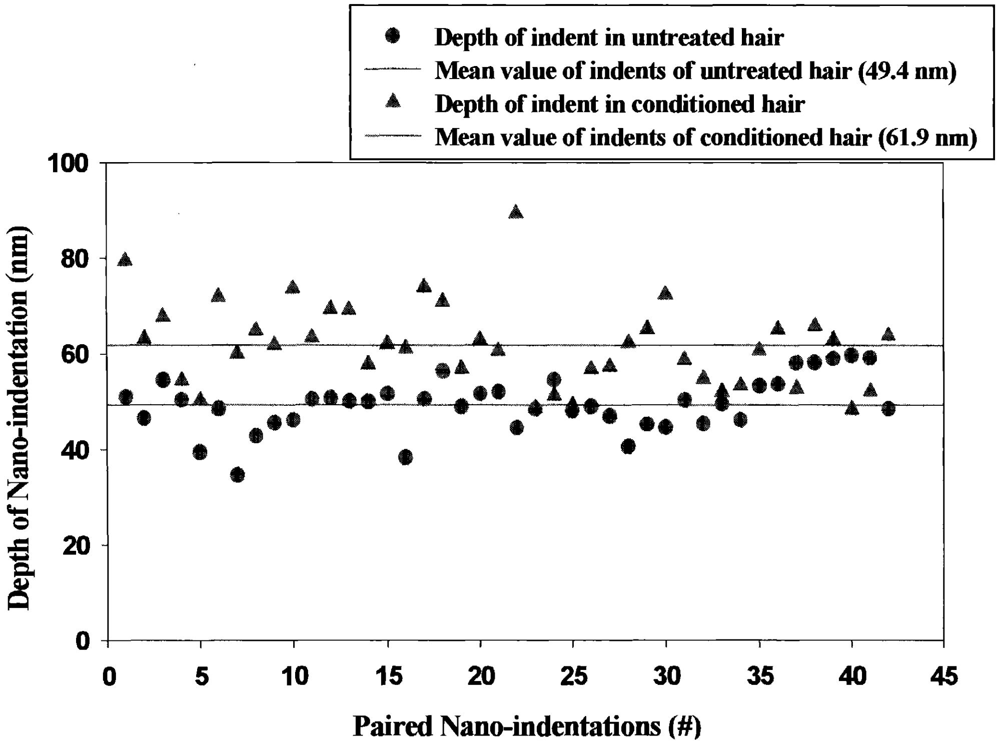


Figure 5. Depth of nano-indentation in untreated and conditioner-treated hair.

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