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Nanomechanical characterization of human hair using nanoindentation and SEM

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Abstract

Human hair is a nanocomposite biological fiber with well-characterized microstructures. Nanomechanical characterization of human hair can help to evaluate the effect of cosmetic products on hair surface, can provide a better understanding of the physicochemical properties of a wide variety of composite biological systems, and can provide the dermatologists with some useful markers for the diagnosis of hair disorders. The paper presents systematic studies of nanomechanical properties of human hair including hardness, elastic modulus and creep, using the nanoindentation technique. The samples include Caucasian, Asian and African hair at virgin, chemo-mechanically damaged and treated conditions. Hair morphology was studied using scanning electron microscopy (SEM). Indentation experiments were performed on both the surface and cross-section of the hair, and the indents were studied using SEM. The nanomechanical properties of hair as a function of hair composition, microstructure, ethnicity, damage and treatment are discussed.

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Keywords: Nanoindentation; Hardness; Elastic modulus; Human hair; Cuticle; Cortex; SEM

1. Introduction

Healthy and beautiful hair is desired. The need for products that improve the look and feel of hair surface has created a huge industry for hair care. Hair care technology has advanced the cleaning, protection, and restoration of desirable hair properties by altering the chemical and physical properties of the hair surface. Shampoo is used to clean hair and conditioner is used to coat the hair with a thin film in order to protect it and provide desirable look and feel [1,2]. Conditioner consists

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of gel network chassis (cationic surfactant, fatty alcohols and water) for superior wet feel and combination of conditioning actives (silicones, fatty alcohols and cationic surfactant) for superior dry feel. The wet feel benefits are creamy texture, ease of spreading, slippery feel while applying, and soft rinsing feel. The dry feel benefits are moistness, softness and dry combing ease. Many other ingredients are added as well to meet the needs of consumers.

The success of a cosmetic product is based not only on its properties, but also on the way it interacts with the biological substrate. One function of conditioner is to interact with the hair surface and soften it. It would be useful if this effect can be evaluated quantitatively by measuring the nanomechanical properties, such as hardness and elastic modulus, of the hair surface before and after conditioner treatment. The uniformity or distribution of the conditioner layer over the hair surface is also an important feature, namely how and where it is localized. In industry, it has been a challenge to locate the conditioner by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The variation of the nanomechanical properties of the conditioner treated hair from one location to another along the hair surface can be the parameters to evaluate the uniformity of conditioner, assuming that small variation indicates good uniformity. Therefore, the nanomechanical characterization of hair surface can help to evaluate the effect of conditioner and its distribution.

In the past, most of the mechanical property studies of human hair were on the macro scale using the conventional methods, such as tension, torsion and bending tests [2–7]. The mechanical properties obtained from these tests are the overall mechanical properties of the hair, not just the hair surface. Recently, a few studies have been conducted on the elasticity of keratin fiber and hair using AFM [8–10]. Although it is possible to extract nanomechanical information like elastic modulus or elasticity from AFM, it is very difficult to measure hardness using an AFM. Depth-sensing nanoindentation measurement techniques are commonly used to measure nanomechanical properties of surface layers of bulk materials and of ultrathin coatings. These techniques are considered to be suitable to measure the nanomechanical properties of human hair [11–13].

The nanomechanical characterization of hair not only can help to evaluate the effect of cosmetic products on hair surface, but also can provide a better understanding of the physicochemical properties of a wide variety of composite biological systems. Human hair is a nanocomposite biological fiber with well-characterized structures, which will be described in detail in the next section, and it can be a good model to study the role of various structural and chemical components in providing mechanical strength for composite biological fibers. For example, human hair has similar structures with wool fiber. There exist some theoretical models for the role of different structural components in contributing to the mechanical properties of wool fibers in the lateral and longitudinal directions, which might also apply to human hair [14]. But the models need direct experimental data, such as hardness and elastic modulus in the micro/nanoscale. In addition, all natural fibers, including human hair, exhibit non-linear viscoleastic behavior [15,16]. That is, the stress is a non-linear function of strain as well as being a function of time. The non-linear viscoelastic behavior of human hair at moderate extensions have been studied [6], but the creep behavior of hair in the lateral direction due to localized nanoindentation has received little attention. The studies of creep behavior of human hair in the micro/nanoscale may also help to understand the non-linear viscoelastic behavior of other composite biological fibers.

Furthermore, the quantitative determination of the mechanical properties of human hair can also provide the dermatologists with some useful markers for the diagnosis of hair disorders and for the evaluation of their response to therapeutic regimens [17,18]. Nikiforidis et al. developed a methodology trying to interpret the stress–strain curves of the elastic and viscous components of the mechanical behavior of human hair obtained during longitudinal stretching, and to determine characteristic parameters which correlate with its structural features. Unfortunately, the diagnostic value of the parameters identified through their proposed methodology is limited because of the lack of homogeneity of hair, since for diagnosis of hair disorders it is important to know whether the change of the mechanical parameters is due to variations of the cross-sectional area of hair medullar (central region) or due to alterations in the cortical microstructures (outer region). These problems can be overcome by using a depth sensing nanoindenter to measure the nanomechanical properties of the cross-section of the hair. Nanoindentation studies on cross-section of glass fibers (8–20 μm in diameter) have been carried out successfully in our group [19].

To summarize, nanomechanical characterization of human hair using nanoindentation technique will probably contribute to at least three areas: hair cosmetology, composite biological system studies and dermatology. In this paper, systematic studies of nanomechanical properties of human hair including hardness, elastic modulus and creep, using nanoindentation technique are presented.

2. Hair structure

Since the physical properties of human hair are closely related to the microstructures, in order to better understand the nanomechanical properties of hair, it is necessary to describe the hair structure first.

Fig. 1 shows a schematic of a human hair fiber with its various layers of cellular structure [1–3]. Hair fibers (about 50–100 μm in diameter) consist of cuticle and cortex, and in some cases medulla in the central region. All of them are composed of dead cells, which are mainly filled with keratin protein. The keratin is characterized by a high content of cystine, an amino acid that has the capacity to cross-link the protein by its intermolecular disulfide linkages. A high cystine content corresponds to rich disulfide cross-links, leading to high mechanical properties. In addition to disulfide bonds, hair is also rich in peptide bonds and the abundant CO– and NH– groups present give

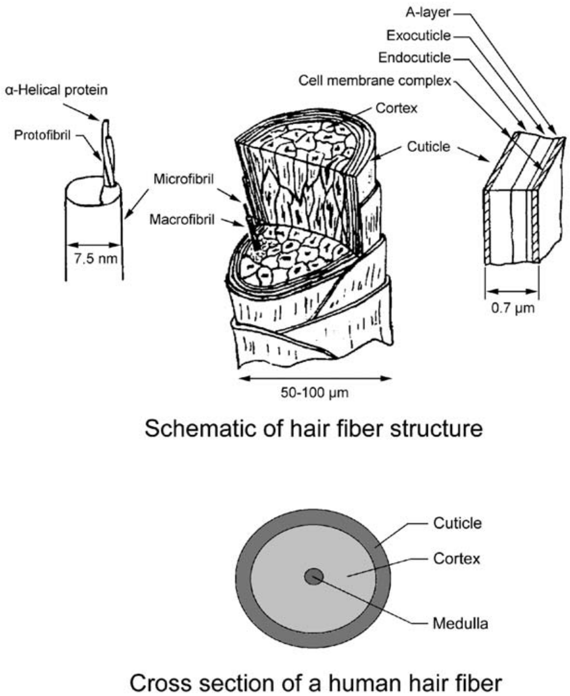


Fig. 1. Schematic of hair fiber structure, and cross-section of human hair fiber [2].

rise to hydrogen bonds between groups of neighboring chain molecules.

Cuticle consists of flat overlapping cells (scales). The cuticle cells are attached at the root end and they point forward the tip end of the hair fiber, like shingles on a roof. Each cuticle cell is approximately 0.3–0.5 μm thick and the visible length of each cuticle cell is approximately 5–10 μm. The cuticle in human hair is generally 5–10 scales thick. Each cuticle cell consists of the cell membrane complex and three major layers: the A-layer, a resistant layer with a high cystine content (>30%); the exocuticle, also rich in cystine (~15%); and the endocuticle, low in cystine content (~3%). The cortex contains cortical cells and the intercellular binding material, or the cell membrane complex. The cortical cells are generally 1–6 μm thick and 100 μm long, which run longitudinally along the hair fiber axis and take up the majority of the inner hair fiber composition [20]. The macrofibrils (about 0.1–0.4 μm in diameter) comprise a major portion of the cortical cells. Each macrofibril consists of intermediate filaments (about 7.5 nm in diameter), previously called microfibrils, and the matrix. The intermediate filaments are low in cystine (~6%), and the matrix is rich in cystine (~21%). The cell membrane complex consists of cell membranes and adhesive material that binds the cuticle and cortical cells together. The intercellular cement of the cell membrane complex is primarily non-keratinous protein, and is low in cystine content (~2%). The medulla of human hair, if present, generally makes up only a small percentage of the mass of the whole hair, and is believed to contribute negligibly to the mechanical properties of human hair fibers.

3. Experimental details

3.1. Test samples

3.1.1. Hair sample preparation

Caucasian, Asian and African hair samples were used in this study. Table 1 presents a list of all samples used. Samples arrived as hair switches approximately 0.3 m long. Although the exact location from the root is unknown, it is estimated that hair samples used for testing were between 0.1 and 0.2 m from the scalp. In most cases, the experiments were conducted on the middle parts of the hair samples (about 10 mm). In the case for comparing the topography and mechanical properties of hair at different locations, the virgin Caucasian hair specimens were also cut from the locations near scalp and near tip. There are three main categories that are of interest for each type of hair ethnicity: virgin, damaged, and treated. Virgin samples are considered to be baseline specimens and are defined as having an intact cuticle and absence of chemical damage. Chemo-mechanically damaged hair fibers have been exposed to one or more cycles of coloring and permanent wave treatment, washing, and drying, as well as combing (to contribute mechanical damage), which are representative of common hair management and alteration. In the case of African damaged hair samples, damage occurred due to chemical straightening. Treated samples were exposed to one rinse/wash cycle of a Procter & Gamble commercial conditioner, Pantene Smooth & Sleek (for details, see Appendix A). All hair samples had undergone two rinse/wash cycles of commercial shampoo application (in the case of treated samples, prior to treatments).

Table 1
List of hair samples used

Ethnicity	Condition
Caucasian	Virgin
	Damaged
	Treated (with conditioner)
Asian	Virgin
	Damaged
	Treated (with conditioner)
African	Virgin
	Damaged
	Treated (with conditioner)

3.1.2. Specimen mounting

For nanoindentation studies, hair specimens were mounted onto Si (1 0 0) wafer using Liquid Paper® correction fluid. A thin layer of the fluid

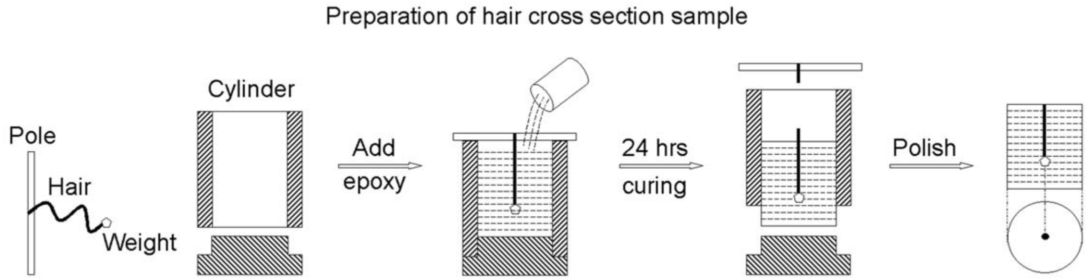


Fig. 2. Schematic of the hair cross-section sample preparation process.

was brushed onto the wafer, and when the fluid hardened into a tacky state, the hair sample was carefully placed. The Liquid Paper® dries quickly to keep the hair firmly in place. For SEM studies, hair specimens were mounted onto Si (1 0 0) wafer using conductive silver paste with the above method.

3.1.3. Cross-section sample preparation

Fig. 2 shows the process of preparing the hair cross-section sample. The Buehler® Epoxicure™ Resin and Buehler® Epoxicure™ Hardener were mixed in a cylinder in the weight ratio of 5:1 to make the hair cross-section metallography sample. The epoxy cures slowly at room temperature. To make sure the hair was put vertically in the epoxy, one end of the hair was attached to a thin pole, and the other end was tied with a weight. After 24 h curing, the hair was cut and the epoxy containing the hair was taken out of the cylinder. The last step was to use the standard metallography polishing technique to polish the epoxy till a clean cross-section interface of hair was obtained. The virgin Caucasian, Asian and African hair were used to make the cross-section samples.

3.2. Experimental techniques

3.2.1. Hardness, elastic modulus and creep measurements

Hardness and elastic modulus of human hair were measured using a nanoindentation technique [11–13] with a Nano Indenter II® (MTS Systems Corp.). A three-sided (triangular-based) pyramidal diamond Berkovich indenter tip (radius 100–200 nm) was used. For nanoindentation on all the virgin hair surface except African hair, a wide load range (0.1–300 mN) was used, in order to study the mechanical property variation of hair surface depending on the indentation depth. In the case of virgin African hair, the load of 300 mN was not used because the hair was too soft to get reasonable data at 300 mN. For the damaged, treated hair and the hair near scalp, in the middle and near tip, 0.1, 1.0, 10, 100 mN normal loads were used. At each load, five indents were made, and the hardness and elastic modulus values were averaged from them and the standard deviations were calculated. In order to study the data variation from hair to hair in the same ethnicity at the same condition, four Caucasian virgin hair, four Caucasian damaged hair and four Caucasian treated hair were chosen. In each case, three hair were chosen from one batch, and the forth one was chosen from another batch. For nanoindentation on virgin hair cross-section samples, only one normal load, 1.0 mN, was used to make indents at cuticle, cortex and medulla.

Creep displacements of various hair as a function of time were measured using the nanoindentation technique [11,12] with the Nano Indenter II®. The same diamond Berkovich indenter tip was used. To do the creep test, a normal load was applied, and then the tip was held for 600 s. The displacement change during the holding time were recorded. The loads used were 0.1, 1.0 and 10 mN. All the hardness, elastic modulus and creep measurements were performed in ambient conditions ($22 \pm 1\,^{\circ}C$, $50 \pm 5\%$ relative humidity).

3.2.2. SEM measurements

Hair morphology, cross-section structure and indents on hair were measured using Philips XL-30 ESEM. The operating accelerating voltage was 10 kV. Before doing SEM, the hair samples were coated with a thin layer of gold (about 5 nm thick) by sputtering using a Pelco® Model 3 Sputter Coater 91000.

4. Results and discussion

4.1. Hair morphology

Fig. 3(a) shows the SEM images of Caucasian, Asian and African hair at virgin, damaged and treated conditions. By comparing the virgin Caucasian, Asian and African hair, it can be seen that the Asian hair is the thickest (about 100 μm), followed by African hair (about 80 μm) and Caucasian hair (about 50 μm). The visible cuticle cell is about 5–10 μm long for the three hair. Fig. 3(b) shows the SEM images of virgin Caucasian hair at three locations: near scalp, middle and near tip. Three magnifications were used to show the significant differences. The hair near scalp had complete cuticles, while no cuticles were found on the hair near tip. This may be because that the hair near the tip experienced more mechanical damage than the hair near the scalp. The hair in the middle experienced intermediate damage, i.e., one or more scales of the cuticles were worn away, but many cuticles stayed complete.

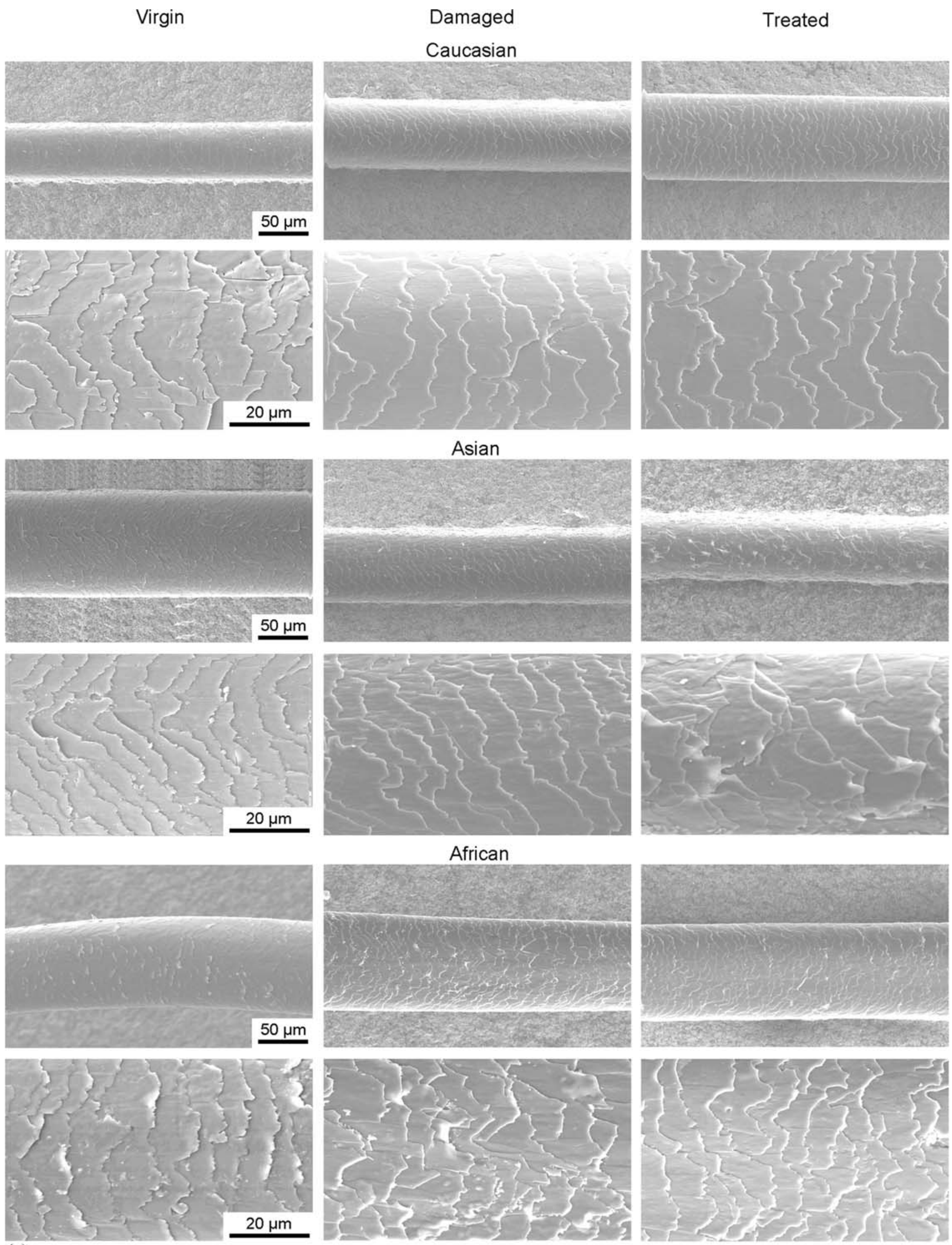
Most of our hair are in the similar stage as the middle part of the hair (see Fig. 3(b)) in terms of damage extent. If some substructures of one cuticle scale, like A-layer or A-layer and exocuticle (see Fig. 1), are gone, or even worse, one or several cuticle scales are worn away, it is impossible to heal the hair biologically, because hair fibers are composed of dead cells. However, it is possible to physically "repair" the damaged hair by using conditioner, one of whose functions is to cover or fill the damaged area of the cuticles. Fig. 3(c) shows the high magnification SEM images of virgin and treated Caucasian hair. The endocuticles (pointed by arrows) were found in both hair. In order for the conditioner to physically repair the hair, it is expected for it to cover the endocuticles. In the case of severely damaged hair, for example, if an edge of one whole cuticle scale worn away, the conditioner may fill that damaged edge. In the SEM image of the treated hair in Fig. 3(c), the substance which stayed near the cuticle edge is probably the conditioner (pointed by an arrow).

Fig. 4 shows the AFM images of various virgin hair, along with the section plots. The arrows point to the position where the section plots were taken from. Each cuticle cell is nearly parallel to the underlying cuticle cell, and they all have similar angles to the hair axis, forming a shingle-like hair surface structure. The visible cuticle cell is approximately 0.3–0.5 μm thick and about 5–10 μm long for all three hair.

4.2. Hardness, elastic modulus and creep of hair surface

Fig. 5 shows the optical micrograph of three indents on virgin Asian hair made at the normal load of 100 mN. The indentation depths and residual depths were about 5 and 3 μm, respectively. The sizes of these indents are about 15–20 μm in diameter. This image clearly shows that the Nano Indenter II system can successfully make indents on human hair surface.

Fig. 6(a) shows the load-displacement curves for virgin, damaged and treated Caucasian hair obtained at four loads: 0.1, 1.0, 10 and 100 mN. The hardness and elastic modulus values corresponding to each load-displacement curve are listed in the figure boxes. As mentioned in the Experimental section, at each load, five indents were made. Fig. 6(a) just presents one representative result for each load. At 0.1 mN, the indentation depths of all these hair were less than 150 nm, which means that the indents were made within one cuticle scale, assuming that the thickness of one cuticle scale is about 0.3–0.5 μm for all these hair samples. At 1.0 mN, the indentation depths were about 0.4–0.6 μm, indicating that indents were probably made through one to two cuticle scales. At 10 mN, the indenter tip penetrated about three to five cuticle scales. At 100 mN, the indentation depths were about 5 μm, which means



(a)

Fig. 3. (a) SEM images of various hair; (b) SEM images of virgin Caucasian hair at three locations; and (c) SEM images of Caucasian, virgin and treated hair.

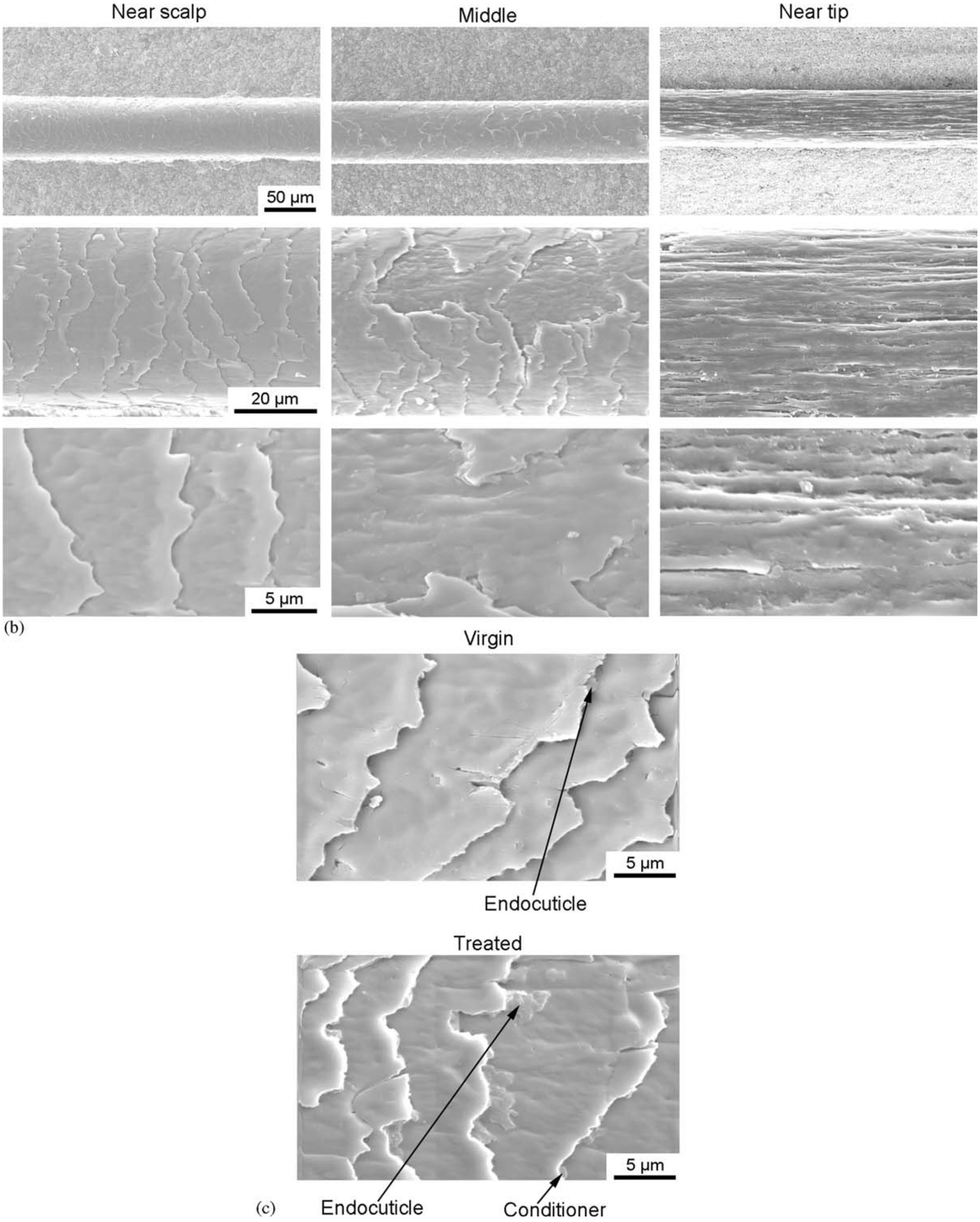


Fig. 3. (*Continued*)

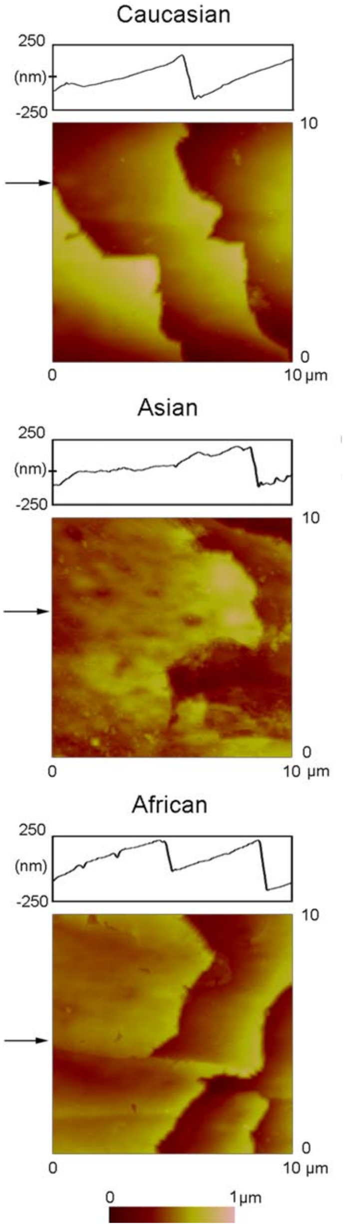


Fig. 4. AFM images of various virgin hair.

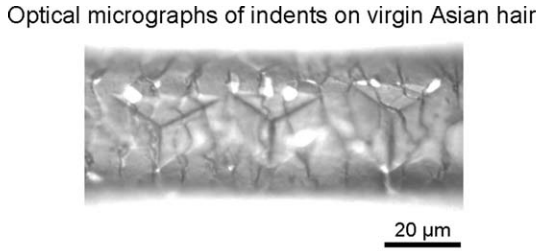


Fig. 5. Image of indents on hair surface.

that the tip probably reached the cortex of the hair, considering that the hair generally has about 5–10 cuticle scales. It is interesting to observe that the loading curves of damaged hair obtained at 0.1 and 1.0 mN are not so smooth as the virgin and treated hair, especially at the beginning, indicating that the damaged hair was very soft at the first 30–50 nm or so, probably because of the chemical damage which caused changes to the exposed surface. At 0.1 and 1.0 mN, the hardness and elastic modulus of treated and damaged hair are lower than the virgin hair, indicating that chemical damage and conditioner treatment led to the softness of the hair surface. Considering human hair as a polymeric cylinder, the absorption of chemicals used in hair coloring and conditioner ingredients in the first micron or so might plasticize the polymer and hence reduce its mechanical properties. At 10 and 100 mN, the hardness and elastic modulus of all three hair look similar. This result indicates that the effective depth of the chemicals/conditioner influence is probably less than 1.5 μm, i.e., the first 3–4 scales of the cuticles probably interact with the chemicals and conditioner ingredients more effectively than the rest of the scales.

Fig. 6(b) shows the hardness and elastic modulus vs. indentation depth for various hair. Every data point (averaged hardness and elastic modulus value), and every error bar in Fig. 6(b) was calculated from five indentations. According to Fig. 6(b), the hardness and elastic modulus of hair decreases as the indentation depth increases. In order to explain this, the indentation process is divided into two stages. In the first stage, the indenter tip penetrated the cuticles scales only, in which the indentation depth was probably less than 5 μm. For one cuticle scale, the mechanical properties are expected to decrease from top layer to bottom layer, because the cystine content, thus the disulfide cross-link density, decreases from the A-layer (cystine content $>30\%$), to the exocuticle (cystine content $\sim 15\%$), and to the endocuticle

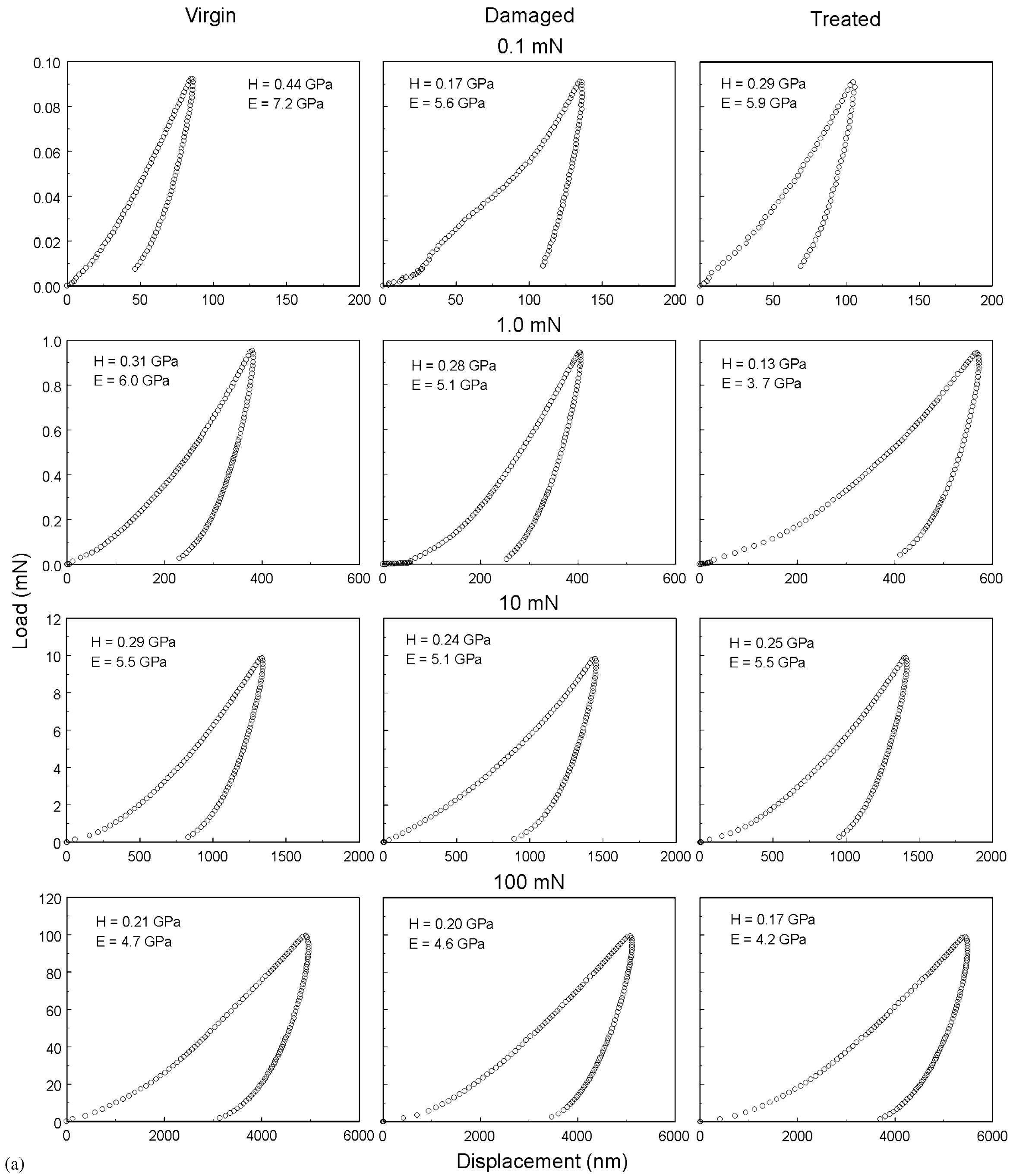


Fig. 6. (a) Load-displacement curves for Caucasian hair; and (b) hardness and elastic modulus vs. indentation depth for various hair.

(cystine content ~3%) (see Fig. 1). The cuticle scales are bound together by the cell membrane complex, one of the weakest parts of the hair fiber in terms of mechanical properties. The intercellular cement of the cell membrane complex is primarily non-keratinous protein, and is low in

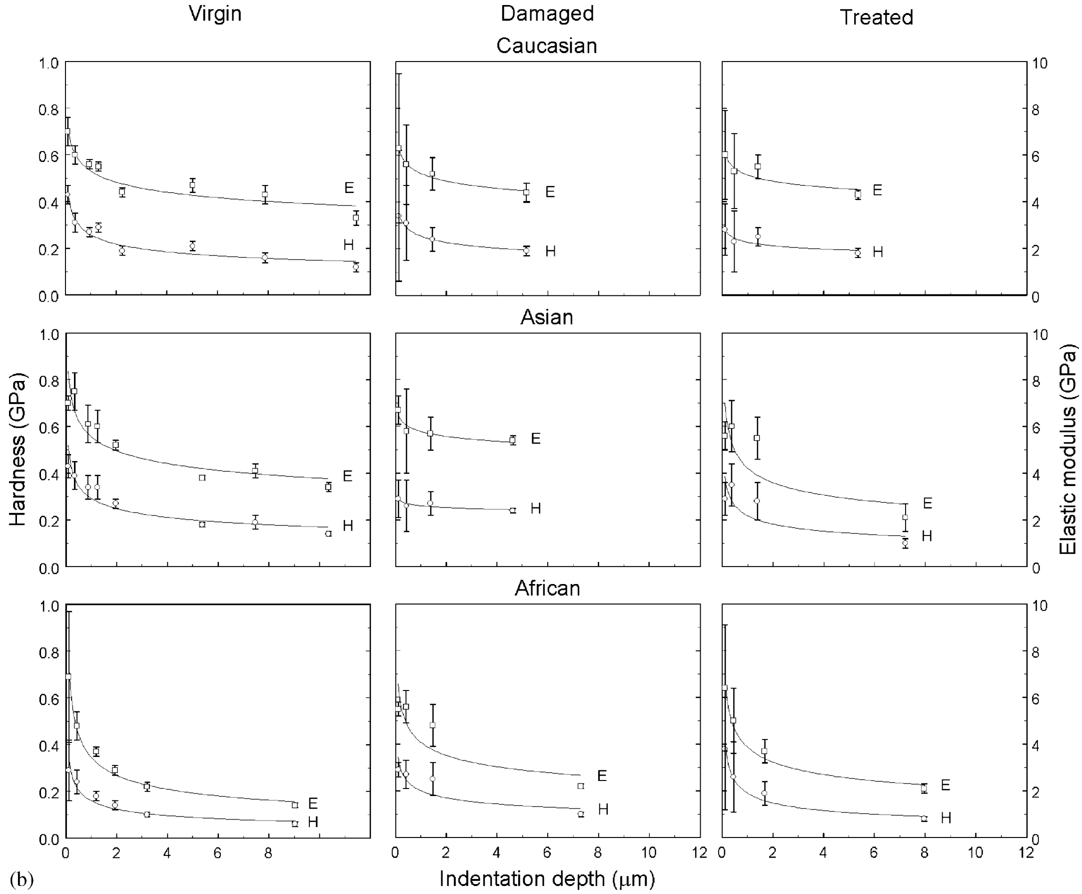


Fig. 6. (*Continued*)

cystine content (~2%). When the indenter tip penetrated the cuticle scales one by one continuously, the number of the cell membrane complex layers penetrated by the tip increased. These weak cell membrane complex layers joined together might lead to a deeper displacement upon indentation, contributing to lower mechanical properties. It is also possible that the outer scales of cuticles have higher mechanical properties than the inner scales. In the second stage, the tip began to penetrate the cortex. In general, the cuticles are richer in disulfide cross-links than the cortex [2,3]. So the mechanical properties of the cortex are expected to be lower than the cuticle. Putting the two indentation processes together, the hardness and elastic modulus of hair will decrease as a function of the indentation depth.

Fig. 6(b) also indicates that at normal loads of 0.1, 1.0 and 10 mN, corresponding to the indentation depth of less than 1.5 μm, the damaged and treated hair generally had lower hardness and elastic modulus, but larger error bars, i.e., larger data deviations, than the virgin hair for each ethnicity. This result means that the effective interaction depths were probably less than 1.5 μm for all three ethnicity of hair, and that the effect or distribution of the conditioner on the hair surface was not uniform. It is believed that most of the important interactions between shampoo/conditioner and hair occur at or near the hair surface (the first few micrometers of the fiber periphery). The nanomechanical characterization of hair surface shows that the effective interaction depth (< 1.5 μm) may be shallower than what was thought before. In general, two types of interaction occur between chemical/conditioner ingredients and hair: adsorption and absorption. It has been suggested that for conditioning ingredients in hair conditioners, adsorption is more critical than absorption, because the conditioning ingredients are relatively large species [2]. If this is the case, then the data variation was probably caused by the non-uniform adsorption of the chemical molecules and the conditioning ingredients to the hair surface. Because the interaction affected the hair up to 1.5 μm deep, absorption should also play an important role here. Transcellular and intercellular diffusion are the two theoretical pathways for absorption to occur. The transcellular route involves diffusion across cuticle cells through both high and low cross-linked proteins. The intercellular diffusion involves penetration between cuticles cells through the intercellular cement and the endocuticle that are low in cystine content (low cross-link density regions). The intercellular diffusion is usually the preferred route for entry of most molecules (especially large ones such as surfactants or even species as small as sulfite near neutral pH). However, for small molecules, transcellular diffusion under certain conditions might be the preferred route, especially if the highly cross-linked A-layer and exocuticle are damaged [2]. Depending on the molecular size and the hair condition, the diffusion pathway and diffusion rate might be different from site to site on the hair surface, thus the distribution of conditioner might not be uniform. To sum up, for damaged and treated hair, since the adsorption and absorption of chemicals and conditioner ingredients were probably not uniform on the hair surface, the nanomechanical properties of the hair surface (depth $<1.5\,\mu m$) were not affected (generally decreased), uniformly, leading to the larger data variation compared to corresponding virgin hair. Our work implies that the nanoindentation technique can be used to quantitatively evaluate the effective depth of the conditioned hair and distribution of conditioner by measuring the hardness and elastic modulus of the hair surface before and after conditioner treatment as a function of depth and location.

No two-hair fibers have exactly the same mechanical properties. In order to study the nanomechanical property variation from hair to hair in the same ethnicity at the same condition, nanoindentation experiments were performed on virgin, damaged and treated Caucasian hair, each of which included hair from different batches. Fig. 7(a) summarizes the hardness and elastic modulus for various batches of Caucasian hair. At each load, only one indentation was made. It was found that the decreasing trend of the hardness and elastic modulus as a function of increasing load, i.e., increasing indentation depth, was the same as Fig. 6(b).

Fig. 7(b) summarizes the hardness and elastic modulus of various hair. In general, the damaged and treated hair had lower nanomechanical properties and larger error bars than the corresponding virgin hair, as discussed above. The data of African hair was a little strange. For example, the treated African hair seemed to have higher hardness than virgin African hair. It should be noted that the African hair is naturally curly and highly elliptical, and it was very difficult to mount them and make indentations on their surface. The curly and highly elliptical surface of African hair might cause the indentation results vary somewhat from the actual values. If we use the hardness and elastic modulus measured at 1.0 mN as the hair surface hardness and elastic modulus, then by comparing the virgin Caucasian, Asian and African hair, we can see that the Asian hair has the highest hardness (0.39 ± 0.06 GPa) and elastic modulus (7.5 ± 0.8 GPa), followed by Caucasian hair with hardness of 0.31 ± 0.04 GPa and elastic modulus of 6.0 ± 0.4 GPa. The African hair seems to have the lowest mechanical properties, whose hardness is 0.24 ± 0.05 GPa and elastic modulus is 4.8 ± 0.6 GPa. Note that all these mechanical properties were measured in the middle part of the hair.

Fig. 7(c) summarizes the hardness and elastic modulus for virgin Caucasian hair at three locations: near scalp, middle and near tip. As expected, the hardness and elastic modulus of hair surface decreases from root to tip, because of the cuticle damage. Considering that the hair near scalp has complete cuticles, while the hair near tip

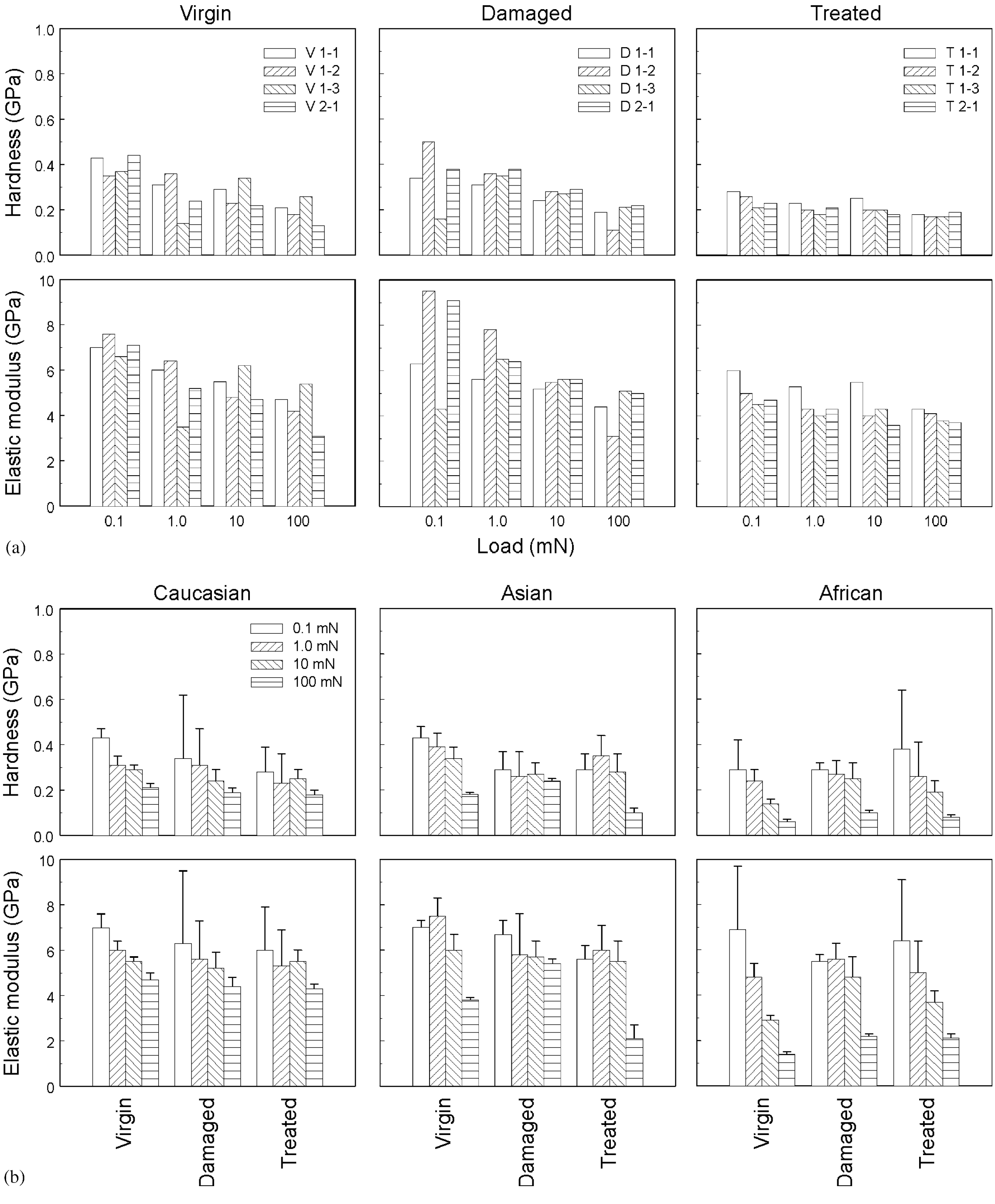
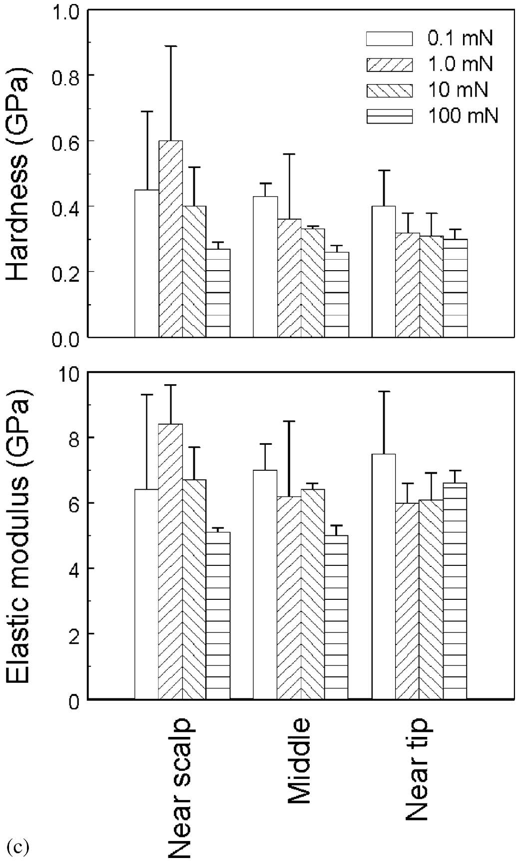


Fig. 7. (a) Summary of hardness and elastic modulus for various batches of Caucasian hair: V1-1, V1-2 and V1-3 stand for three hair from virgin hair batch No. 1, and V2-1 stands for one hair from virgin hair batch No. 2. D stands for damaged hair and T stands for treated hair; (b) summary of hardness and elastic modulus of various hair; and (c) summary of hardness and elastic modulus for virgin Caucasian hair at three locations.



(c)

Fig. 7. (*Continued*)

only has exposed cortex (see Fig. 3(b)), it is probably a good way to compare the nanomechanical properties of hair cuticle and cortex in the lateral direction by comparing the nanomechanical properties of hair near scalp and hair near tip. At 1.0 mN, the cuticle (hair near scalp) has higher hardness (0.6 ± 0.29 GPa) and elastic modulus (8.4 ± 1.2 GPa) than cortex (hair near tip), whose hardness is 0.3 ± 0.06 GPa, and elastic modulus is 6.0 ± 0.6 GPa. This result clearly suggests that the cuticles contribute more to the hair lateral mechanical properties than the cortex, which is in good agreement with the theoretical models for wool fibers [14].

Fig. 8 shows the creep displacement vs. time curves for various hair. The normal load used for creep tests was 10 mN. In all cases, the displacement increased as time passed. The creep behavior of hair may arise from several sources. Hair is rich in peptide bonds and the abundant CO– and NH– groups present give rise to hydrogen bonds between groups of neighboring chain molecules. Other linkages, such as side-chain interactions of the disulfide type, and the chain folding may also present in hair. When hair was compressed, the creep behavior was a result of deformation and relaxation of the chemical bonds, the polypeptide chains and the non-crystalline regions [6]. It should be noted that at normal load lower than 10 mN, the creep behavior was not obvious. Assuming that the diameter of Caucasian, Asian and African hair was about 50, 100 and 80 μm, respectively, the compression ratio of the indented area of these hair at 10 mN at the beginning of the creep tests were about: Caucasian (~2.6%), Asian (~1.3%) and African (~2.5%). This may suggest that if the local compression ratio was less than these values for corresponding hair, the deformation and relaxation of the chemical bonds, the polypeptide chains and the non-crystalline regions might be too small to cause the creep behavior to occur. According to the creep displacement vs. time curves, it is difficult to correlate the creep behavior of each hair with its ethnicity and condition (virgin, damage or treated).

4.3. Hair cross-section structure and mechanical properties

Fig. 9 shows the SEM images of virgin hair cross-section. These SEM images may represent the typical shape of Caucasian (nearly oval), Asian (nearly round) and African (oval-flat) hair. Regarding the diameter, the Asian hair seems to be the thickest, followed by African and Caucasian hair, which is in good agreement with the SEM studies of the hair surface (see Fig. 3(a)). The center column of Fig. 9 shows the cortex and medulla of each hair. The arrows point to the indents made at the cortex. The medulla of African hair is not so obvious, and it is believed that not all the hair has medulla [2]. The right column shows the images of the cuticles. The top-right image clearly shows that the cuticle of Caucasian hair is about 6–7 scales thick, and each cuticle cell is about 0.3–0.5 μm thick. Note that the cuticle scales

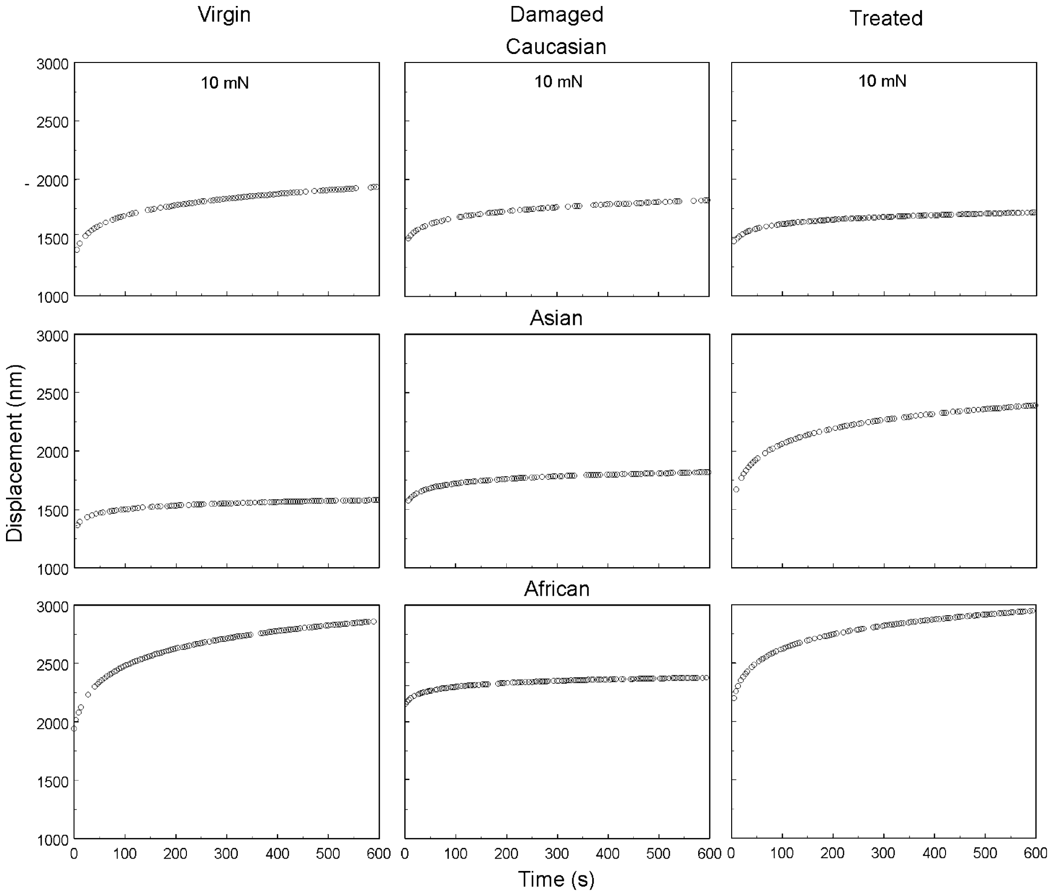


Fig. 8. Creep displacement vs. time curves for various hair.

were separated due to polishing, implying that the binding strength of the cell membrane complex between the cuticle scales might not be very strong. The information obtained from the hair cross-section studies was summarized in Table 2. Note that this summary is based on limited data.

The hardness and elastic modulus of hair cuticle, cortex and medulla were measured from the cross-section samples, and Fig. 10 shows the hardness and elastic modulus plots across various virgin hair. As expected, the cuticles have the highest mechanical properties, followed by cortex and medulla. Table 3 summarizes the hardness and elastic modulus of various hair. The hardness of cuticles was taken from the hair surface measurements (see Fig. 7(b)). By comparing the mechanical properties of Caucasian, Asian and African hair cortex, it can be seen that the Asian cortex appears to have the highest properties, followed by Caucasian and African hair. This trend is in agreement with the trend for the hair surface measurement results (see Fig. 7(b)). Table 3 shows that the hardness of cuticles is greater than cortex, but the elastic modulus of cortex is comparable to cuticle. Note that the elastic modulus of cortex listed in Table 3 is in the longitudinal direction. Comparing the hardness (0.3 ± 0.06 GPa) and elastic modulus (6.0 ± 0.6 GPa) of Caucasian cortex in the lateral direction (see Fig. 7(c)) with its hardness (0.27 ± 0.02 GPa) and elastic modulus (6.5 ± 0.5 GPa) in the longitudinal direction, it can be seen that hardness and elastic modulus of the hair cortex in the longitudinal direction are lower and higher, respectively, than the lateral direction.

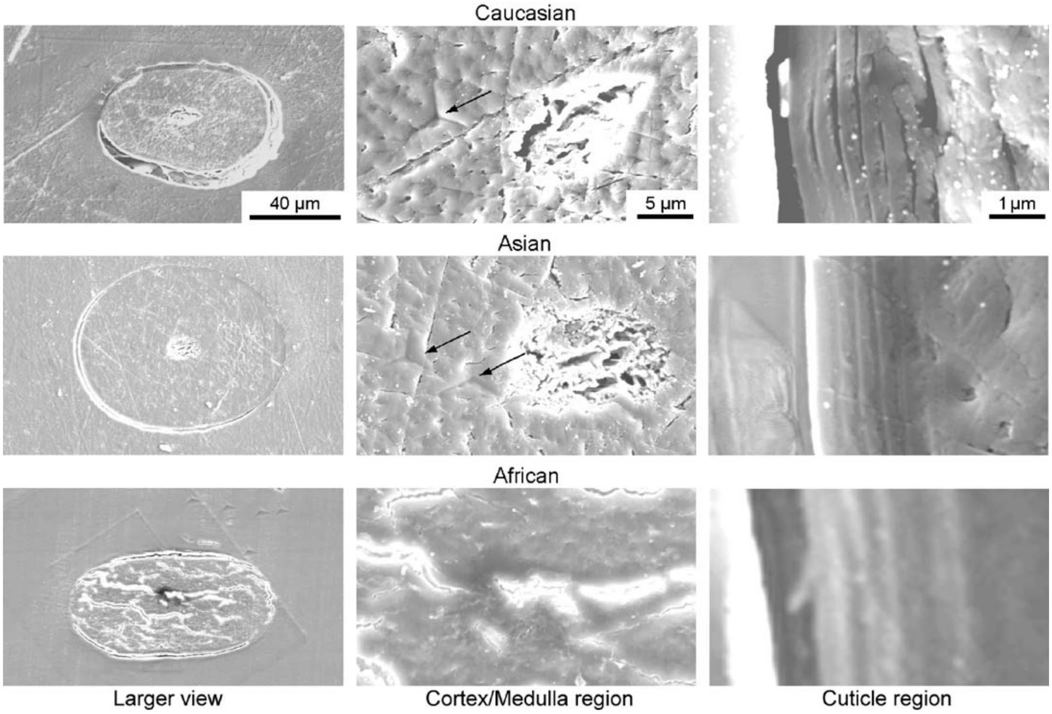


Fig. 9. SEM images of virgin hair cross-section.

Table 2
Variation in cross-sectional dimensions of human hair

	Shape	Maximum diameter (D_1) (μm)	Minimum diameter (D_2) (μm)	Ratio D_1/D_2	Number of cuticle scales	Cuticle scale thickness (μm)
Caucasian	Nearly oval	74	47	1.6	6–7	0.3–0.5
Asian	Nearly round	92	71	1.3	5–6	0.3–0.5
African	Oval-flat	89	44	2.0	6–7	0.3–0.5

Average length of visible cuticle scale: about 5–10 μm.

In these cross-section studies, the nanomechanical properties of hair cuticle, cortex and medulla were measured quantitatively using nanoindentation technique, and correlated well with the corresponding microstructure. If there is hair disorder causing the microstructure of cuticle, cortex or medulla to change, the hardness and elastic modulus of cuticle, cortex or medulla should change accordingly. Therefore, the methodology of measuring the hardness and elastic modulus of cuticle, cortex and medulla by nanoindentation may provide the dermatologists with some useful markers for the diagnosis of hair disorders and for the evaluation of their response to therapeutic regimen.

5. Conclusions

In this paper, hair morphology and nanomechanical properties of human hair, including hardness, elastic modulus, and creep have been measured

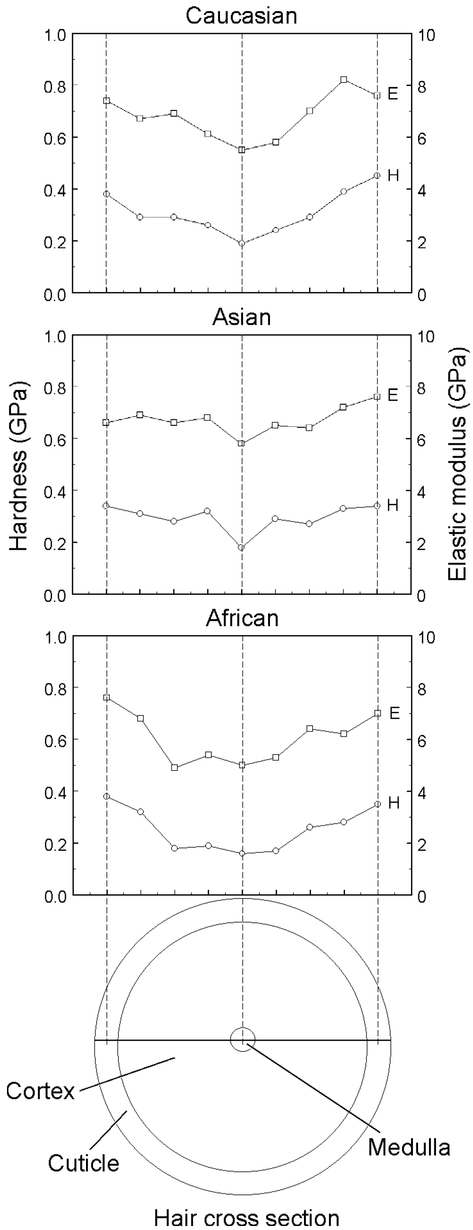


Fig. 10. Hardness and elastic modulus plots across various hair.

using SEM and nanoindentation. The conclusions from this study are as follows.

(1) The SEM studies of hair cross-section and AFM studies of hair surface show that the cuticle is about 5–7 scales thick, and each cuticle cell is about 0.3–0.5 μm thick. The visible length of each cuticle cell is about 5–10 μm long. It appears that the morphology of hair is different from root to tip. That is, the hair near scalp has complete cuticles, and the hair in the middle has worn cuticles, and the hair near tip seldom has cuticles. The size and shape of Caucasian, Asian and African hair have been measured from the hair surface and cross-section. Asian hair seems to be the thickest (nearly round), followed by African hair (oval-flat) and Caucasian hair (nearly oval).
(2) The chemical damage and conditioner treatment caused the hardness and elastic modulus of hair surface to decrease within a depth of less than 1.5 μm. That is, the first 3–4 cuticle scales may interact with the chemicals and conditioner ingredients more effectively than the rest of the scales. The decreases of mechanical properties are believed to be due to absorption of low levels of individual conditioner molecules into the outer part of the cuticle. For damaged and treated hair, since the adsorption and absorption of chemicals and conditioner ingredients were probably not uniform on the hair surface, the hardness and elastic modulus of the hair surface were not affected uniformly, leading to larger mechanical property variation as compared to virgin hair. Our work suggests that the nanoindentation technique can be used to quantitatively evaluate the effective depth of conditioner treated hair and distribution of conditioner by measuring the hardness and elastic modulus of the hair surface before and after conditioner treatment as a function of depth and location.
(3) It is found that the hair cuticle has higher hardness and elastic modulus than cortex in the lateral direction. Hardness and elastic modulus of the hair cortex in the longitudinal direction are lower and higher, respectively, than the lateral direction.
(4) The hardness and elastic modulus of hair decreased as the indentation depth increased. The cystine content variations in cuticle

Table 3
Summary of hardness and elastic modulus of human hair

	Hardness (GPa)			Elastic modulus (GPa)		
	Cuticle[a]	Cortex[b]	Medulla[b]	Cuticle[a]	Cortex[b]	Medulla[b]
Caucasian	0.32 ± 0.04	0.27 ± 0.02	~0.19	6.0 ± 0.4	6.5 ± 0.5	~5.5
Asian	0.39 ± 0.06	0.30 ± 0.02	~0.18	7.5 ± 0.8	6.7 ± 0.3	~5.8
African	0.24 ± 0.05	0.23 ± 0.06	~0.16	4.8 ± 0.6	5.8 ± 0.7	~5.0

Mean and $\pm 1\sigma$ values are presented.
[a]Obtained from the hair surface at normal load of 1.0 mN.
[b]Obtained from the hair cross-section at normal load of 1.0 mN.

substructures (A-layer, exocuticle, endocuticle, cell membrane complex) and cortex were proposed to be responsible for the result. The mechanical properties of hair surface also decreased from root to tip, because the cuticle damage became more severe from root to tip.

(5) The Caucasian, Asian and African hair seems to have different nanomechanical properties in the lateral direction. It appears that Asian hair surface has the highest hardness (0.39 ± 0.06 GPa) and elastic modulus (7.5 ± 0.8 GPa), followed by Caucasian hair with hardness of 0.31 ± 0.04 GPa and elastic modulus of 6.0 ± 0.4 GPa. The African hair seems to have the lowest mechanical properties, whose hardness is 0.24 ± 0.05 GPa and elastic modulus is 4.8 ± 0.6 Gpa.

(6) The creep behavior was observed for all hair in the lateral direction at low local compression ratio (about 1–3%). It appears that if the local compression ratio was lower than 1%, the creep was negligible. This may be because that the deformation and relaxation of the chemical bonds, the polypeptide chains and the non-crystalline regions was too small at very low compression ratio to cause the creep behavior to occur.

(7) The methodology of measuring the hardness and elastic modulus of cuticle, cortex and medulla using nanoindentation technique may provide the dermatologists with some useful markers for the diagnosis of hair disorders and for the evaluation of their response to therapeutic regimen.

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Appendix A. Shampoo and conditioner treatment procedure

The appendix outlines the steps involved in washing hair switches with shampoo and conditioner.

A.1. Shampoo treatments

Shampoo treatments consisted of applying a commercial shampoo evenly down a hair switch with a syringe. The hair was lathered for 30 s, rinsed with tap water for 30 s, then repeated. The amount of shampoo used for each hair switch was 0.1 cm^3 shampoo per gram of hair. Switches were hanged to dry in an environmentally controlled laboratory, then wrapped in aluminum foil.

A.2. Conditioner treatments

A commercial conditioner was applied 0.1 cm^3 of conditioner per gram of hair. The conditioner was applied in a downward direction (scalp to tip) thoroughly throughout the hair switch for 30 s, then allowed to sit on the hair without manipulation for another 30 s. The switch was then rinsed thoroughly for 30 s. Switches were hanged to dry in an environmentally controlled laboratory, then wrapped in aluminum foil.

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