Nanoscale characterization of human hair and hair conditioners

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Abstract

Human hair is a nanocomposite biological fiber. Hair care products such as shampoos and conditioners, along with damaging processes such as chemical dyeing and permanent wave treatments, affect the maintenance and grooming process and are important to study because they alter many hair properties. Nanoscale characterization of the cellular structure, mechanical properties, and morphological, frictional, and adhesive properties (tribological properties) of hair are essential to evaluate and develop better cosmetic products, and to advance the understanding of biological and cosmetic science. The atomic/friction force microscope (AFM/FFM) and nanoindenter have become important tools for studying the micro/nanoscale properties of human hair. In this review article, we present a comprehensive review of structural, mechanical, and tribological properties of various hair and skin as a function of ethnicity, damage, conditioning treatment, and various environments.

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1. Introduction

Everybody wants beautiful, healthy hair and skin. For most people, grooming and maintenance of hair and skin is a daily process. The demand for products that improve the look and feel of these surfaces has created a huge industry for hair and skin care. Beauty care technology has advanced the cleaning, protection, and restoration of desirable hair properties by altering the hair surface. For many years, especially in the second half of the 20th century, scientists have focused on the physical and chemical properties of hair to consistently develop products which alter the health, feel, shine, color, softness, and overall aesthetics of the hair. Hair care products such as shampoos and conditioners aid the maintenance and grooming process. Shampoos clean the hair and skin oils and conditioners repair hair damage and make the hair easier to comb; prevent flyaway; add feel, shine, and softness. Mechanical processes such as combing, cutting, and blowdrying serve to style the hair. Chemical products and processes such as chemical dyes, colorants, bleaches, and permanent wave treatments enhance the appearance and hue of the hair. Of particular interest is how all these common hair care items deposit onto and change hair properties, since these properties are closely tied to product performance. The fact that companies like Procter & Gamble, L’Oreal, and Unilever have hair care product sales consistently measured in the billions of dollars [http://www.pg.com; http://www.loreal.com; http://unilever.com] suggests that understanding the science behind human hair has more than just purely academic benefits, as well.

While products and processes such as combing, chemical dyeing, and permanent wave treatment are used to enhance appearance and style of the hair, they also contribute a large amount of chemical and mechanical damage to the fibers, which leads to degradation of structure and mechanical properties. As a result, the fibers become weak and more susceptible to breakage after time, which is undesirable for healthy hair. Shampoos and conditioners, which typically serve cleaning and repairing functions to the hair surface, respectively, have a distinct effect on mechanical properties as well.

The tribology of the hair also changes as a function of the various hair care products and processes. Fig. 1 illustrates schematically various functions, along with the macro- and micro/nanoscale mechanisms behind these interactions, that make surface roughness, friction, and adhesion very important to hair and skin [39]. For a smooth wet and dry feel, friction between hair and skin should be minimized in wet and dry environments, respectively. For a good feel with respect to bouncing and shaking of the hair during walking or running, friction between hair fibers and groups of hair fibers should be low. The friction one feels during combing is a result of interactions between hair and the comb material (generally a plastic), and this too needs to be low to easily maintain, sculpt, and comb the hair. To minimize entanglement, adhesive force (the force required to separate the hair fibers) needs to be low. In other cases, a certain level of adhesion may be acceptable and is often a function of the hair style. For individuals seeking “hair alignment,” where hair fibers lay flat and parallel to each other, a small amount of adhesive force between fibers...
may be desired. For more complex and curly styles, even higher adhesion between fibers may be optimal.
Early research into human hair was done primarily on the chemical and physical properties of the hair fiber itself. Key topics dealt with analysis of chemical composition in the fiber, microstructure, and hair growth, to name a few. Until about 2000, most information about the detailed structure of human hair was obtained from scanning electron microscope (SEM) and transmission electron microscope (TEM) observations [70,62,71,81]. Mechanical properties were also of interest. Most of the mechanical property measurements of human hair were on the macroscale and used conventional methods, such as tension, torsion and bending tests [62,72,73,2,35]. The mechanical properties obtained from these tests are the overall mechanical properties of the hair, not just the hair surface. Efforts were also made to study the effects of environmental and chemical damage and treatment, such as dyeing, bleaching, and polymer application; these topics have stayed a mainstream area of investigation due to the availability and formation of new chemicals and conditioning ingredients. Tribology has generally been studied via macroscale friction force of hair. As a matter of fact, much of the tribological work performed by the hair care industry today still focuses on the measurement of macroscale friction, particularly between a skin replica and a hair swatch of interest [62]. The intrinsic differences of the hair as a function of ethnicity eventually became a concern as well. For instance, research has shown that African–American hair has higher resistance to combing, higher static charge, and lower moisture content than Caucasian hair [75]. Because of differences like these, a growing number of hair care products specifically tailored for ethnic hair care have been developed and sold with commercial success.

Modern research since the late 1990s has been primarily concerned with using micro/nanoscale experimental methods such as atomic force/friction force microscopies (AFM/FFM) and nanoindentation to answer the complex questions surrounding the structure and behavior of the hair. Nanoscale characterization of the cellular structure, mechanical properties, and tribological properties of hair are essential to evaluate and develop better cosmetic products, and to advance the understanding of composite biological systems, cosmetic science, and dermatology. AFM/FFM have been used to effectively study the structure of the hair surface and cross section. AFM provides the potential for being able to see the cellular structure and molecular assembly of hair, for determining various properties of hair, such as elastic modulus and viscoelastic properties, and for investigating the physical behavior of various cellular structure of hair in various environments [21,12]. As a non-invasive technique, AFM has been used to evaluate the effect of hair treatment and can be operated in ambient conditions in order to study the effect of environment on various physical properties. AFM studies on hair fibers have been carried out for surface topography measurements [68,39] and friction, adhesion and wear properties of hair and skin and the effects of hair care products on hair [39-41,22,42,47]. Roughness parameters have been measured to compare changes due to damaging processes. Friction force has been measured to understand damage or conditioner distribution and its effect on hair tribology. Adhesive force mapping has shown useful to observe the conditioner distribution as well. Surface charge of human hair has a significant effect on manageability, flyaway behavior, feel and appearance. It is known that interaction of hair with dissimilar materials, such as plastic combs, hands, and latex balloons creates a charge on hair [49,50]. Physical wear has been shown to cause surface potential change in conductors and semiconductors [26,14,15] including hair [49].

The nanoindenter has been used to characterize the nanomechanical behavior of the hair surface and cross section using nanoindentation and nanoscratch techniques.
These properties are important for evaluating cosmetic products by comparing the nanomechanical properties, such as hardness, elastic modulus, and scratch resistance, of the hair surface before and after chemical damage or conditioner treatment. Since hair is a nanocomposite biological fiber with well characterized structures, which will be described in details in the next section, it is a good model to study the role of various structural and chemical components in providing mechanical strength for composite biological fibers [81]. 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 [69,58].

In this review article, we present a comprehensive study of various hair and skin structural, mechanical, and tribological properties as a function of ethnicity, damage, conditioning treatment, and various environments. Various cellular structure (such as the cortex and the cuticle) of human hair and fine sublamellar structures of the cuticle, such as the A-layer, the exocuticle, the endocuticle, and the cell membrane complex are easily identified and studied. Nanomechanical properties including hardness, elastic modulus, tensile deformation, creep, and scratch resistance are discussed. Nanotribological properties including surface roughness, friction, adhesion, and wear are presented, as well as investigations of conditioner localization and thickness. To study the electrostatic charge build up on hair, surface potential studies are presented.

2. Human hair, skin, and hair care products

2.1. Human hair and skin

Fig. 2a shows a schematic of a human hair fiber with its various layers of cellular structure [86,56,62,27,38,68]. Hair fibers (about 50–100 μm in diameter) consist of the cuticle and cortex, and in some cases medulla in the central region. All are composed of dead cells, which are mainly filled with keratin protein. Table 1 displays a summary of the chemical species of hair [21]. Depending on its moisture content, human hair consists of approximately 65–95% keratin proteins, and the remaining constituents are water, lipids (structural and free), pigment, and trace elements. Proteins are made up of long chains of various mixtures of the some 20 or 50 amino acids. Each chain takes up a helical or coiled form. Among numerous amino acids in human hair, cystine is one of the most important amino acids. Every cystine unit contains two cysteine amino acids in different chains which lie near to each other and are linked together by two sulfur atoms, forming a very strong bond known as a disulfide linkage,
In addition to disulfide bonds, hair is also rich in peptide bonds and the abundant CO- and NH-groups present give rise to hydrogen bonds between groups of neighboring chain molecules. The distinct cystine content of various cellular structure of human hair results in a significant effect on their physical properties. A high cystine content corresponds to rich disulfide crosslinks, leading to high mechanical properties. The species responsible for color in hair is the pigment – melanin, which is located in the cortex of the hair in granular form.

An average head contains over 100,000 hair follicles, which are the cavities in the skin surface from which hair fibers grow. Each follicle grows about 20 new hair fibers in a lifetime. Each fiber grows for several years until it falls out and is replaced by a new fiber. Hair typically grows at a rate on the order of 10 mm/month.
The 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 tiles 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 various sublamellar layers (the epicuticle, the A-layer, the exocuticle, the endocuticle and inner layer) and the cell membrane complex (see Fig. 2). Table 2 displays the various layers of the cuticle, their respective cystine levels [62] and other details. The outer epicuticle layer is covered with a thin layer of covalently attached lipid (fatty acid), predominantly 18-Methyl Eicosanoic Acid (18-MEA) (see Table 1). This layer constitutes the outer β-layer of the cuticular cell membrane complex, which acts as a boundary lubricant, responsible for low friction and provides a hydrophobic surface. The A-layer is a component of high cystine content (≈30%) and located on the outer-facing aspect of each cell. The A-layer is highly crosslinked which gives this layer considerable mechanical toughness and chemical resilience, and the swelling in water is presumed to be minimal. The exocuticle, which is immediately adjacent to the A-layer, is also of high cystine content (≈15%). On the inner facing aspect of each cuticle cell is a thin layer of material which is known as the inner layer. Between the exocuticle and inner layer is the endocuticle which is low in cystine (≈3%). The cell membrane complex (CMC) itself is a lamellar structure,
which consists of the inner β-layer, the δ-layer and the outer β-layer. The outer β-layer of the CMC separates the cuticle cells from each other. Low cohesive forces are expected between the lipid-containing outer β-layer and the δ-layer of CMC, which provides a weak bond. It may result into cuticular delamination during mechanical wear, with the potential advantage of revealing a fresh layer of 18-MEA to the newly exposed surface [68].

Fig. 3 shows the SEM images of virgin Caucasian, Asian, and African hair [81]. 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. A listing of various cross-section dimensional properties are presented in Table 3 [81]. While Caucasian and Asian hair typically have similar cross-sectional shape (Asian hair being the most cylindrical), African hair has a highly elliptical shape. African hair is much more curly and wavy along the hair fiber axis than Caucasian or Asian hair.

Chemically, all ethnic hair are found to have similar protein structure and composition [53,24,25,57]. African hair has less moisture content than Caucasian hair. The shape (diameter, ellipticity, and curliness) of various ethnic hair depends on several factors, including the shape of the hair follicle and its opening; these vary from one person to another and also between races [32,79]. The pronounced ellipsoidal cross section of hair shaft in African hair could be caused by a heterogeneous and asymmetric fiber framework, in addition to internal mechanical stresses [78]. Previously, it was though that elliptical cross section of hair is responsible for curl. While circular cross sections (Asian and Caucasian) generally have straight hair, curly hair has a predominantly elliptical cross section.
(African). However, recent studies suggest that hair follicle shape and not the cross section is responsible for hair curl [79]. This means that if the follicle is straight, even an elliptical cross section could give rise to straight hair. Both in-vitro growth studies and computer aided three dimensional reconstruction [45] support this claim. Curvature of the curly hair is programmed from the basal area of follicle. This bending process is apparently linked to a lack of symmetry in the lower part of the bulb, affecting the hair shaft cuticle.

Fig. 4 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 during its life 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. If some substructures of one cuticle scale, like A-layer or A-layer and exocuticle (see Fig. 2a), 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. 5 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, 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. 5, the substance which stayed near the cuticle edge is probably the conditioner (pointed by an arrow).
Fig. 6 shows the AFM images of various virgin hair, along with the section plots [39]. 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 tile-like hair surface structure. The visible cuticle cell is approximately 0.3–0.5μm thick and about 5–10μm long for all three hair.

2.1.2. The cortex and medulla

The cortex contains cortical cells and the intercellular binding material, or the cell membrane complex. The cortical cells are generally 1–6μm thick and 100μm long, which run longitudinally along the hair fiber axis and take up the majority of the inner hair fiber composition [61]. The macrofibrils (about 0.1–0.4μm in diameter) comprise a major portion of the cortical cells. Each macrofibril consists of intermediate filaments (about 7.5nm 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.

Fig. 7a shows the SEM images of virgin hair cross section [81] and Fig. 7b shows the TEM images of a cross section of human hair [71].
2.1.3. Skin

Skin covers and protects our bodies. The skin at the forehead and scalp areas are of most interest when dealing with human hair, since most of the hair care products are developed specifically for head hair. The skin of the hand and fingers is also of importance.

Fig. 6. AFM images of various virgin hair [39].
because the “feel” of hair is often sensed by physically touching the fibers with these regions. In general, skin is composed of three main parts: epidermis, dermis, and subcutaneous tissue (L’Oreal); see Fig. 8.

The epidermis contains four distinct cellular layers: basal, spinous, granular, and horny. In the basal layer, melanocytes deliver the pigment melanin to keratinocytes. Keratinocyte cells that have been cornified are referred to as corneocytes [60]. Hexagonally shaped corneocyte cells compose the horny layer, or stratum corneum. The stratum corneum is the outer layer of the skin; at about 15-μm thick, it acts as a mechanical, thermal, and chemical barrier from environmental factors and contamination. The complex organization of corneocytes and intercellular matrix contribute to the success of the barrier [82]. In fact, Wertz et al. [83] developed a structural model which observes the matrix as a lamellar
phase composition of various lipids which provide a glue-like system to provide a barrier effect.

The dermis structure is known for its ability to handle most of the physical stresses imposed on the skin, and takes up roughly 90% of the mass [60]. The dermis is divided into an outermost papillary layer and underlying reticular layer.

2.2. Hair care: cleaning and conditioning treatments, and damaging processes

2.2.1. Cleaning and conditioning treatments: shampoo and conditioner

Shampoos are used primarily to clean the hair and scalp of dirt and other greasy residue that can build up after time. Shampoos also have many secondary functions including controlling dandruff, reducing irritation, and even conditioning. Conditioners, on the other hand, are used primarily to give the hair a soft, smooth feel which results in easier hair combing. Secondary functions include preventing “flyaway” hair due to static electricity, giving the hair a shiny appearance, and protecting the hair from further damage by forming a thin coating over the fibers.

Further developments in marketing and aesthetic factors (brand name, fragrance, feel, and color of the shampoos and conditioners) have created new market segments. In many instances, these factors have become primary reasons for use.

2.2.1.1. Shampoo: constitution and main functions. The following discussion is based on Gray [31,32]. As stated above, shampoos serve various cleaning functions for the hair
and scalp. In the past, typical shampoos were mainly soap based products. However, soaps did not have very good lathering capability, and often left a residual “scum” layer on the hair that was undesirable and could not be rinsed off.

In modern shampoos, advances in chemistry and technology have made it possible to replace the soap bases with complex formulas of cleansing agents, conditioning agents, functional additives, preservatives, aesthetic additives and even medically active ingredients.

2.2.1.2. Conditioner: constitution and main functions. As stated earlier, many shampoos have certain levels of conditioning agents which mimic the functions of a full conditioner product. Conditioner molecules contain cationic surfactants which give a positive electrical charge to the conditioner. The negative charge of the hair is attracted to the positively charged conditioner molecules, which results in conditioner deposition on the hair; see Fig. 9. This is especially true for damaged hair, since damaging processes result in hair fibers being even more negatively charged. The attraction of the conditioner to hair results in a reduction of static electricity on the fiber surfaces, and consequently a reduction in the “fly away” behavior. The conditioner layer also flattens the cuticle scales against each other, which improves shine and color. The smooth feel resulting from conditioner use gives easier combing and detangling in both wet and dry conditions.

Conditioner consists of a gel network chassis (cationic surfactants, fatty alcohols, and water) for superior wet feel and combination of conditioning actives (cationic surfactants, fatty alcohols, and silicones) for superior dry feel. Fig. 10 shows the transformation of the

![Fig. 9. Negatively charged hair and the deposition of positively charged conditioner on the cuticle surface [42].](image1)

![Fig. 10. Conditioner formation from emulsion to gel network [12].](image2)
cationic surfactants and fatty alcohol mixture into the resulting gel network, which is a frozen lamellar liquid crystal gel phase [12]. The process starts as an emulsion of the surfactants and alcohols in water. The materials then go through a strictly controlled heating and cooling process: the application of heat causes the solid compounds to melt, and the solidification process enables a setting of the lamellar assembly molecules in a fully extended conformation, creating a lamellar gel network. When this network interacts with the hair surface, the high concentration of fatty alcohols make it the most deposited ingredient group, followed by the silicones and cationic surfactants. Typical deposition levels for cationic surfactant, fatty alcohol, and silicone are around 500–800 ppm, 1000–2000 ppm, and 200 ppm, respectively. Typical concentrations are approximately 2–5 wt%, 5–10 wt%, and 1–10 wt%, respectively [42].

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 easier dry combing. Each of the primary conditioner ingredients also has specific functions and roles that affect performance of the entire product. Table 4 displays the functions of the major conditioner ingredients and their chemical structure [42]. Cationic surfactants are critical to the forming of the lamellar gel network in conditioner, and also act as a lubricant and static control agent, since their positive charge aids in counteracting the negative charge of the hair fibers. Fatty alcohols are used to lubricate and moisturize the hair surface, along with forming the gel network. Finally, silicones are the main source of lubrication in the conditioner formulation.

2.2.2. Damaging processes

In Section 2.2.1 we discussed some of the products which aid in “treating” the hair. There are other hair care products and processes which, while creating a desired look or style to the hair, also bring about significant damage to the fibers. Most of these processes occur on some type of periodic schedule, whether it be daily (while combing the hair), or monthly (haircut and coloring at a salon). In general, hair fiber damage occurs most readily by mechanical or chemical means, or by a combination of both (chemical-mechanical).

2.2.2.1. Mechanical damage. Mechanical damage occurs on a daily basis for many individuals. The damage results from large physical forces or temperatures which degrade and wear the outer cuticle layers. Common causes are

- combing (generally with plastic objects, and often multiple times over the same area lead to scratching and wearing of the cuticle layers)
- scratching (usually with fingernails around the scalp)
- cutting (affects the areas surrounding the fiber tips)
- blowdrying (high temperatures thermally degrade the surface of the hair fibers)

2.2.2.2. Permanent wave treatment. Permanent wave treatments saw many advances in the beginning of the 20th century, but have not changed much with the invention of the Cold Wave around the turn of that century. Generally speaking, the Cold Wave uses mercaptans (typically thioglycolic acid) to break down disulphide bridges and style the hair without much user interaction (at least in the period soon after the perm application) [31]. The
<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Chemical structure</th>
<th>Purpose/Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td></td>
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<tr>
<td>Cationic surfactants</td>
<td>Stearamidopropyl dimethylamine</td>
<td>– Aids formation of lamellar gel network</td>
</tr>
<tr>
<td></td>
<td></td>
<td>– Lubricates and static control agent</td>
</tr>
<tr>
<td></td>
<td>Behenyl amidopropyl dimethylamine glutamate (BAPDMA)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Behentrimonium chloride (BTMAC) CH₃(CH₂)₂₇N(Cl)(CH₃)₃</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohols</td>
<td>Stearyl alcohol (C₁₈OH)</td>
<td>– Aids formation and moisturizes</td>
</tr>
<tr>
<td></td>
<td>Cetyl alcohol (C₁₆OH)</td>
<td>– Aids formation of lamellar gel network along with cationic surfactant</td>
</tr>
<tr>
<td>Silicons</td>
<td>PDMS blend (dimethicone)</td>
<td>– Primary source of lubrication</td>
</tr>
<tr>
<td></td>
<td></td>
<td>– Gives hair a soft and smooth feel</td>
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Cold Wave process does not need increased temperatures (so no thermal damage to the hair), but generally consists of a reduction period (whereby molecular reorientation to the cuticle and cortex occurs via a disulfide-mercaptan interchange pathway [62]) followed by rinsing, setting of the hair to the desired style, and finally neutralization to decrease the mercaptan levels and stabilize the style. The chemical damage brought on by the permanent wave can increase dramatically when not performed with care.

2.2.2.3. Chemical relaxation. Commonly used as a means of straightening hair (especially in highly curved, tightly curled African hair), this procedure uses an alkaline agent, an oil phase, and a water phase of a high viscosity emulsion to relax and reform bonds in extremely curly hair. A large part of the ability to sculpt the hair to a desired straightness comes from the breakage of disulfide bonds of the fibers.

2.2.2.4. Coloring and dyeing. Hair coloring and dyeing have become extremely successful hair care procedures, due in part to “over-the-counter” style kits which allow home hair care without professional assistance. The most common dyes are para dyes, which contain paraphenylenediamine (PPD) solutions accompanied by conditioners and antioxidants. Hydrogen peroxide (H$_2$O$_2$) is combined with the para dyes to effectively create tinted, insoluble molecules which are contained within the cortex and are not small enough to pass through the cuticle layers, leaving a desired color to the hair. Due to the levels of hydrogen peroxide, severe chemical damage can ensue in the cuticle and cortex.

2.2.2.5. Bleaching. Like dyeing, bleaching consists of using hydrogen peroxide to tint the hair. However, bleaching can only lighten the shade of hair color, as the H$_2$O$_2$ releases oxygen to bind hair pigments [31]. Bleaching may also be applied to limited areas of the hair (such as in highlights) to create a desired look. The chemical damage brought on by bleaching leads to high porosity and severe wear of the cuticle layer.

3. Experimental

The SEM has long been the standard means of investigating the surface topography of human hair. The SEM uses an electron beam to give a high resolution image of the sample, but cannot provide quantitative data regarding the surface. SEM requires the hair sample to be covered with a very thin layer of a conductive material and needs to be operated under vacuum during both metallization and measurements. Surface metallization and vacuum exposure could potentially induce modifications to the surface details. TEM examinations provide fine detailed internal structure of human hair. However, thin sections of 50–100 nm thickness and heavy metal compounds staining treatment are required for TEM examinations. The cutting of these thin sections with the aid of an ultra-microtome is not an easy task. Moreover, since both SEM and TEM techniques cannot be used to measure the physical properties (e.g., mechanical and tribological) of various cellular structure of human hair of interest and do not allow ambient imaging conditions, many outstanding issues remain to be answered. For example: How do the various cellular structures of hair behave physically in various environments (temperature, humidity, etc.)? How do they swell in water? For conditioner treated hair, how thick is the conditioner layer and how is the conditioner distribution on hair surface?
AFM is now commonly used for morphological, structural, tribological and mechanical characterization of surfaces [6–9]. As a non-invasive technique, AFM has been used to evaluate the effect of hair treatment since it can be used to study the effect of environment on various physical properties. A schematic of an AFM imaging a hair fiber is shown in Fig. 11. AFM/FFM uses a sharp tip with a radius of approximately 10–50 nm. This significant reduction in tip to sample interaction compared to the macroscale allows the simulation of single asperity contact to give detailed surface information. Contact mode allows simultaneous measurement of surface roughness and friction force. Different AFM operating modes, tapping mode and torsional resonance (TR) mode can be used for measurements of material stiffness and viscoelastic properties mapping using amplitude and phase angle imaging.

When skin comes in contact with hair, actual contact occurs over a large number of asperities. During relative motion, friction and adhesion are governed by the surface interactions which occur at these asperities. Until about 2000, much of the work in the industry has focused on the measurement of macroscale friction, particularly between a skin replica and a hair swatch of interest [62]. Fig. 12 shows schematics of typical macro- and micro/nanoscale test apparatuses. However, there are many problems associated with performing these types of measurements. Factors such as topographical variations, lumping of the hair fibers, the large size of the synthetic skin, and traditional measurement system errors can all lead to uncertainty in the data.

Depth-sensing nanoindentation measurement techniques are now commonly used to measure nanomechanical properties of surface layers of bulk materials and of ultrathin coatings [7,9,16]. More recently, nanoindentation technique has been used to investigate

Fig. 11. Schematic diagram of AFM operation with human hair sample.
nanomechanical properties (such as hardness, Young’s modulus, creep, and scratch resistance) of various cellular layers of glass fibers, keratin fibers, and hair surface/cross-section [44,59,81,80]. In-situ tensile loading experiments in the AFM have been carried out to study the progress of deformation and morphological changes in the hair fiber [67].

For the research reported in this article, all hair samples arrived as hair swatches 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. The main hair categories of interest are: virgin (untreated), virgin (treated with 1 cycle of commercial conditioner), chemo-mechanically damaged (untreated), chemically damaged (untreated), mechanically damaged (untreated), and chemo-mechanically or chemically damaged (treated with 1 or 3 cycles of commercial conditioner or experimental conditioners). 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 were 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. Chemically damaged hair fibers were not exposed to the combing sequence in their preparation. In the case of African damaged hair
samples, chemical damage occurred only by chemical straightening. Mechanically damaged hair fibers were exposed to combing sequence to cause mechanical damage and were observed under an optical microscope at 100× to have mechanical damage. All treated hair samples were treated with either one or three rinse/wash cycles of a conditioner similar to a Procter & Gamble commercial product (with PDMS blend silicone), or were treated with two combinations of silicone types (PDMS, blend of low and high molecular weight silicone, or an amino silicone).

Collagen film is typically used as a synthetic hair material for testing purposes. Polyurethane films represent synthetic human skin. They are cast from human skin and have a similar surface energy, which also makes them suitable test specimens when real skin cannot be used. To characterize surface roughness of human skin, it was also replicated using a two-part silicone elastomer putty (DMR-503 Replication Putty, Dynamold, Inc., Fort Worth, Texas). The thickness of the film was approximately 3 mm.

In order to simulate hair conditioner–skin contact in AFM experiments, it is important to have contact angle and surface energy of an AFM tip close to that of skin. Table 5 shows the contact angles and surface energies of materials important to the nanocharacterization

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Contact angle and surface energy of hair and relevant materials associated with nanotribological characterization of hair</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Contact angle (°)</td>
</tr>
<tr>
<td></td>
<td>Dry</td>
</tr>
<tr>
<td>Virgin Caucasian hair</td>
<td>103\textsuperscript{a}</td>
</tr>
<tr>
<td>Virgin treated</td>
<td>88\textsuperscript{a}</td>
</tr>
<tr>
<td>Chemically damaged</td>
<td>79\textsuperscript{a}</td>
</tr>
<tr>
<td>Chemically damaged, treated</td>
<td>95\textsuperscript{a}</td>
</tr>
<tr>
<td>Mechanically damaged</td>
<td>92\textsuperscript{a}</td>
</tr>
<tr>
<td>Asian</td>
<td>92\textsuperscript{a}</td>
</tr>
<tr>
<td>African</td>
<td>80\textsuperscript{a}</td>
</tr>
<tr>
<td>PDMS (bulk)</td>
<td>105\textsuperscript{c}</td>
</tr>
<tr>
<td>Human skin</td>
<td></td>
</tr>
<tr>
<td>– Forehead</td>
<td>55\textsuperscript{e}</td>
</tr>
<tr>
<td>– Forearm</td>
<td>88\textsuperscript{f}</td>
</tr>
<tr>
<td>– Finger</td>
<td>84\textsuperscript{f}</td>
</tr>
<tr>
<td>104\textsuperscript{g} (after soap washing)</td>
<td>0.027\textsuperscript{g}</td>
</tr>
<tr>
<td>58\textsuperscript{g} (before soap washing)</td>
<td>0.024\textsuperscript{g}</td>
</tr>
<tr>
<td>Si\textsubscript{3}N\textsubscript{4} tip</td>
<td>48\textsuperscript{h}</td>
</tr>
<tr>
<td>Si tip</td>
<td>51\textsuperscript{j}</td>
</tr>
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</table>

\textsuperscript{a} Lodge and Bhushan [48].
\textsuperscript{b} LaTorre et al. [42].
\textsuperscript{c} Bhushan and Burton [11].
\textsuperscript{d} Jalbert et al. [37].
\textsuperscript{e} Lerebour et al. [43].
\textsuperscript{f} Schott [65].
\textsuperscript{g} Ginn et al. [30].
\textsuperscript{h} Tao and Bhushan [76].
\textsuperscript{i} Yanazawa [85].
\textsuperscript{j} Tao and Bhushan [77].
of the hair samples: Untreated, damaged and treated human hair; PDMS, which is used in conditioners; skin, which comes into contact with hair; and Si$_3$N$_4$ and Si AFM tips used for nanotribological measurements. The dynamic contact angle of various human hair reports in Table 5 were measured by Lodge and Bhushan [47] using the Wilhelmy balance method. This method uses a microbalance to measure the force exerted on a single fiber when it is immersed into the wetting liquid of interest (de-ionized water). This measured force is related to the wetting force of the liquid on the fiber, and the dynamic contact angle can be calculated. They reported a significant directionality dependence. The values reported here compare well with other values reported in the literature [55,42]. The data reported for PDMS (bulk) and live skin in-situ were obtained using the standard sessile-drops method using a contact angle goniometer [11,30,65,43]. In the measurement technique developed by Tao and Bhushan [76,77] for dynamic contact angle of the AFM, by tips advancing and receding the AFM tip across the water surface, the meniscus force between the tip and the liquid was measured at the tip–water separation. The water contact angle was determined from the meniscus force.

4. Structural characterization using an AFM

A schematic diagram in Fig. 2a provides an overall view of various cellular structure of human hair. Human hair is a complex tissue consisting of several morphological components, and each component consists of several different chemical species. Table 1 presented earlier summarizes the main chemical species present in human hair.

Traditionally, most cellular structure characterizations of human hair or wool fiber were done using SEM and TEM. More recently, the cellular structure of human hair has been characterized using AFM and TR mode II (described earlier) [21,12]. In Section 4.1, structure of hair cross section and longitudinal section is presented; and in Section 4.2, structure of various cuticle layers of human hair is presented.

4.1. Structure of hair cross section and longitudinal section

4.1.1. Cross section of hair

Fig. 13a shows the AFM images of Caucasian hair cross section. The hair fiber embedding in epoxy resin can be easily seen. From TR amplitude image and TR phase image, the cortex region, the cuticle region and epoxy resin region are easily identified. In the cuticle region, five layers of cuticle cells are seen, and the total thickness of the cuticle region is about 2 $\mu$m for this sample. In the detailed images of the cuticle region, three layers of cuticle cells are shown, and various sublamellar structure of the cuticle can be seen. The thickness of the cuticle cell varies from 200 nm to 500 nm. Cortex region shows very fine circular structure of size about 50 nm, which represents the transverse face of the macrofibril and matrix. At this scale, no intermediate filament structure can be revealed.

4.1.2. Longitudinal section of hair

Fig. 13b shows the AFM images of longitudinal section of virgin Caucasian hair. Different regions (cortex region, the cuticle region and embedding epoxy resin) are easily seen. As shown in the detailed image of the cuticle region, various sublamellar structure of the cuticle, the A-layer, the exocuticle, the endocuticle and the cell membrane complex, which cannot be easily revealed in TR surface height image, are easily resolved in TR amplitude
Fig. 13. (a) Cross-section images of virgin Caucasian hair and fine detailed images of the cuticle region and cortex region. (b) Longitudinal section images of virgin Caucasian hair and fine detailed images of the cuticle region and cortex region. Note that the longitudinal section is not perfectly parallel to the long axis of the hair fiber but with a small angle, therefore, the thickness of sublamellar layers of the cuticle is not the real thickness [21].
image and TR phase image because of different contrast. Most sublamellar structure features of the cuticle shown in the TEM image of Fig. 7b can be identified in the TR amplitude and phase angle images. Previously, these sublamellar structures were only able to be
distinguished by TEM [71]. Various cellular sublamellar structure in the cuticle have very different chemical content [62,71]: the A-layer is rich in disulfide crosslinks due to a very high cystine content of up to 35%; The exocuticle is also rich in disulfide crosslinks (15% cystine); in contrast, the endocuticle is relatively lightly crosslinked containing only about 3% cystine. Consequently, these layers exhibit distinct stiffness and viscoelastic properties, and TR mode II imaging technique (TR amplitude and phase angle images) can easily detect these differences. Note that this longitudinal section is not perfect parallel to the long axis of the hair fiber but with a small angle, therefore, the thickness of various sublamellar layers of the cuticle does not represent the real thickness. In the cortex region, two different morphological regions can be seen: the macrofibril and the matrix. The macrofibril, which is a bundle of the intermediate filament, aligns parallel to each other and looks like a tree trunk; the matrix surrounds macrofibril region. The matrix region has high cystine content of compared to low cystine content of macrofibril region. This chemical content difference between the macrofibril and the matrix make it possible to reveal the fine internal cellular structure of hair using AFM TR mode II technique.

4.2. Structure of various cuticle layers

4.2.1. Virgin hair

Fig. 14 shows the AFM images of surface of virgin Caucasian hair. Two typical sample positions are shown: position 1 is near root end of hair and position 2 is near tip end of hair. In position 1, one cuticle edge is shown, which is also seen in the TR amplitude and phase images as the black strips because of the topographic effect near the cuticle edge. The topographic effect tends to be significant only when there is a large local geometry change. The cuticle edge shows little natural weathering damage and is still intact with a step height of about 500 nm, and the general cuticle surface which is covered with a lipid layer (the outer \( \beta \)-layer) is relative uniform at large scale. In contrast, the surface near tip of hair (position 2) shows lots of damage which may be simply because of natural weathering and mechanical damage from the effects of normal grooming actions, such as combing, brushing, and shampooing. Parts of the cuticle outer sublamellar layers were removed and underneath layers (the A-layer, the endocuticle, the inner layer) are exposed. Because different chemical content of various sublamellar layer of the cuticle results in different stiffness and viscoelastic properties, large contrast can be seen in TR amplitude and TR phase angle images. Note that the surface height within each individual sublamellar layers (the A-layer, the outer \( \beta \)-layer, the inner layer) is relativity uniform, therefore the topographic effect on the TR amplitude and phase is minimum. Detail images of the outer \( \beta \)-layer, the A-layer and the endocuticle are shown at the bottom of Fig. 14. All these layers show distinct morphology which can be readily revealed in the TR amplitude and phase angle images: the outer \( \beta \)-layer shows very fine granular structure; the A-layer shows little discriminable features; and the endocuticle has much rougher granular structure [70,71] than that of the outer \( \beta \)-layer. Previous friction force microscopy (FFM) studies [68] on keratin fibers indicated that for untreated (virgin) fibers, no image contrast was observed on the outer-facing surfaces of the scales. These results indicate that the outer lipid layer may form fine domains, which results in the fine granular structure shown in the TR amplitude and phase images (Fig. 14). TR mode II technique has higher sensitivity compared to FFM technique, therefore, the fine chemical distribution, which normally cannot be detected by FFM and other techniques, can readily be revealed.
Fig. 14. Images of surface of virgin Caucasian hair. Two typical samples are shown: near root end in which intact cuticle edges are seen and near tip end in which damage occur, and part of the cuticle top layers were removed and underneath sublamellar layers are exposed. Detailed images of the outer β-layer, the A-layer and the endocuticle exposed near tip end are shown at the bottom [21].
4.2.2. Chemically damaged hair

Fig. 15 shows the AFM images of surfaces of chemically damaged Caucasian hair. Two typical samples are shown. More damage can be seen compared to the surface of virgin hair. More cuticle edges were removed and often larger areas of rough granular endocuticle layer were exposed (see Sample I). Of the components within each cuticle cell (the A-layer, the exocuticle, the endocuticle, etc.), the endocuticle is the least crosslinked [62]. Under wet conditions it will swell preferentially and is the preferred plane for lamellar fracture under mechanical stress. Indeed, many examples have been observed where the cuticle has come off to leave this granular endocuticle layer of approximately half of the thickness of original scale and located at the scale margins. As shown in sample II, the endocuticle layers were further eliminated, entire pieces of cuticles were removed and some fine lines on cuticle surface which delineate the original boundaries of the cuticle edges are clearly seen in TR amplitude images. These lines are referred to cuticle edge “ghost” in literatures [70,68]. The actual fracture occurs at the interface between the outer $\beta$-layer and the $\delta$-layer (see Fig. 2). The outer $\beta$-layer was originally present, but because of its location, i.e. under the original overlying cuticle but close to the scale edge, it may have undergone oxidative loss through environmental or chemical exposure.

For easy visualization, Fig. 16 shows a schematic which illustrates the progress of hair damage. Virgin hair has intact smooth cuticle edge; as damage occurs (natural weathering or mechanical damage), parts of the cuticle outer sublamellar layers wear off and underneath layers (for example, the endocuticle) are exposed. Further damage will cause entire piece of cuticle to be broken off and the ghost which delineate the original boundary of the cuticle edge is seen.

4.2.3. Conditioner treated hair

Various sublamellar layers of cuticle can be exposed on the surfaces of virgin hair and chemically damaged hair depending on the degree of damage. Because of distinct chemical nature, these layers may have different interaction with conditioner (or other hair care products) which will affect the adsorption of conditioner on hair surface. Fig. 17 shows the AFM surface images of two samples of chemically damaged treated hair. In sample I, intact cuticle edges can be seen. From TR phase angle image, higher contrast can be seen near cuticle edges. It will be presented later that conditioner is unevenly distributed across the hair surface, and thicker conditioner layer can be found near cuticle edges [39,40]. This build up of conditioner might be simply caused by the physical entrapment at the steps of the cuticle edges. Uneven thickness of conditioner caused the contrast on TR phase angle images. In sample II, a sharp cuticle edge and a cuticle ghost edge can be readily seen in TR amplitude image. No endocuticle or other sublamellar layers could be found because further treatments removed these layers. As shown in TR phase angle image of sample II, the region between cuticle edge and cuticle ghost edge shows different contrast from other part of hair surface. This newly formed region surface may have exposed the epicuticle layer, while the other parts of hair were still covered with the outer $\beta$-layer. The outer $\beta$-layer is basically a covalent attached lipid covered layer, which is hydrophobic. The interaction between conditioner and the outer $\beta$-layer or other sublamellar layers of the cuticle (such as the epicuticle) could be very different; therefore, the adsorptions of conditioner on these surfaces are different.

Fine details of chemically damaged treated general cuticle surface (the outer $\beta$-layer) are shown at the bottom of Fig. 17. Compared to the fine granular structure of the outer
Fig. 15. Images of surface of chemically damaged Caucasian hair. Two typical images are shown: sample I in which large areas of the cuticle tops sublamellar layers are removed and much rougher endocuticle layer is exposed; and sample II in which entire pieces of the cuticle are removed and only the cuticle ghost edges are left. Detailed images of the outer $\beta$-layer, the endocuticle and the epicuticle are shown at the bottom [21].
beta-layer shown in the Fig. 14, no discriminated features can be seen now since the entire surface is covered with a layer of conditioner.

In summary, although the morphology of the fine cellular structure of human hair has traditionally been investigated using SEM and TEM, these techniques have limited capability to in-situ study environment effects on the physical behavior of hair. AFM TR mode can be used to characterize the fine cellular structure of human hair, and many features previously only seen with SEM and TEM can be identified. The AFM technique provides the possibility to further in-situ studies of the effects of environment (temperature, humidity, etc.) and hair-care product treatment on physical behavior of human hair.

4.2.4. Effect of humidity on morphology and cellular structure of hair surface

Fig. 18 shows the TR mode phase contrast images of various hair surfaces at different humidities. The phase contrast images of virgin hair surfaces at different humidities show distinct contrast, indicating a very fine granular structure. Interestingly, this fine granular structure is hardly affected by the humidity changes as shown in the TR phase contrast images at different humidities. The hydrophobic nature of the intact lipid layer minimizes the effect of water. On the other hand, damaged hair surface shows some contrast at low (5–10%) and medium (40–50%) humidity, but no longer has the fine granular structure as virgin hair surface. Damaged hair surface underwent chemical treatments, which might have partially destroyed the lipid layer on hair surface, therefore, no fine liquid domain can be observed. Some of the inner cellular structures of hair, which are partially hydrophilic were also exposed. Therefore, damaged hair surface can adsorb more water at high (80–90%) humidity. In this case, TR mode phase contrast measurement can no longer detect the contrast of different surface domain (content), but the relatively uniformly adsorbed water layer.

Treated hair shows different morphology at different humidities. Treated hair surface is covered with a layer of conditioner, which can adsorb large amount of water at medium and high humidity. This thick condition (and water) layer smears the phase contrast of TR mode images as shown in Fig. 18, which is similar to the case of damaged hair at high
humidity. However, large phase contrast can be observed at low humidity. At low humidity, the conditioner layer will lose water and is no longer able to retain the water content. The large phase contrast indicates that the conditioner gel network has collapsed after staying at low humidity and formed some kind of isolated conditioner gel network domains. Those domains have distinct chemical content and have different lateral stiffness and viscoelastic properties.

The surface height of cross section of virgin hair at two humidities is shown in Fig. 19. The cortex, layers of the cuticle an deembedding epoxy can be seen. At high humidity, the cortex and cuticle can adsorb a large amount of water, which will consequently weaken the hydrogen bonds and salt bonds between the protein molecules in hair cellular structure.
4.3. Summary

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).

The cross section and longitudinal section of virgin Caucasian human hair were investigated using TR mode II. The cortex and the cuticle, the macrofibril and the matrix of human Caucasian hair were readily revealed. Various sublamellar cellular structures of cuticle, such as the A-layer, the exocuticle, the endocuticle, and the cell membrane...
complex, are easily observed because of their distinct stiffness and viscoelastic properties. The surface features of various Caucasian human hair (virgin, chemically damaged, and chemically damaged treated) were readily revealed. Sublamellar layers show distinct contrast in TR amplitude and phase angle images. The fine granular structure of the outer $\beta$-layer, which has not previously been seen by SEM, TEM, and other AFM studies, is a result of the fine domain formation of lipid layer. Chemically damaged hair surfaces show much more damage; larger areas of the endocuticle were exposed. The endocuticle has much rougher structure than general cuticle surface (such as the outer $\beta$-layer), which could be the part of reason why damaged hair loses shine. Conditioner unevenly distributes on damaged treated hair surface; thicker conditioner films are found near the cuticle edges. At high humidity, the cortex and cuticle can adsorb water, which will consequently weaken the hydrogen bonds and salt bonds between the protein molecules in hair cellular structure. The effect is more significant in chemically damaged and treated hair.

5. Nanomechanical characterization using nanoindentation, nanoscratch, and AFM

Nanomechanical characterization of human hair using nanoindentation and nanoscratch provides valuable information about the hair fiber itself, as well as how damage and treatment affect important mechanical properties of the fiber [81,80]. In Section 5.1, the hardness, Young’s modulus and creep results for both the hair surface and cross section are discussed. In Section 5.2, the coefficient of friction and scratch resistance of the hair surface is presented for unsoaked and soaked hair. In Section 5.3, stress–strain curves and AFM topographical images of virgin and damaged hair during tensile deformation are presented.

5.1. Hardness, Young’s modulus, and creep

5.1.1. Hair surface

Fig. 20 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 $\mu$m 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. 21a shows the load–displacement curves for virgin, chemo-mechanically damaged and virgin treated Caucasian hair obtained at two loads: 0.1 and 10 mN. (Loads of 1 and 100 mN were also studied; data not shown.) The hardness and elastic modulus values corresponding to each load–displacement curve are listed in the figure boxes. As mentioned in Section 3, at each load, five indents were made. Fig. 21a just presents one representative result for each load. At 0.1 mN, the indentation depths of all these hair were less than

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**Fig. 20.** Image of indents on hair surface made using a nanoindenter [81].

**Fig. 21.** (a) Load–displacement curves for Caucasian virgin, chemo-mechanically damaged, and virgin treated hair at two peak loads; (b) hardness and elastic modulus vs. indentation depth for various virgin, chemo-mechanically damaged and treated hair [81].
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 that the tip probably reached the cortex of the hair, considering that a hair fiber generally has about 5–10 cuticle scales. It is interesting to observe that the loading curves of chemomechanically damaged hair obtained at 0.1 mN and 1.0 mN are not so smooth as the virgin and virgin treated hair, especially at the beginning, indicating that the chemomechanically 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 virgin treated and chemomechanically 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 mN 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. 21b 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. 21b was calculated from five indentations. According to Fig. 21b, 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 crosslink density, decreases from the A-layer, to the exocuticle, and to the endocuticle (see Fig. 2a and Table 2). The cuticle scales are bound together by the cell membrane complex, one of 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 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 crosslinks than the cortex [62,27], 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. 21b 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 chemo-mechanically damaged and virgin 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 were 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 [62]. 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 crosslinked proteins. The intercellular diffusion involves penetration between cuticles cells through the intercellular cement and the endocuticle that are low in cystine content (low crosslink 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 crosslinked A-layer and exocuticle are chemomechanically damaged [62]. 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 chemomechanically damaged and virgin 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 μm) were not affected (generally decreased) uniformly, leading to the larger data variation compared to corresponding virgin hair. This 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.

Fig. 22a summarizes the hardness and elastic modulus of various hair. In general, the chemomechanically damaged and virgin 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 virgin 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 the hardness and elastic modulus measured at 1.0 mN is taken as the hair surface hardness and elastic modulus, then by comparing the virgin Caucasian, Asian and African hair, it is seen 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. 22b 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 only has exposed cortex, 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 [84].

Fig. 23 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 (Fig. 2b). Other linkages, such as side-chain interactions of
the disulphide type, and the chain folding may also be 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 [2]. 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 μm, 100 μm, 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, chemo-mechanically damaged or virgin treated).

5.1.2. Cross section

Fig. 7a presented previously 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. The center column of Fig. 7a 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 [62]. 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 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 hardness and elastic modulus of hair cuticle, cortex and medulla were measured from the cross-section samples, and Fig. 24 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 6 summarizes the hardness and elastic modulus of various hair [81]. The hardness of cuticles was taken from the hair surface measurements (see Fig. 22a). 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. 31a). Table 6 shows that the hardness of cuticles is greater than cortex, but the elastic modulus of cortex is comparable to cuticle [81]. 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. 31a) 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.

5.1.3. Effect of humidity and temperature on Young’s modulus

Fig. 25a shows effective Young’s modulus mappings of chemically damaged treated hair at different humidities obtained from force calibration plots [12]. At different humidities, the maps are distinctly different. As humidity increases, the effective Young’s modulus of hair surface decreases significantly. The effective Young’s modulus of hair surface at 80–90% humidity is only half the value at 5–10% humidity. At high humidity, the water content in conditioner gel network will increase significantly; therefore, the conditioner layer on hair surface is thicker and softer, consequently a lower value of effective Young’s modulus. At low humidity, the conditioner gel network may desorb most of the water content, which results in the collapse of the gel network. Consequently, the conditioner layer no longer acts as a soft protection layer, instead as a hard, thin shell on the hair surface.

Fig. 25b summarizes the effective Young’s modulus of various hair surfaces at different humidities. Young’s modulus of damaged hair is lower than virgin hair and it decreases dramatically at high humidity. Since the hydrophobic lipid protection layer of damaged hair has been depleted or damaged, the hydrophilic molecules of the inner cellular structure of hair are exposed to water. Water can adsorb and diffuse easily into hair via the defects on the surface, therefore softening the hair. Treated hair has smaller effective Young’s modulus than virgin hair at 50% humidity because of the soft physisorbed conditioner gel network layer on the surface. The layer remains intact at high humidity and protects the hair surface from excess water adsorption and diffusion (penetration). However, at low humidity, the gel network is no longer able to retain the water content. It will
lose most of the water content and collapse, and behave as a hard shell on hair surface. Therefore, treated hair surface at low humidity has the same effective Young’s modulus as that of virgin hair.

Fig. 24. Hardness and elastic modulus plots across various virgin, chemo-mechanically damaged and virgin treated hair [81].
Table 6
Summary of hardness and elastic modulus of human hair

<table>
<thead>
<tr>
<th></th>
<th>Hardness (GPa)</th>
<th></th>
<th>Elastic modulus (GPa)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cuticle(^a)</td>
<td>Cortex(^b)</td>
<td>Medulla(^b)</td>
<td>Cuticle(^a)</td>
</tr>
<tr>
<td>Caucasian</td>
<td>0.32 ± 0.04</td>
<td>0.27 ± 0.02</td>
<td>~0.19</td>
<td>6.0 ± 0.4</td>
</tr>
<tr>
<td>Asian</td>
<td>0.39 ± 0.06</td>
<td>0.30 ± 0.02</td>
<td>~0.18</td>
<td>7.5 ± 0.8</td>
</tr>
<tr>
<td>African</td>
<td>0.24 ± 0.05</td>
<td>0.23 ± 0.06</td>
<td>~0.16</td>
<td>4.8 ± 0.6</td>
</tr>
</tbody>
</table>

Mean and ±1σ 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.

Fig. 25. (a) Effective Young’s modulus maps of Caucasian chemically damaged treated hair at different humidities [12], and (b) effective Young’s modulus of Caucasian virgin, chemically damaged, and damaged treated hair samples at different humidities [12].
The effective Young’s modulus of the cross section of virgin hair is shown in Fig. 26. As humidity increases, the Young’s modulus decreases and the differences between various layers (the cortex, the cuticle, and the epoxy) disappear. Human hair consists of various chemical and physical bonds (salt bond, hydrogen bond, and disulfide bond). The strength of these bonds will be strongly affected by the level of water content.

The effective Young’s modulus of various hair surfaces were also measured at different temperatures. Three different temperatures are studied: room temperature, human body temperature and a high temperature which represents the temperature under direct sunshine. Fig. 27 summarizes the findings for virgin, damaged, and conditioner treated hair at those temperatures. For virgin or damaged hair surfaces, temperature has little effect on the Young’s modulus due to small range of temperature studied. The effective Young’s modulus of conditioner treated hair surface increases as the temperature increases. At high
temperature, the conditioner layer is no longer able to retain the water content and collapses to form a hard shell covering the surface. Therefore, conditioner treated hair has high effective Young’s modulus at high temperature.

5.2. Scratch resistance

Nanoscratch technique is capable of simulating the scratch phenomena on hair surface on the nanoscale by scratching the hair surface using a conical diamond tip (radius about 1 μm) and recording the coefficient of friction, in-situ scratch depth and residual depth.

5.2.1. Nanoscratch on single cuticle cell

Fig. 28 shows the coefficient of friction and scratch depth profiles as a function of normal load and tip location on a single cuticle cell of Caucasian and Asian hair (virgin, chemo-mechanically damaged and virgin treated). The scratch direction is from left to right. The scratch length was 5 μm and the normal load was increased from 0.01 to 1 mN during scratching. The coefficient of friction of all the hair samples ranged from 0.3 to 0.6 [80]. The coefficient of friction of virgin treated Caucasian hair (~0.3) is lower than virgin Caucasian hair (~0.4), and the coefficient of friction of virgin treated Asian hair (~0.3) is also lower than virgin Asian hair (~0.5). The conditioner acts as a thin layer of lubricant on hair surface and it reduces the coefficient of friction of hair during scratch. The coefficient of friction of chemo-mechanically damaged hair depends on the type and

![Comparison of coefficient of friction and scratching](image-url)
extent of damage. If the chemical damage softens the hair surface, then during scratching, the tip plows into the hair easily, leading to higher coefficient of friction. If the damage hardens the hair surface or does not change the mechanical properties of the hair surface, then the coefficient of friction probably will decrease or stay the same during scratch.

The scratch depth profiles include the profiles obtained before (pre-scratch), during (in-situ scratch) and after (post-scratch) scratching at scratch length of 5 μm and a maximum normal load of 1 mN as indicated in Fig. 28. Reduction in scratch depth is observed after scratching as compared to that of during scratching. This reduction in scratch depth is attributed to an elastic recovery after removal of the normal load. The post-scratch depth indicates the final depth which reflects the extent of permanent damage and plowing of the tip into the hair surface. The scratch depth profiles show that at the very beginning of the scratch for all the hair samples, the in-situ displacement (30–200 nm) increased rapidly at very low load. After that, it increased gradually. This observation indicates that the top about 200 nm of the hair surface may be softer than the underlying layer. The scratch depth profiles also show that the reference surface profile before scratch is not very flat, indicating that human hair has a rough surface. AFM studies have shown that the RMS roughness of Caucasian and Asian hair surface ranges from 7 nm to 48 nm [39]. At 1 mN, the in-situ scratch depths of all the hair samples range from 300 nm to 600 nm, and the residual depths range from 50 nm to 200 nm. Since the thickness of one cuticle cell is about 300–500 nm, during the 1 mN nanoscratch test, the scratch tip might only penetrate one cuticle cell layer.

5.2.2. Nanoscratch on multiple cuticle cells

Most of the time when we comb our hair, the comb is scratching multiple cuticle cells. Fig. 29a shows the coefficient of friction and scratch depth profiles as a function of normal load and tip location on multiple cuticle cells of chemo-mechanically damaged Caucasian hair obtained in two scratch tests: scratch along cuticle and scratch against cuticle, and Fig. 30b shows the SEM images of the hair surface after scratch. The coefficient of friction obtained when the tip scratched the hair against cuticle is significantly higher than the coefficient of friction obtained when the tip scratched the hair along cuticle, which is known as the “directionality effect”. This is understandable because when the tip scratches the hair surface against cuticle, the 300–500 nm high cuticle “wall” resists the tip to move, leading to higher coefficient of friction [80].

By observing the surface profiles (before scratch) of Fig. 29a, we can clearly see the shape (height and visible length) of each cuticle cell, i.e., the height is about 300–500 nm, and the visible length is about 5–10 μm, which is in good agreement with SEM and AFM data. The scratch tip acts as a surface profiler before scratching. During scratching, the in-situ displacement increased up to about 3 μm at 10 mN, while the residual depth is about 1.5 μm. Considering that the thickness of cuticle is about 1.5–5 μm, it is likely that during the 10 mN scratch test, the tip reached the cortex. The SEM images (Fig. 29b) clearly show that in both the along cuticle and against cuticle cases, the cuticle cells were worn away. The topography of the exposed surface is totally different from the cuticle topography and it is believed that the exposed surface is the cortex. It can also be seen from Fig. 29b that the scratching against cuticle caused much more damage to the hair than along cuticle.

Given the fact that the “directionality effect” is universal for each human hair from all races and that the scratching along cuticle is more relevant to our daily life, we now focus
on the scratch tests along cuticle. Fig. 30a shows the coefficient of friction and scratch depth profiles as a function of normal load and tip location on multiple cuticle cells of chemo-mechanically damaged Caucasian hair obtained in two scratch tests: scratch along cuticle and scratch against cuticle; (b) SEM images of the hair surface after scratch [80].

For example, the SEM image of chemo-mechanically damaged Caucasian hair shows two scratches, and the scratch wear track on the right side corresponds to the scratch depth profile. For Caucasian hair, the averaged coefficient of friction of virgin treated hair (~0.4) is lower than virgin hair (~0.7). For Asian hair, the averaged coefficient of friction of virgin treated hair (~0.5) is also lower than virgin hair (~0.8). The trend corresponds well with the nanoscratch results on single cuticle. Based on this data, it is clear that the conditioner treatment indeed can reduce the coefficient of friction of hair surface upon scratching. Regarding the chemo-mechanically damaged hair, since the coefficient of friction of chemo-mechanically damaged hair varies depending on the type and extent of damage (as discussed above), it is difficult to make comparison with the virgin or virgin treated hair.

It is worth mentioning that the coefficient of friction of human hair measured by nanoscratch technique is on the microscale, and not on the nanoscale, since the tip radius is
1 μm and the normal load range is 1–10 mN. It will be shown later that the coefficient of friction of conditioner treated hair measured using an AFM tip (radius 30–50 nm), is higher than virgin hair [39]. In the nanoscale, the increase in friction force is due in part to an increase in meniscus effects which increase the adhesive force contribution to friction at sites where conditioner is deposited or accumulated on the hair surface. This adhesive force is of the same magnitude as the normal load, which makes the adhesive force

Fig. 30. (a) Coefficient of friction, scratch depth profiles and SEM images of Caucasian and Asian hair (virgin, chemo-mechanically damaged and virgin treated). (b) High magnification SEM images of damaged Caucasian and Asian hair after scratch [80].
contribution to friction rather significant. On the microscale, however, the adhesive force is much lower in magnitude than the applied normal load, so the adhesive force contribution to friction is negligible over the hair surface. On the microscale, the conditioner acts as a thin layer of lubricant, decreasing the friction.

Fig. 30b shows the high magnification SEM images of chemo-mechanically damaged Caucasian hair and chemo-mechanically damaged Asian hair after scratch. It is interesting to find that the failure mechanisms for these two hair are different. For Caucasian hair, it seems that the tip plowed the cuticle cells continuously during scratching and the plowed cuticle cells were accumulated at the end of the scratch. As discussed before (also see the Fig. 29), the exposed surface of the Caucasian hair is believed to be the cortex. For Asian hair, the tip did not plow the cuticle cells continuously. Instead, the tip only broke the top cuticle cell of each cuticle and carried away the broken cuticle cells until the end of the scratch. In this case, the tip did not reach the cortex during scratching. In order to explain this, we need to look at the nanomechanical properties of Caucasian and Asian hair. According to mechanical property data reported earlier [81], the cuticle of Asian hair has a higher hardness (0.39 ± 0.06 GPa) than Caucasian hair (0.24 ± 0.05 GPa). So the Asian hair may be more “brittle” than Caucasian hair during scratch. That may be the reason why Asian hair is fractured easier than Caucasian hair during scratch. However, it must be noted that our observation is based on limited number samples and experiments. Since human hair varies from one hair to another even in the same race, it is hard to draw a general conclusion on hair failure mechanism in terms of the hair race. What we can say is that the hair fails differently during scratching, depending on the nanomechanical properties of the cuticle of the hair.
Fig. 31 shows the schematic of the various failure mechanisms during nanoscratching on hair. The top and middle figures show the scratch along cuticle, and the bottom diagram shows the scratch against cuticle. In the case of scratching along cuticle, if the hair cuticle is soft (top figure), then the scratch tip will plow the cuticle and carry away the worn cuticle cells (scales). If the load is high enough, then the tip can reach the cortex during scratching. After scratching, a newly exposed surface will be created and some pileup is formed at the end of the scratch wear track. If the hair cuticle is hard (middle figure), then the scratch tip will fracture the cuticle cells instead of plowing deep into them. After scratching, for each cuticle cell undergoing scratching, part of it is carried away by the tip, resulting in the formation of small pileup at the end of the scratch wear track, and
leaving behind a series of incomplete cuticle cells. In the case of scratching against cuticle (bottom figure), the tip will plow the cuticle cells (whether soft or hard) and create a newly exposed surface with large wedge formation and pileup at the end of the scratch wear track.

In the studies reported earlier, nanomechanical measurements have also been performed on African hair [81]. In this study, the curly shape and structure made it very difficult to perform the nanoscratch on its surface.

5.2.3. Soaking effect

Fig. 32a and b compare the coefficient of friction and scratch depth profiles of unsoaked and soaked Caucasian obtained on single cuticle cell (at 1 mN) and multiple cuticle cells (10 mN loads), respectively. At 1 mN, (see Fig. 32a), the coefficient of friction of virgin and chemo-mechanically damaged Caucasian hair increased from ~0.4 to ~0.7 after soaking, while the coefficient of friction of virgin treated hair (~0.3) does not change much. It is known that the human hair swells in water. In this work, the hair was only soaked in deionized water for 5 min. After the sample was soaked, it took a few minutes to mount the sample and run the scratch tests. In this case, it is possible that only a few hundred nanometer of the hair surface contained considerable amount water and were softened. During scratching, it is easier for the tip to plow into the softer hair surface, leading to higher coefficient of friction. This may be the reason that for 1 mN scratch in which the maximum in-situ scratch depths were less than 600 nm, the coefficient of friction of virgin and

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![Fig. 32. Comparison of nanoscratch results on chemo-mechanically damaged Caucasian unsoaked and soaked hair samples (a) Scratch on single cuticle cell (1 mN load); (b) Scratch on multiple cuticle cells (10 mN load) [80].](image-url)
chemo-mechanically damaged hair increased. For virgin treated hair in the 1 mN scratch test, however, some of the conditioner molecules might occupy the pathways of water molecules so that the swelling of virgin treated hair was not as significant as virgin and chemo-mechanically damaged hair. Therefore, the virgin treated hair shows little change of coefficient of friction after soaking. At 10 mN, (see Fig. 32b), the coefficient of friction of all three hair does not change considerably after soaking. This may indicate that the 5 min soaking did not affect the hair surface deeply. Table 7 summarizes the coefficient of friction and scratch depths of Caucasian (unsoaked and soaked) and Asian (unsoaked) hair [80].

5.3. In-situ tensile deformation studies on human hair using AFM

Fig. 33 presents stress strain curves for five types of hair. The stress strain curve of human hair is similar to that of wool and other such keratinous fibers [86]. When a keratin fiber is stretched, the load elongation curve shows three distinct regions as marked in Fig. 33 (28,4). In the pre-yield region, also referred to as the Hookean region, stress and strain are proportional, and an elastic modulus can be found. In this region, there is the homogenous response of alpha keratin to stretching. The resistance is provided by hydrogen bonds that are present between turns and stabilize the alpha helix of keratin. The yield region represents transition of keratin from the alpha form to the beta form, the chains unfold without any resistance, and hence the stress does not vary with strain. The beta configuration again resists stretching. So, in the post-yield region, the stress again increases with strain until the fiber breaks. This alpha to beta transition of keratin is
Table 7 Summary of coefficient of friction and scratch depths of Caucasian (unsoaked and soaked) and Asian (unsoaked) hair

<table>
<thead>
<tr>
<th>Max. normal load/No. of cuticle cells</th>
<th>Unsoaked Caucasian</th>
<th>Soaked Caucasian</th>
<th>Unsoaked Asian</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hair condition</td>
<td>Virgin</td>
<td>Damaged</td>
<td>Treated</td>
</tr>
<tr>
<td>Average coefficient of friction</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Max. in-situ depth (nm)</td>
<td>280</td>
<td>440</td>
<td>650</td>
</tr>
<tr>
<td>Max. residual depth (nm)</td>
<td>25</td>
<td>100</td>
<td>150</td>
</tr>
</tbody>
</table>
the reason for the unique shape of the stress strain curve of hair. Typically, yield begins around 5% and post-yield begins at around 15% strain. There is no apparent difference in tensile properties of the different hair types. In the dry state, the tensile properties of hair are significantly contributed by the cortex. Hair fibers oxidized with diperisophthalic acid, which causes almost total removal of cuticle, have shown no significant change in mechanical properties [63]. In the case of conditioner treatment and mechanical damage, the change occurs only in the cuticle. Hence, it is logical that the mechanical properties do not experience measureable change. In the case of chemical damage, apart from cuticle damage, oxidation of the cystine in keratin to cysteic acid residues occurs, and hence disrupts the disulfide crosslinks. However, the disulfide bonding does not influence tensile properties of keratin fibers in the dry state, though some effect is seen in the wet state (62). Since all experiments in the present study were carried out in the dry state, it is again logical that no change in the mechanical properties was observed.

Fig. 34 shows AFM topographical images, and 2D profiles at indicated planes, of a given control area with increasing strain, of the virgin, chemically damaged, and mechanically damaged types of hair. The common effect of stretching, observed for all hair types, is the lifting of the outer cuticle layer with increasing strain.

In the case of virgin hair (Fig. 34a), this is seen to be the only effect of tension. The cuticle lift off is sudden and occurs consistently at around 20% strain. As mentioned earlier, human hair cuticles have a lamellar structure. The various layers of human hair vary in their cystine content. This causes variation in their mechanical strength. The epicuticle and exocuticle are high in cystine content and are extremely rigid. The endocuticle and cell membrane complex are low in cystine content and are more extensible. Stretching hair, sets up interlayer shear forces due to this difference in extensibility [64]. At 20% strain delamination occurs, and the inner cuticle layers separate from the outer ones. This causes
outer cuticle lift off and hence the change in height and slope observed in the AFM images and corresponding cross-sectional profiles.
Fig. 34b and c shows topographical images of chemically damaged hair and mechanically damaged hair, respectively. Apart from the lift off discussed earlier, another noticeable effect in both cases is the disappearance of some cuticle edges and the appearance of sponge-like scales instead. Sponge-like scales in the cuticle have been observed earlier, these are thought to be remains of cuticle cells, which have split up to the endocuticle
Chemical and mechanical damage cause cuticle damage and weakening. Hence in the case of damaged hair, along with failure and delaminations in the endocuticular region, fracture of the outer cuticle occurs to expose the inner cuticle. This shows up as the sponge-like scales observed.
Comparing mechanical damage and chemical damage, it is seen that the fracture occurs earlier in mechanically damaged hair (10%) than in chemically damaged hair (20%). This could be because, in mechanically damaged hair, parts of the cuticle have already broken away, and cuticle damage is more extensive than in chemically damaged hair.

Conditioner in the case of virgin and chemically damaged treated hair has no apparent effect on the lift off or fracture phenomenon (data not shown). Conditioner coats the cuticle and improves its tribological properties. However, it does not chemically or physically alter appreciably the cuticles.

5.4. Summary

Nanoindenter has been used to perform nanomechanical studies on human hair. 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 $\mu$m. That is, the first 3–4 cuticle scales may interact with the chemicals and conditioner ingredients more effectively than the rest of the scales. It is found that the hair cuticle has higher hardness and elastic modulus than cortex in the lateral direction. The hardness and elastic modulus of hair decreased as the indentation depth increased. The cystine content variations in cuticle substructures (A-layer, exocuticle, endocuticle, cell membrane complex) and cortex are proposed to be responsible for the observation. Humidity and temperature had an effect on mechanical properties. The Young’s modulus of damaged treated hair decreases dramatically at high humidity. Little temperature effect was observed on the Young’s modulus.

Nanoscratch tests were performed on single and multiple cuticles of various hair, in both unsoaked and soaked conditions. The coefficient of friction of virgin treated hair is lower than virgin hair for Caucasian and Asian hair in both cases of single cuticle scratch and multiple cuticle scratch. This thin conditioner layer acts as a layer lubricant, reducing the coefficient of friction during scratching. In-situ displacement (30–200 nm) increased greatly at very low initial load and then increased gradually, indicating that the first approximately 200 nm of the hair surface should be softer than the underlying layer. The nanoscratch tests on multiple cuticles clearly show the directionality effect on the coefficient of friction. It is found that the hair surface fails differently during scratching, depending on the nanomechanical properties of the cuticle of the hair. For a hair with hard cuticle, the cuticle cells tend to be fractured during scratching. For a hair with soft cuticle, the scratch tip usually plows and wears away the cuticle cells continuously until it reaches the cortex. The effect of 5 min soaking in de-ionized water on coefficient of friction and scratch resistance of human hair is limited within a shallow region (about 600 nm deep) of the hair surface. In this case, the coefficient of friction of virgin and chemomechanically damaged Caucasian hair increases after soaking because of the swelling of the water, which softens the hair surface.

Human hair shows a stress strain curve typical of keratinous fibers. Transition of alpha keratin to beta keratin in the yield region is the reason for the unique shape of the curves. Chemical damage, mechanical damage and conditioner treatment have no obvious effect on the stress strain curve or tensile properties. This is because such treatments affect the cuticle predominantly and tensile properties of human hair in dry state are governed by the cortex. Tensile stress in general causes lift off of the outer cuticle. The lift off is sudden and occurs consistently at around 20% strain. This lift off occurs in all types of hair studied, and is due to interlayer shear forces and consequent separation between inner and
outer cuticle layers at 20% strain. Chemical damage and mechanical damage cause weakening of the outer cuticle. Along with lift off, fracture of the outer cuticle to expose endocuticular layers occurs. Fracture occurs sooner (about 10% strain) in mechanically damaged hair than chemically damaged hair (about 20% strain).

6. Multi-scale tribological characterization

6.1. Macroscale tribological characterization

Tribology is very important to hair care and product development. While current state of the art is to use AFM to measure nanoscale tribological properties of hair in contact with an AFM tip, macroscale tribological measurements provide an excellent simulation of skin–hair and hair–hair contacts [18]. The friction and wear of hair were measured using a flat-on-flat tribometer. Friction and wear studies on various hair are presented, including effect of load, velocity, and skin size. In addition, the effect of humidity and temperature on hair tribological properties is discussed.

6.1.1. Friction and wear studies of various hair

Fig. 35a shows coefficient of friction measured from hair strands sliding against a polyurethane film (simulated skin) [18]. The data shows that the coefficient of friction of virgin Caucasian hair was about 0.14 along cuticle and about 0.23 against cuticle. As with most animal fibers, human hair shows a directionality friction effect; that is, it is easier to move a surface over hair in a root-to-tip direction than in a tip-to-root direction because of anisotropic orientation of hair cuticles [62,6,8]. The data shows that the flat-on-flat tribometer can measure the directionality dependence of friction. Note that in Fig. 35a, the hair strands were used and all the hair was separated from each other, so during the friction test, there was no interaction between hair and hair. The output signals of normal force and friction force are smooth and the coefficient of friction has small variation.

In industry, many friction tests of hair are performed on bundle of hair, in which some hair is overlapping on each other. So the hair–hair interaction occurs during the friction test and variation in the data is large. Fig. 35b shows the coefficient of friction obtained from bundle of hair. It can be seen that the output signal of normal force fluctuated a lot, and the output signal of friction force is not smooth, leading to big variation of the coefficient of friction. Both the coefficient of friction along cuticle and against cuticle are greater for bundle of hair compared to hair strands, because of the hair–hair interaction during friction tests. It has been observed that if a bundle of hair is used for friction test, the data has much poorer reproducibility than if hair strands are used. This may be because that when a bundle of hair is used, the hair is placed randomly and the hair to hair position is hard to repeat, but for hair strands, the hair to hair position is easy to control since they are separated and parallel to each other. Therefore, in the paper, hair strands were used to make further measurements.

Fig. 36a shows the coefficient of friction of polyurethane film vs. hair and hair vs. hair. In the case of polyurethane film vs. hair, the chemo-mechanically damaged hair has the highest coefficient of friction, followed by virgin and virgin treated hair, indicating that the conditioner can reduce the friction of hair. The hair vs. hair results show the same trend as polyurethane film vs. hair, but the coefficient of friction of hair vs. hair is higher than the corresponding polyurethane film vs. hair. Fig. 36b compares the coefficient of
friction of polyurethane film vs. Caucasian hair at dry and wet conditions. Obviously, the coefficient of friction at wet conditions is higher than dry conditions, due to the swelling of hair. When the hair is swollen, the hair cuticle will be lifted up and the real contact area will be increased, leading to higher coefficient of friction.

Fig. 37 shows the coefficient of friction of polyurethane vs. various hair. For all hair, the chemo-mechanically damaged hair has highest coefficient of friction, followed by virgin hair and virgin treated hair. Note that the coefficient of friction can vary about 10–15% within a given ethnic group. Fig. 38a shows the coefficient of friction of Caucasian hair during wear tests. The coefficient of friction does not change during 24 h for both virgin and virgin treated hair. From the optical micrographs in Fig. 38b, it can be seen that after wear tests, some cuticles were damaged. Polyurethane film is soft and does not create much damage to hair. Since the observed damaged area was small, it may not affect the overall coefficient of friction.
6.1.2. Effect of temperature and humidity on hair friction

Fig. 39 shows the effect of temperature and humidity on hair friction. The coefficient of friction of hair is a strong function of humidity, and it increases as the relative humidity increases. In addition, the differential friction effect also increases with increasing relative humidity, as shown in Fig. 39. It is interesting to find that the differential friction effect of virgin treated hair is less dependent on relative humidity than virgin hair. This may be because some of the conditioner molecules occupied the pathways of water molecules so that the swelling of hair was not as significant as virgin hair.

For virgin hair, the temperature has no effect on coefficient of friction. This is in agreement with Scott and Robbins’s work [66]. For virgin treated hair, it is found that the coefficient of friction increases as the temperature increases. After the hair was treated with conditioner, the hair surface properties might be changed, which could be affected by
temperature. For instance, a higher temperature might lead to softer treated hair surface, leading to higher coefficient of friction.

6.2. Nanotribological characterization using an AFM

Nanoscale tribological characterization is essential to study the hair and evaluate/develop better cosmetic products. This becomes especially important when studying the effects of damage and conditioner treatment. How common hair care products, such as conditioner, deposit onto and change hair roughness, friction, and adhesion are of interest, since these properties are closely tied to product performance. Other important issues, such as the thickness distribution of conditioner on the hair surface which is important in determining the proper functions of conditioner, have been important to cosmetic scientists for decades.

In this section, the roughness, friction, adhesion, and wear of various hair are studied [39,40,42,47]. In Section 7, a new method based on the AFM technique for determining thin liquid film thickness is developed, and the conditioner thickness distribution, adhesive force and the effective Young’s modulus of various hair samples are presented [21,22,47]. The binding interactions between the conditioner molecules and hair surface are discussed as well.

6.2.1. Various ethnicities

Topographical images of Caucasian, Asian, and African hair were taken with scan sizes of $20 \times 20 \mu m^2$, as shown in Fig. 40. Lighter areas of the images correspond to higher topography, and darker areas correspond to lower topography. Only virgin and chemo-mechanically damaged hair are shown in Fig. 40 because virgin treated samples closely resemble virgin hair samples. One can see the variation in cuticle structure even in virgin hair. Cracking and miscellaneous damage at the cuticle edges is evident at both virgin and chemo-mechanically damaged conditions. In virgin hair, the damage is likely to be caused by mechanical damage resulting from daily activities such as washing, drying, and
combing. Most of the virgin cuticle scales that were observed, however, were relatively intact. Long striations similar to scratches, and “scale edge ghosts” (outlines of a former overlying cuticle scale edge left on the underlying scale before it was broken away) were found on the surface. In some instances, the areas surrounding the cuticle edges appeared to show residue or debris on the surface, which is most likely remnants of a previous cuticle or the underside of the cuticle edges that are now exposed (such as the endocuticle). Caucasian and Asian virgin hair displayed similar surface structure, while the African hair samples showed more signs of endocuticular remains along the scale edges. One can also see more curvature in the cuticle scales of African hair, which is attributed to its elliptical cross-sectional shape and curliness, which can partially uplift the scales in different places. With respect to chemo-mechanically damaged hair, it is observed that several regions seem to exist in these hair samples, ranging from intact cuticle scales to high levels of wear on

Fig. 38. (a) Coefficient of friction of virgin and virgin treated Caucasian hair during wear test, (b) optical micrographs of Caucasian hair before and after wear test [18].
the surface. In many cases these regions occur side by side. This wide variation in chemomechanically damaged cuticle structure results in a wider range of tribological properties.

Fig. 39. Effect of humidity and temperature on coefficient of friction of virgin Caucasian hair [18].
Fig. 40. Surface roughness of virgin and chemo-mechanically damaged Caucasian, Asian, and African hair at 5, 10, and 20 \( \mu m^2 \) scan sizes [39].
on the micro/nanoscale for these fibers. Caucasian and Asian chemo-mechanically damaged hair showed more worn away cuticle scales than in chemo-mechanically damaged African hair, which showed mostly endocuticle remnants. This is most likely due to the different effects that chemical straightening has on the hair versus multiple cycles of perming the hair.

A more focused look into roughness and friction on the cuticle surface can be found by comparing Caucasian, Asian, and African virgin and chemo-mechanically damaged hair, Fig. 41, and virgin and virgin treated hair, Fig. 42. Virgin hair was used as the baseline to compare variations in roughness and friction force against modified hair (chemo-mechanically damaged or virgin treated). Scan size of $10 \times 10 \, \mu m^2$ is displayed. Above each AFM and FFM image are cross-sectional plots of the surface (taken at the accompanying arrows) corresponding to surface roughness or friction force, respectively. From the surface roughness images, the step heights of one or more cuticle edges can be clearly seen. Step heights range from approximately 0.3–0.5 $\mu m$.

If the surface is assumed to have Gaussian height distribution and an exponential autocorrelation function, then the surface can be statistically characterized by just two parameters: a vertical descriptor, height standard deviation $\sigma$, and a spatial descriptor, correlation distance $\beta^*$ [6,8]. The standard deviation $\sigma$ is the square root of the arithmetic mean of the square of the vertical deviation from the mean line. The correlation length can be referred to as the length at which two data points on a surface profile can be regarded as being independent, thus serving as a randomness measure [6,8]. Table 8 displays these roughness parameters for each ethnicity as a function of hair type (virgin, chemo-mechanically damaged, and virgin treated) [39]. Virgin hair was shown to generally have the lowest roughness values, with virgin treated hair closely resembling virgin hair. Chemo-mechanically damaged hair showed a significantly higher standard deviation of surface height. This variation is expected because of the non-uniformity of the mechanical and chemical damage that occurs throughout a whole head of hair as well as each individual fiber. This is in agreement with the images of chemo-mechanically damaged hair shown previously, where regions of intact cuticle and severe degradation of the surface are intermingled. The trends observed for standard deviation were not as evident for the correlation length $\beta^*$. For each ethnicity, chemo-mechanically damaged and virgin treated hair showed similar $\beta^*$ values.

From Fig. 41, friction forces are generally seen to be higher on chemo-mechanically damaged hair than on virgin hair. Although friction forces were similar in magnitude, it was observed that the friction force on the cuticle surface of chemo-mechanically damaged hair showed a much larger variance, which contributed to the higher friction values. Another contribution to the higher friction could be that the tiny peaks developed after damage also create a ratchet mechanism on a nanoscale, which affects the friction between the AFM tip and the surface. These peaks could then add to the friction signal. The damage of the hair by chemical and mechanical means have shown high reproducibility in the lab in terms of structure alteration, which explains the similar friction properties no matter the ethnicity for chemo-mechanically damaged hair. With virgin and virgin treated hair, however, it is unknown what prior mechanical damage and sun exposure the fibers have seen, and varies largely on the individuals. Thus, across ethnicity there is variability in friction force for those hair.

Perhaps the most notable difference between virgin and virgin treated hair fibers can be seen in the friction force mappings of Fig. 42. Although quite comparable in surface
roughness, close examination of the virgin treated hair surface shows an increase in friction force, usually only surrounding the bottom edge of the cuticle. This was unlike virgin
Fig. 42. (a) Surface roughness and friction images for virgin and virgin treated Caucasian, Asian, and African hair at 10 µm² scan sizes. Shown above each image is a cross section taken at the corresponding arrows to show roughness and friction force information [39].
hair, where friction generally remained constant along the surface, and unlike chemo-
mechanically damaged hair, where there was large variability which was random over
the entire surface.

Fig. 43 presents friction force curves as a function of normal load for Caucasian virgin,
chemo-mechanically damaged, and virgin treated hair to further illustrate the previous dis-
cussion. One can see a relatively linear relationship between the data points for each type
of hair sample. When plotted in such a way, the coefficient of friction is determined by the
slope of the least squares fit line through the data. If this line is extended to intercept
the horizontal axis, then a value for adhesive force can also be calculated, since friction force
\( F \) is governed by the relationship
\[
F = \mu (W + F_m) ,
\]
where \( \mu \) is the coefficient of friction, \( W \) is the applied normal load, and \( F_m \) is the adhesive
force [6,8].

One explanation for the increase in friction force of virgin treated hair on the micro/
nanoscale is that during tip contact meniscus forces between the tip and the condi-
tioner/cuticle become large as the tip rasters over the surface, causing an increase in the
adhesive force. This adhesive force is of the same magnitude as the normal load, which
makes the adhesive force contribution to friction rather significant. Thus, at sites where
conditioner is accumulated on the surface (namely around the cuticle scale edges), friction
force actually increases. On the macroscale, however, the adhesive force is much lower in
magnitude than the applied normal load, so the adhesive force contribution to friction is
negligible over the hair swatch. As a result, virgin treated hair shows a decrease in friction
force on the macroscale, which is opposite the micro/nanoscale trend. The friction and
adhesion data on the micro/nanoscale is useful, though, because it relates to the presence
of conditioner on the cuticle surface and allows for obtaining an estimate of conditioner
distribution.

Table 8

<table>
<thead>
<tr>
<th></th>
<th>Virgin hair</th>
<th>Chemo-mechanically damaged hair</th>
<th>Virgin treated hair (commercial conditioner)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma ) (nm)</td>
<td>12 ± 8</td>
<td>17 ± 10</td>
<td>12 ± 4</td>
</tr>
<tr>
<td>( b' ) (( \mu )m)</td>
<td>0.61 ± 0.3</td>
<td>1.0 ± 0.3</td>
<td>0.90 ± 0.3</td>
</tr>
<tr>
<td>( \sigma ) (nm)</td>
<td>9.7 ± 4</td>
<td>33 ± 15</td>
<td>7.1 ± 0.1</td>
</tr>
<tr>
<td>( b' ) (( \mu )m)</td>
<td>0.73 ± 0.3</td>
<td>0.94 ± 0.3</td>
<td>0.97 ± 0.3</td>
</tr>
<tr>
<td>( \sigma ) (nm)</td>
<td>12 ± 5</td>
<td>21 ± 16</td>
<td>11 ± 4</td>
</tr>
<tr>
<td>( b' ) (( \mu )m)</td>
<td>0.92 ± 0.3</td>
<td>0.78 ± 0.3</td>
<td>0.89 ± 0.2</td>
</tr>
</tbody>
</table>

Average coefficient of friction \( \mu \)

Caucasian 0.02 ± 0.01
Asian 0.03 ± 0.01
African 0.04 ± 0.02

Adhesive force \( F_m \) (nN)

Caucasian 25
Asian 31
African 35

\[ F = \mu (W + F_m) , \]

where \( \mu \) is the coefficient of friction, \( W \) is the applied normal load, and \( F_m \) is the adhesive
force [6,8].
It is also observed from Fig. 43 that while chemo-mechanically damaged hair displays a higher friction force on the application of normal load, and consequently a higher coefficient of friction, chemo-mechanically damaged hair friction is not as strongly dependent on adhesive force contribution as the virgin and virgin treated hair. Average values for $\mu$ were calculated and are compiled in Figs. 43 and 44 and Table 8 for all hair ethnicities and types [39]. Error bars represent $\pm 1\sigma$ on the average coefficient value. The coefficients of friction for virgin, chemo-mechanically damaged, and virgin treated Caucasian hair are
0.02, 0.13, and 0.03, respectively. For virgin, chemo-mechanically damaged, and virgin treated Asian hair, coefficients of friction are 0.03, 0.13, and 0.06, respectively. Finally, virgin, chemo-mechanically damaged, and virgin treated African hair coefficients of friction are 0.04, 0.14, and 0.05, respectively. Chemo-mechanically damaged hair presents the highest coefficient of friction, but also displays the largest standard deviation, due to the large variations in chemical and mechanical damage that each hair or hair bundle experiences. Coefficient of friction of virgin treated hair is slightly larger than that of virgin hair for all ethnicities. While the coefficient of friction is similar in virgin and virgin treated
hair, the adhesive force contribution to friction for Caucasian virgin treated hair is higher than in Caucasian virgin hair, when calculated according to the method described above. However, this was not always the trend for Asian and African virgin treated hair samples. It should be noted that since in friction force measurement the tip moves laterally over the surface, this might cause a smearing out of the conditioner layer which accounts for the inconsistent trend. In the adhesive force mappings described in the next section, where determination of adhesive force does not depend on this lateral movement, all virgin treated hair samples showed higher adhesion than their virgin hair counterparts.

A force calibration plot (FCP) technique and resulting adhesive force maps (commonly called force-volume maps) can be used to understand the adhesive forces between the AFM tip and the sample [7,9,13,46]. Shown in Fig. 45 are FV maps and an example of the individual force calibration plots from which the maps were created. Adhesive force distribution for chemo-mechanically damaged hair was shown to be comparable to virgin hair adhesive force values, but slightly lower. A significant increase in adhesive force over the entire mapping was found in all cases of virgin treated hair as compared to virgin hair, especially in Asian and African hair. Conditioner distribution can be seen from these images. This technique shows promise to be very useful in further study of the distribution of materials and hair care products on the surface of the hair.

A typical value for the adhesive force of each FV map was calculated. Values are shown in the plot of Fig. 45, along with surface roughness and coefficient of friction data for all hair samples. Adhesive force values are also tabulated in Table 8.

6.2.1.1. Directionality effects of friction on the micro/nanoscale. The outer surface of human hair is composed of numerous cuticle scales running along the fiber axis, generally stacked on top of each other. As previously discussed, the heights of these step changes are approximately 300 nm. These large changes in topography make the cuticle an ideal surface for investigating the directionality effects of friction using AFM/FFM.

The directionality effect of friction on the macroscale has been well studied in the past. It was shown by Robbins [62] and Bhushan et al. [18] that rubbing the hair from the tip to the root (against the cuticle steps) results in a higher coefficient of friction than rubbing the hair from root to tip (with the cuticles). On the micro/nanoscale, it is important to distinguish how material effects and topography-induced effects contribute to the directionality effect of friction force when scanning over and back across a small surface region [6–9]. Fig. 46 shows surface roughness, friction force, and surface slope maps of a Caucasian virgin hair fiber, each coupled to their accompanying 2D cross-sectional profiles. The scan size of $5 \times 5 \mu m^2$ provides one cuticle step height to be studied. As the tip rasters over the step in the trace mode (i.e. from left to right), a small decrease in the friction force is observed as the tip follows the step downward. When the tip comes back in the retrace mode (i.e. right to left), climbing up the sharp peak results in a high friction signal. However, because of the sign convention of the AFM/FFM that causes a reversal in the sign when traversing the opposite direction, this signal is now observed to be highly negative. The interesting difference between the two profiles lies in the fact that the magnitude of the decrease in friction when going up the step is much larger than the magnitude of the friction when the tip is going down the step, yet both signals are in the same direction. The important result is that even by subtracting the two signals (T-R), there is still a gross variation in the image due to topography effects. These topography effects yield friction
Fig. 45. Force volume maps of virgin, chemo-mechanically damaged, and virgin treated hair at each ethnicity. Examples of the individual force calibration plots, which make up the FV maps, are presented for Caucasian hair of each type [39].
variations in the same direction, whereas material effects show up in opposite directions. It can be shown that the cuticle edge provides a local ratchet and collision mechanism that increases the friction signal at that point. It was concluded that surface slope variation always correlates to friction force variations with respect to topography effects, and the data presented in Fig. 46 shows the same trend when comparing trace and negative retrace slope profiles.

6.2.2. Virgin and chemically damaged Caucasian hair (with and without commercial conditioner treatment)

The hair surface is negatively charged and can be damaged by a variety of chemical (permanent hair waving, chemical relaxation, coloring, bleaching) and mechanical (combing, blowdrying) factors [62,19,31]. Fig. 47 shows the transformation and wear of the cuticles scales before and after damage. Chemical damage causes parts of the scales to fracture and reveal underlying cuticle remnants. Conditioner application provides a protective coating to the hair surface for prevention of future damage.
Shown in Fig. 48 are surface roughness and friction force plots for virgin, virgin treated, chemically damaged, chemically damaged treated (1 cycle conditioner), and chemically damaged treated (3 cycles conditioner). Above each AFM and FFM image are cross-sectional plots of the surface (taken at the accompanying arrows) corresponding to surface roughness and friction force, respectively. Although virgin and virgin treated hair are quite comparable in surface roughness maps, examination of the treated hair surface shows an increase in friction force, especially in the area surrounding the scale edge bottom level. These frictional patterns observed in treated hair were not like anything observed in the virgin or chemically damaged cases. Images of all hair types have shown friction variation due to edge contributions and cuticle mechanical damage that has left only remnants of cuticle sub layer (such as the endocuticle). Further investigation of the corresponding treated hair roughness images showed this increase in friction was not due to a significant change in surface roughness, either. One explanation for the increase in friction force of treated hair on the micro/nanoscale is that during tip contact meniscus forces between the tip and the conditioner/cuticle become large as the tip rasters over the surface, causing an increase in the adhesive force. This adhesive force is of the same magnitude as the normal load, which makes the adhesive force contribution to friction rather significant. Thus, at sites where conditioner is accumulated on the surface (namely around the cuticle scale edges), friction force actually increases. On the macroscale, however, the adhesive force is much lower in magnitude than the applied normal load, so the adhesive force contribution to friction is negligible over the hair swatch. As a result, treated hair shows a decrease in friction force on the macroscale, which is opposite the micro/nanoscale trend.

Fig. 47. Schematic of the effect of damage to the cuticle scales and the deposition of conditioner on the cuticle surface. The cross section of the hair with and without conditioner is shown below [42].
Fig. 48. Surface roughness and friction force images for Caucasian virgin, virgin treated, chemically damaged, damaged treated (1 cycle conditioner), and damaged treated (3 cycles conditioner) hair at 5 μm scan sizes. Shown above each image is a cross section taken at the corresponding arrows to show roughness and friction force information [40].
In general, friction forces are higher on chemically damaged hair than on virgin hair. Although friction forces were similar in magnitude, it was observed that the friction force on the cuticle surface of chemically damaged hair showed a much larger variance, which contributed to the higher friction values. Chemically damaged treated hair shows a much stronger affinity to the conditioner. It is widely known that the cuticle surface of hair is negatively charged. This charge becomes even more negative with the application of chemical damage to the hair. As a result, the positively charged particles of conditioner have even stronger attraction to the chemically damaged surface, which explains the increased presence of conditioner (and corresponding higher friction forces) when compared to virgin treated hair. With the application of three conditioner cycles on chemically damaged treated hair, friction force is still higher near the cuticle edge, however it is also increased all over the cuticle surface, showing a more uniform placement of the conditioner.

Fig. 49 shows adhesive force maps for the various hair, which gives a measurement of adhesive force variation on the surface. Fig. 50 presents surface roughness, coefficient of friction, and adhesive force plots for the various virgin and chemically damaged hair discussed above. The data is also presented in Table 9 [40]. Surface roughness for human hair is characterized by a vertical descriptor, height standard deviation $\sigma$, and a spatial descriptor, correlation distance $\beta^*$ [6,8]. The standard deviation $\sigma$ is the square root of the arithmetic mean of the square of the vertical deviation from the mean line. The correlation length can be referred to as the length at which two data points on a surface profile can be regarded as being independent, thus serving as a randomness measure. These two parameters are all that is needed if the surface is assumed to have Gaussian height distribution and an exponential autocorrelation function [6,8]. Virgin and virgin treated hair showed similar $\sigma$ values, while $\beta^*$ was higher in virgin treated hair. Chemically damaged hair and both types of chemically damaged treated hair showed similar roughness values, although $\sigma$ was higher for the treated cases. The chemically damaged hair presented in this work is different from the chemo-mechanically damaged hair studied in [39]. It seems that chemically damaging the surface does not lead to as much wear and surface roughness increase as the combination of both chemical and mechanical damage. Thus, it should be noted (and it is understandable) that there are differences between the chemo-mechanically and chemically damaged hair.

Coefficient of friction of virgin and virgin treated hair is similar, but slightly higher for the treated cases. Chemically damaged hair shows a much higher coefficient of friction, and with more variation in the values since the chemical damage varies throughout each individual fiber. An interesting finding was that, contrary to the virgin and virgin treated hair results, coefficient of friction for chemically damaged hair decreased with application of conditioner treatment (both 1 and 3 cycles). One possible explanation is that because the stronger negative charge on chemically damaged hair results in better attraction of conditioner, this leads to higher adhesive force but, more importantly, lower shear strength on the surface. This creates an overall effect of lubrication and ultimately lowers the coefficient of friction.

Average adhesive force values were taken from the adhesive force maps described previously. Virgin treated hair shows a higher adhesive force than virgin hair due to the meniscus effects that come about from AFM tip interaction with the conditioner on the cuticle surface [6,8]. The same trend is true and even more evident for chemically damaged treated hair compared to chemically damaged hair. A possible reason that 1 cycle of conditioner on chemically damaged hair showed higher average adhesive force than 3 cycles
Fig. 49. Adhesive force maps displaying variations in adhesive force on the cuticle surface of Caucasian virgin, virgin treated, chemically damaged, damaged treated (1 cycle conditioner), and damaged treated (3 cycles conditioner) hair. Treated hair is shown to have higher adhesive force due to meniscus effects [40].
could be because the three cycles generally places the conditioner more uniformly on the surface rather than accumulating it most near the bottom surface near the cuticle edge, which is where the adhesive force maps were generally taken. Nevertheless, the increased adhesive force shown in the plots is a clear indication of conditioner present on the hair surface, and its localization can be observed.

6.2.2.1. Effect of relative humidity, temperature, and soaking, and durability measurements.

Fig. 51 displays the effect of relative humidity on friction force and adhesive force. Coefficient of friction remained relatively constant for virgin and virgin treated hair. However, chemically damaged hair experienced a large increase in coefficient of friction at the high humidity, while chemically damaged treated hair experienced the opposite trend. This clearly shows that heavy moisture in the air plays a role on the frictional properties of chemically damaged hair. When combined with conditioner, a lubricating effect once again dominates as the water helps form a liquid layer which is more easily sheared. In terms of adhesive force, most samples showed a decrease in adhesive force with high humidity. It is expected that as water builds up on a surface, meniscus effects diminish and as a result do not readily contribute to adhesive force. Thus, the adhesive force is expected to come down at very high humidity.

Fig. 52 displays the effect of temperature on friction force and adhesive force. The coefficient of friction generally decreased with increasing temperature. As the hair fiber heats up, conditioner which is present on the surface decreases in viscosity, causing a thinner
film and lower friction force. The lower friction force ultimately leads to lower coefficient of friction values. Adhesive force was shown to decrease with increasing temperature as well. This was especially evident for treated hair fibers, whereas large adhesive force at room temperature decreased rapidly to adhesion values similar to non-treated fibers. It is most likely that at higher temperatures the thinning conditioner layer causes a reduced surface tension, which directly relates to the drop in adhesive force.

Virgin, chemically damaged, and chemically damaged treated hair samples were soaked in de-ionized water for five minutes. Their corresponding coefficient of friction was measured and compared to coefficient of friction values for dry samples which were adjacent to the wet samples on the respective hair fiber. Fig. 53 shows the results for two hair samples of each hair type. Virgin hair exhibits a decrease in coefficient of friction after soaking. Virgin hair is more hydrophobic (see Table 5), so more of the water is present on the surface.
and results in a lubrication effect after soaking. Chemically damaged hair tends to be hydrophilic due to the chemical degradation of the cuticle surface, and results in absorption of water after soaking. This softens the hair, which leads to higher friction, even with conditioner treatment. This is yet another indication that virgin and chemically damaged hair have significantly different surface properties which in many cases results in opposite trends for their nanoscale tribological properties. Adhesive force for virgin hair remained approximately the same before and after soaking, while it decreased for chemically damaged and chemically damaged treated hair after soaking.

Fig. 54 shows the durability effects on friction force for various hair. Above the graph are pictures of unworn and worn virgin hair, with the cuticle edge serving as a reference point. Before testing, the surface is relatively smooth and void of any large debris or wear. After 1000 cycles at approximately 10 µN load with a stiff silicon AFM tip, however, the interaction has caused degradation and wear (scratch) marks on the cuticle scale. This is
the type of wear one could potentially see if hair were to come in contact with sand from a day spent at the beach, among other activities. Virgin hair shows an obvious increase in friction force signal as the scratch mark digs further into the surface. By this time the lubricious lipid layer on the surface of the virgin cuticle has been worn away and the friction force comes close to the magnitude of chemically damaged hair friction force at the onset of cycling. When conditioner is applied to the virgin hair, however, the wear does not show up as an increase in the friction force. Thus, conditioner serves as a protective covering to the virgin hair and helps protect the tribological properties when wear ensues.

6.2.3. Various hair types treated with various conditioner matrices

LaTorre et al. [42] measured nanotribological properties of various conditioner matrices and compared their performance with a commercial conditioner. As mentioned earlier,
a conditioner primarily consists of cationic surfactants, fatty alcohols, and PDMS blend silicone (dimethicone) (Table 4). They studied two different silicones – a PDMS (blend of low and high MW) silicone and an amino silicone added to BTMAC surfactant. Motivation for selection of amino silicone was that it may attach to the damaged hair surface and improve nanotribological performance and durability.

Fig. 55 displays the representative surface roughness and friction force maps for chemically damaged hair, commercially treated hair, PDMS blend silicone treated hair, and amino silicone treated hair [42]. When conditioner is applied to the surface, a pattern of high friction is shown in the area surrounding the bottom edge of the cuticle. This is believed to be an area of conditioner accumulation which causes increased friction due to meniscus effects. Friction maps for PDMS blend silicone do not show this increase as readily, suggesting that this type of silicone is not a contributor of high friction force on the nanoscale. This can be due to the fact that a PDMS type silicone is fairly mobile on the surface and thus does not cause the same meniscus effects as the AFM tip rasters through it. The amino group typically is less mobile and harder to move, which accounts for a different slip plane flow than PDMS silicone.
Fig. 56a displays the adhesive force maps for chemically damaged hair and the different treatments [42]. As shown in the legend, a lighter area corresponds to a higher tip pull-off force (adhesive force). Chemically damaged untreated hair has relatively low adhesive force, and is more or less consistent over the hair surface. In nearly all cases, addition of a conditioner treatment caused an increase in meniscus forces, which in turn increased the adhesive pull-off force between the AFM tip and the sample. Observing the chemically damaged treated hair, the uneven distribution of the conditioner layer is seen. This uneven distribution is also most evident for the amino silicone images, in which the less mobile silicone brings about a distinguishable change in adhesion over the surface. For the PDMS blend silicone, it is seen that adhesion over the surface is much more consistent than the amino silicone, where various areas of high adhesion occur.

It is important to note that while adhesive force maps presented are representative images for each treatment, adhesive force varies significantly when treatments are applied to the hair surface. Fig. 56b shows histograms of all adhesive force data for chemically damaged, chemically damaged treated, PDMS blend silicones, and amino silicones [42]. Chemically damaged treated hair shows a much larger range of adhesive force values and a normal distribution, which suggests that the conditioner layer is normally distributed. The histogram for PDMS blend silicone treatment shows a normal distribution at the larger adhesive force values, but also shows another peak at low adhesion values. Amino silicone treated hair follows a normal distribution, but it is interesting to note the distinct groupings of the adhesion values and the spacing between them. This is further
Fig. 56. (a) Adhesive force maps for Caucasian chemically damaged hair with various treatments; (b) adhesive force histograms [42].
evidence that the amino silicone groups most likely attach immediately to the hair surface
and are less mobile than PDMS silicone, causing distinct regions of high and low adhesion
values over the cuticle surface.

Fig. 57 displays a summary of the data collected for all chemically damaged hair sam-
pies and their treatments [42]. The figure also includes the macroscale coefficient of friction
data obtained using a technique similar to the macroscale measurement technique. Table 10 reviews some of the observations and corresponding mechanisms which help
to explain the trends found [42]. The application of the commercial conditioner to the
chemically damaged hair caused a decreased coefficient of friction and a large increase
in adhesive force. The decreased coefficient of friction may be explained by the fact that
the chemically damaged hair accumulates much of the positively charged conditioner on
the surface due to its highly negative charge, which in turn makes it easier to shear the
liquid on the surface, causing lower coefficient of friction. However, the nanoscale pull-
off force (adhesive force) is much larger than on the untreated hair because of meniscus
effects. In general, adhesive force varied widely, but typically showed a significant increase
with the presence of conditioner. As discussed previously, this is a clear sign that meniscus
effects are influencing the pull-off force between the tip and the sample.

In most cases, the macroscale and microscale coefficient of friction followed the same
trend, in which a decrease was observed with the addition of the PDMS blend or amino
silicones to the surfactant. The silicones are typically used as a major source of lubrication
and thus give the conditioner more mobility on the hair surface compared to just surfac-
tants and fatty alcohols. The inverse trend was seen only for the amino silicone group.

The amino silicones have a strong electrostatic attraction to the negatively charged hair
surface, which in turn creates higher binding forces and less mobility. The dampened
mobility of the amino silicone, with respect to hair surface and tip, may account for this
wide variation in coefficient of friction and large adhesive force values. In terms of adhe-
sive force, it was previously observed in Fig. 56a that the amino silicone treatments
showed much more distinct regions of higher and lower adhesion compared to PDMS
blend silicones. This non-uniform amino silicone thickness distribution on hair is also
believed to be caused by the inhibited mobility, as the molecules immediately attach to
the hair at contact and do not redistribute as a uniform coating. The increased polarity
of the amino silicones compared to the PDMS blend can also be a major contributor of
the higher friction and adhesion at high deposition levels.

In respect to roughness, the vertical standard deviation decreased slightly with most
treatments, although standard deviations were similar. The spatial parameter increased
slightly with treatments, but the variation also becomes extremely high.

6.2.4. Skin

Synthetic materials were also studied for surface roughness and friction force informa-
tion, shown in Fig. 58a. While macroscale dimples could be seen on the surface of collagen
film, it was interesting to find similar pits and dimples on the micro/nanoscale, conse-
quently with a large variation in dimple size and depth. Polyurethane films are shown
to have quite different topography and friction forces, while their coefficient of friction
is very similar. Human skin shows a rougher texture with higher peaks, Fig. 58b. The
roughness parameters for the collagen and polyurethane films, and also for human skin,
are presented in Table 11 [39]. Surface height standard deviation σ was approximately
three times larger than that of virgin hair for both synthetic materials. However, the
Fig. 57. Coefficient of friction, adhesive force, and surface roughness plots for Caucasian chemically damaged hair with various treatments.
correlation length $\beta^*$ was lower than what was typically observed in hair. The average coefficient of friction for these synthetic materials are shown in Fig. 59 plotted next to virgin Caucasian hair as a reference. These values were calculated using the slope of the friction force curves, described previously. Both collagen and polyurethane films displayed similar coefficient of friction values of 0.22 and 0.24, respectively. Virgin hair displays a much lower coefficient of friction than both materials, approximately eight times lower.

<table>
<thead>
<tr>
<th>Observation</th>
<th>Mechanism</th>
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<tbody>
<tr>
<td>Damaged vs. damaged treated hair</td>
<td>The conditioner layer deposited on the surface of the damaged hair results in a lower shear strength which in turn lowers the coefficient of friction, while meniscus effects increase the pull-off (adhesive) force between the tip and hair sample</td>
</tr>
<tr>
<td>PDMS blend vs. amino silicone</td>
<td>A stronger electrostatic attraction exists which results in stronger binding forces (which leads to higher adhesion) for amino silicone</td>
</tr>
<tr>
<td>Amino silcones interact strongly with negatively charged hair surface</td>
<td>Less mobility with amino silcones, so molecules attach to hair at contact and do not redistribute easily</td>
</tr>
<tr>
<td>Amino silicone thickness distribution on hair is less uniform than with PDMS blend</td>
<td></td>
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</tbody>
</table>

6.3. Scale effects

6.3.1. Directionality dependence of friction

Human hair has been shown in the past to have a directionality friction effect on the macroscale, making it easier to travel over the hair surface from root-to-tip than in the opposite direction due to the tile-like orientation of cuticles [62,18]. The outer surface of human hair is composed of numerous cuticle scales running along the fiber axis, generally stacked on top of each other. As previously discussed, the heights of these step changes are approximately 300 nm. These large changes in topography make the cuticle an ideal surface for investigating the directionality effects of friction [41]. The first row of Fig. 60a displays a low resolution SEM micrograph and a friction profile for macroscale coefficient of friction measurements. Note that this data is taken for measurements where multiple fibers are in contact with the synthetic skin upper specimen at the same time, and does not correspond directly with the SEM micrograph. With an applied normal load of 50 mN and 3 mm travel, it is observed that the friction force produced when scanning from root-to-tip (referred to as “along cuticle”) is lower than that when scanning against cuticle. This is a direct consequence of the literally thousands of scale edges which come in contact with the synthetic skin. When traveling against cuticle, these edges act as tiny resistors to motion as they are forced backwards and uplifted from their interface with the underlying cuticle layers. The resistance to motion of so many cuticle edges at the same time becomes “additive” and results in higher values of friction, corresponding to higher coefficient of friction than when traveling along cuticle. For along cuticle travel, these
Fig. 58. (a) Surface roughness and friction force images for collagen and polyurethane films at 5 and 10 μm² scan sizes. Shown above each image is a cross section taken at the corresponding arrows to show roughness and friction force information; (b) surface roughness for human skin at 5 and 10 μm² scan sizes. Note that vertical scales in 2D section profiles are doubled [39].
edges are forced downward against the underlying cuticle layers so that the resistance effect of these edges is limited, which results in lower friction values.

The second row of Fig. 60a shows an AFM height map corresponding to the microscale friction profile shown to its right. (These measurements were made using an AFM tip mounted with 4 \( \mu \text{m} \) radius silica ball.) Due to the size of the hair, it was only possible to capture a rectangular height map as shown. It is evident that the 100 \( \mu \text{m} \) travel results in the involvement of several cuticle scales. The applied normal load for the microscale friction profile (about 20 \( \text{nN} \)) is significantly reduced from that of the macroscale value, which consequently yields much lower friction forces. In the along cuticle direction, we can see small fluctuations in the friction data over the scan distance. These are caused by local variations in surface roughness, system noise, and changes due to traveling over the scale edges. However, when scanning against the cuticle, distinctly large spikes in the data are observed at roughly 5–10 \( \mu \text{m} \) intervals. This is clearly the effects of the scale edges coming in contact with the AFM microscale tip and causing local collisions and ratcheting of the tip. Because of the sign convention of the AFM that causes a reversal in the sign when traversing the opposite direction, this signal is now observed to be highly negative. These edge effects are hence the primary item responsible for the higher friction and coefficient of friction observed in the against cuticle direction.

Directionality effects on nanoscale hair friction have previously been reported by LaTorre and Bhushan [39]. As shown in the bottom row of Fig. 60a, the scan size of 5 \( \times \) 2.5 \( \mu \text{m}^2 \) provides one cuticle scale edge to be studied (the height map is rectangular only to be consistent with the microscale image in the middle row). As the tip rasters in
Fig. 60. (a) Directionality effects of virgin Caucasian hair friction on various scales; (b) microscale coefficient of friction data for Caucasian virgin, chemically damaged, virgin treated, damaged treated (1 cycle conditioner) and damaged treated (3 cycles conditioner) hair showing directionality effects [41].
the along cuticle direction, a small decrease in the friction force is observed as the tip follows the scale edge on a downward slope. When the tip comes back in the against cuticle direction, colliding with the scale edge and climbing up the sharp peak results in a high friction signal. As discussed above, because of the sign convention of the AFM/FFM that causes a reversal in the sign when traversing the opposite direction, this signal is now observed to be highly negative. The interesting difference between the two profiles lies in the fact that the magnitude of the decrease in friction when going up the step is much larger than the magnitude of the friction when the tip is going down the step, yet both signals are in the same direction. It is thus shown that the cuticle edge provides a local ratchet and collision mechanism that increases the friction signal at that point and clearly shows the directionality dependence caused by edge effects.

Coefficient of friction data showing directionality dependence on the macroscale for various virgin, damaged, and treated hair has been reported previously [18]. Fig. 60b shows a summary of the microscale coefficient of friction data for the various hair samples of this study. In most cases, the coefficient of friction has more than doubled when scanning in the against cuticle direction. A more in depth discussion on the coefficient of friction trends between the different hair types will follow. For now, however, it is important to realize that there is strong directionality dependence on coefficient of friction data for hair, especially on the microscale. On the nanoscale, while directionality dependence of friction force has been studied, actual coefficient of friction data is generally only measured on a small scan area which does not include the cuticle edge, so that only the true cuticle surface is involved [39]. Hence, nanoscale coefficient of friction directionality data similar to Fig. 60b is not shown.

6.3.2. Scale effects on coefficient of friction and adhesive force of various hair

Given the fact that the “directionality effect” is now observed to be universal for all types of hair and on all scales, and since the along cuticle direction is more relevant to our daily life (i.e. combing), we now focus on coefficient of friction data along cuticle.

As described earlier, microscale and nanoscale coefficient of friction is taken as the slope of the least squares fit line of a friction force vs. normal force data curve. Fig. 61a shows these types of raw data curves for various representative hair samples using both microscale (top plot) and nanoscale (bottom plot) AFM tips. The nanoscale data was taken from raw data used in LaTorre and Bhushan [41]. One can see a relatively linear relationship between the data points for each type of hair sample. If the least squares fit lines of Fig. 61a are extended to intercept the horizontal axis (indicated by the dotted lines), then a value for adhesive force can also be calculated, since friction force $F$ is governed by the relationship

$$F = \mu(W + F_a),$$

where $\mu$ is the coefficient of friction, $W$ is the applied normal load, and $F_a$ is the adhesive force [6,8]. These adhesive force values serve as average adhesive force values over the course of the full scan profile, and differ slightly from the force calibration plots of Fig. 61b. From Fig. 61a, it is observed in both plots that treated hair fibers, whether virgin or chemically damaged, have much higher average adhesive force values as compared to their untreated counterparts. Chemically damaged hair is observed to have the highest coefficient of friction (highest slope) on both the micro- and nanoscales. As explained in LaTorre and Bhushan [39,40] and LaTorre et al. [42], chemical damage to the hair causes
Fig. 61. (a) Friction force vs. normal load curves for micro- and nanoscale coefficient of friction of Caucasian virgin, chemically damaged, virgin treated, damaged treated (1 cycle conditioner) and damaged treated (3 cycles conditioner) hair; (b) Adhesive force comparison of virgin and virgin treated hair using micro- and AFM tips and force calibration plot technique [41].
the outer lubricious layer of the cuticle to wear off, resulting in an increased coefficient of friction.

Force calibration plots yield adhesive force values at a single point and are considered to be more relevant for measurement of the pull-off force between the tip and hair surface. Since it has been previously shown that treating both virgin and chemically damaged hair with conditioner results in large increases in adhesive force using both micro- and nano-scale AFM tips, we will focus only on the force calibration plots of the virgin and virgin treated hair to discuss mechanisms for this trend. The first plot in Fig. 61b shows a typical virgin hair force calibration plot with the microscale AFM tip. We can see that on the application of 1 cycle conditioner treatment to the virgin hair, the microscale adhesive force jumps to about 230 nN. This is clearly the effects of meniscus forces brought about by the presence of the conditioner layer on the cuticle surface which interacts with the tip [22,39,40]. With the nanoscale tip (bottom row of Fig. 61b), increase in adhesive force is again seen with conditioner treatment.

It is important to notice that that adhesive force values on the microscale are always larger than those on the nanoscale for a given hair. To explain the scale dependency of adhesive force, we can model the hair-conditioner–tip interaction as a sphere close to a surface with a continuous liquid film [22]. The adhesive force $F_a$, is the force needed to pull the sample away from the tip (which is the same as the adhesive force calculated with force calibration plots). $F_a$ is the sum of van der Waals force $F_{vdw}$ mediated by adsorbed water or conditioner layer and the meniscus force $F_m$ due to Laplace pressure ($F_a = F_{vdw} + F_m$). The meniscus force $F_m$ is given by

$$F_m = 2\pi R \gamma (1 + \cos \theta),$$

where $R$ is the tip radius, $\gamma$ is the surface tension of the conditioner, and $\theta$ is the contact angle between the tip and conditioner [8]. The increase in adhesive force calculated by force calibration plots with the microscale AFM tip compared to the nanoscale AFM tip is in large part due to the increased radius $R$ of the microscale ball, which consequently induces larger $F_m$.

Fig. 62 displays the coefficient of friction and adhesive force data on macro-, micro-, and nanoscales [41]. Scale dependence is clearly observed. Macroscale data for virgin and virgin treated hair were taken from Bhushan et al. [18]. The values for other hair were taken in part from the indexed coefficient of friction values in LaTorre and Bhushan [40] which were transformed into actual values (as described previously). No adhesive force data is presented for the macroscale data because the adhesive force contribution to friction is considered to be negligible compared to the applied normal load. On the micro- and nanoscales, however, the magnitude of the adhesive force is the same as that of the applied normal load, so they have significant contributions on the coefficient of friction data, and thus are presented. Microscale values are taken from the raw data represented in Fig. 61a and b. Nanoscale data was taken from LaTorre and Bhushan [40].

Macroscale coefficient of friction (COF) data is shown in the top row of Fig. 62. Chemically damaged hair has higher coefficient of friction than virgin hair, 0.24 compared to 0.14. Coefficient of friction decreases with the application of 1 cycle of conditioner for both virgin and chemically damaged hair. When 3 cycles of conditioner are applied to chemically damaged hair, there is only a slight decrease compared to 1 cycle application, 0.14–0.13. Thus, the data readily reveals that conditioner treatment decreases coefficient for friction of hair. The main mechanism for this macroscale trend is that lubrication with
a thin conditioner layer occurs over a large contact area, and thus the conditioner layer shears easily to create a lubricious effect [40]. It is important to note that the magnitude of the coefficient of friction values is higher on the macroscale than on the other scales.
for all hair types. Bhushan et al. [17] have previously outlined several differences in operating conditions which can be responsible for higher macroscale friction values. The one most relevant to our situation is that coefficient of friction increases with an increase in the AFM tip radius. Nanoscale friction data is taken with a sharp AFM tip, while the macro- and microscale tests have contacts which range from nanoasperities to much larger asperities which may be responsible for larger values of friction force on these scales. The combination of higher normal loads with a larger contact area (due to contact with multiple fibers at the same time) may also be responsible for increased coefficient of friction on the macroscale.

The coefficient of friction trends are similar on the microscale. On the microscale, virgin hair coefficient of friction was 0.08, while application of 1 cycle conditioner decreased the coefficient of friction only slightly to 0.07. From Fig. 62 it is important to note the large standard deviation on the virgin treated value. The corresponding adhesive force data in the same row is useful to better understand this behavior. It is shown that the virgin treated hair has a large adhesive force contribution (due to meniscus effects caused by the conditioner layer) which is having significant effects on the variation of friction force, and consequently the coefficient of friction. The chemically damaged hair has the largest coefficient of friction of the set, 0.16. Application of one conditioner cycle brought the value down to 0.08, while it was even lower for three conditioner cycles, 0.06. Adhesive force increased significantly with conditioner application; for virgin hair, adhesive force increased from about 50 nN to 220 nN due to the meniscus effects that come about from AFM tip interaction with the conditioner on the cuticle surface. Likewise, the adhesive force for chemically damaged hair was about 65 nN and jumped to 190 nN and 100 nN for 1 and 3 cycles of conditioner treatment, respectively. A possible reason that 1 cycle of conditioner on damaged hair showed higher average adhesive force than 3 cycles could be because the 3 cycles generally places the conditioner more uniformly on the surface rather than accumulating it most on the bottom surface near the cuticle edge, which is where the adhesive force maps were generally taken. Nevertheless, the increased adhesive force shown in the plots is a clear indication of conditioner present on the hair surface [40].

On the nanoscale, coefficient of friction of virgin and virgin treated hair is similar, but slightly higher for the treated cases. This is opposite of the trend on the macroscale and slightly different than that observed on the microscale. These meniscus bridges require more force to break through than with untreated hair, which causes the coefficient of friction to be similar to the untreated value, instead of experiencing a significant decrease which is traditionally expected. Damaged hair shows a much higher coefficient of friction, and with more variation in the values since the chemical damage varies throughout each individual fiber. Contrary to the virgin and virgin treated hair nanoscale results, coefficient of friction for damaged hair decreased with application of conditioner treatment (both 1 and 3 cycles), which agrees well with macro- and microscale trends.

There are several reasons that nanoscale coefficient of friction trends for virgin treated and chemically damaged treated hair are different. The effects of chemical damage play a large role. It is widely known that the cuticle surface of any hair is negatively charged. This charge becomes even more negative with the application of chemical damage to the hair. As a result, the positively charged particles of conditioner have even stronger attraction to the chemically damaged surface, which explains the increased presence of conditioner when compared to virgin treated hair. With the application of three conditioner cycles on damaged treated hair, there is an even more uniform placement of the conditioner. This leads
to high adhesive force due to meniscus effects (similar to that of virgin treated hair) but more importantly, lower shear strength on the surface. This creates an overall effect of lubrication as the tip travels across the cuticle surface and ultimately lowers the coefficient of friction.

Another reason for the difference in nanoscale trends between virgin and chemically damaged hair may have to do with drastic differences in hydrophobicity of the two hair types. Virgin hair has been shown to be hydrophobic, with a contact angle around 100° (Table 5). Chemically damaged hair, however, is hydrophilic, with a contact angle around 70°. The conditioner gel network is primarily composed of water, together with fatty alcohols, cationic surfactants, and silicones. Thus, the hydrophobicity of the hair will be relevant to not only how much conditioner is deposited, but also how it diffuses into the hair and bonds to the hair surface. For virgin treated hair, the conditioner deposits in certain locations, especially near the cuticle edge, but due to the hydrophobicity of the cuticle does not spread out as readily as with chemically damaged hair. For chemically damaged hair, the conditioner spreads out a bit more uniformly and in more places over the cuticle surface due to both the hydrophilicity and the stronger negative charge which attracts more conditioner deposition. Thus, as the tip scans over the virgin treated surface, the conditioner does not smear as readily, causing the tip to have to break the tiny meniscus bridges formed with the conditioner. This results in increased adhesive force, which contributes to higher friction force. This ends up increasing the coefficient of friction to about the same level as the untreated virgin hair, instead of a reduction in coefficient which is typically expected for a lubricated surface. In the case of chemically damaged hair, however, the conditioner layer is already more spread out, especially in the case of 3 cycles of treatment. As the tip scans over the surface, the overall effect is one of reduced shear strength, i.e. the conditioner layer, albeit not fully continuous, smears with tip travel and causes reduced coefficient of friction between the tip and the hair. With 3 cycles the conditioner thickness increases slightly, and the layer is even more uniformly distributed over the surface, which causes a further reduction in coefficient of friction, much like the results seen on both the micro- and macroscale.

Fig. 63 shows schematically the mechanisms responsible for the reverse trends seen on the nanoscale for virgin treated hair [41]. In the top cartoon of Fig. 63, the thin layer of conditioner acts as a lubricant over the hair fiber, limiting the dry contact with the synthetic skin block and creating easier relative motion, which decreases coefficient of friction compared to the untreated hair. This is true on the macroscale for both virgin and chemically damaged hair. On the microscale, the same trend is experienced; that is, the 4 μm radius of the AFM ball comes in contact with multiple cuticle scales at the same time, causing an overall lubrication effect for both virgin treated and chemically damaged treated hair as the thin conditioner layer is sheared to created easier relative motion. It is important to note, however, that adhesive forces due to meniscus effects are the same magnitude as the applied microscale normal load.

On the nanoscale (bottom cartoon of Fig. 63), we see different trends for virgin treated and chemically damaged treated hair. As discussed earlier, the hydrophobicity of the virgin hair causes different deposition of conditioner. The AFM tip has to break the tiny meniscus bridges formed with the conditioner as it scans across the hair surface, which increases adhesive force contribution and results in an increased coefficient of friction. For hydrophilic chemically damaged hair, there is more uniform deposition and better smearing of the conditioner layer, which serves to lower coefficient of friction between the tip and the cuticle surface.
6.4. Summary

A flat-on-flat tribometer has been used to measure macroscale friction and wear of the polyurethane film (synthetic skin) vs. hair and hair vs. hair. In the case of polyurethane film vs. hair, the chemo-mechanically damaged hair shows highest coefficient of friction, followed by virgin and virgin treated hair. The coefficient of friction obtained in the case of hair vs. hair is greater than that of polyurethane film vs. hair. After 24 h skin vs. hair wear test, the coefficient of friction did not change, while some of the cuticles were damaged.

AFM contact mode has been used to perform nanotribological studies on various hair and skin. Friction force and the resulting coefficient of friction are seen to be higher on chemo-mechanically damaged hair than on virgin hair, due to the increase in surface roughness and a change in surface properties that results from exposure to chemical damage. Generally speaking, the average coefficient of friction is similar between virgin and virgin treated hair of each ethnicity. However, in virgin treated hair there is an increase
in friction forces around the cuticle edges and surrounding area. It is currently believed that the increase in friction force is due in part to an increase in meniscus effects which increase the adhesive force contribution to friction at sites where conditioner is deposited or accumulated on the surface, namely around the cuticle scale edges. This adhesive force is of the same magnitude as the normal load, which makes the adhesive force contribution to friction rather significant. On the macroscale, however, the adhesive force is much lower in magnitude than the applied normal load, so the adhesive force contribution to friction is negligible over the hair swatch. As a result, treated hair shows a decrease in friction force on the macroscale, which is opposite the micro/nanoscale trend. The friction and adhesion data on the micro/nanoscale is useful, though, because it relates to the presence of conditioner on the cuticle surface and allows for obtaining an estimate of conditioner distribution. Studies using force calibration plot technique showed a decrease in adhesive force with damaged hair, and significantly higher adhesive force for treated hair. This increase on the micro/nanoscale is most likely due to meniscus force contributions from the accumulation and localization of a conditioner layer on the hair surface. Thus, the presence of conditioner can be detected by this increasing adhesive force. The directionality dependence of friction is evident when the cuticle edge is examined using FFM.

Chemically damaged treated hair shows a much stronger affinity to conditioner than virgin hair. The negative charge of hair fibers becomes even more negative with the application of chemical damage to the hair. As a result, the positively charged particles of conditioner have even stronger attraction to the chemically damaged surface, and this results in an increased presence of conditioner (and corresponding higher friction forces) when compared to virgin treated hair. With the application of three conditioner cycles on chemically damaged treated hair, friction force increases all over the cuticle surface, showing a more uniform placement of the conditioner. Contrary to the virgin and virgin treated hair results, coefficient of friction for chemically damaged hair decreased with application of commercial conditioner treatment (both 1 and 3 cycles). One possible explanation is that because the stronger negative charge on damaged hair results in better attraction of conditioner, this leads to higher adhesive force but, more importantly, lower shear strength on the surface.

Environmental effects were studied for various hair. The coefficient of friction generally decreased with increasing temperature. After soaking hair in de-ionized water, virgin hair exhibits a decrease in coefficient of friction after soaking. Virgin hair is more hydrophobic (based on contact angle data), so more of the water is present on the surface and results in a lubrication effect after soaking. Chemically damaged hair tends to be hydrophilic due to the chemical degradation of the cuticle surface, and results in absorption of water after soaking. This softens the hair, which leads to higher friction, even with conditioner treatment. Durability tests show that once conditioner is applied to virgin hair, wear does not show up as an increase in friction force. Thus, conditioner serves as a protective covering to the virgin hair and helps protect the tribological properties when wear ensues.

In most cases, a decrease in coefficient of friction was observed on chemically damaged hair with the addition of the PDMS blend or amino silicones to the BTMAC surfactant. The silicones are typically used as a major source of lubrication and thus give the conditioner more mobility on the hair surface compared to just surfactants and fatty alcohols. The inverse trend was seen only for the amino silicone group. The dampened mobility of the amino silicone, with respect to hair surface and tip, may account for this wide variation in coefficient of friction. Adhesive force varied widely, but typically
showed a significant increase with the presence of conditioner ingredients. This is a clear sign that meniscus effects are influencing the pull-off force between the tip and the sample. The amino silicones showed much more distinct regions of high and low friction and adhesion, which shows that there is less mobility of these molecules and much less redistribution as they coat the hair. Force calibration plots indicate that commercial conditioner containing only non-polar silicones and experimental conditioner containing polar amino silicones exhibit distinct affinity for chemically damaged hair surface. Commercial conditioner physically adsorbed on hair surface via van der Waals attractions can be easily squeezed out from the contact region under the load; on the other hand, amino silicones in experimental conditioner are substantive to the hair surface and cannot escape from the contact region under the load because of the strong electrostatic binding between the polar amino groups of silicone molecules and hair surface. Amino silicones provide much better load-bearing capacity and works as a cushion preventing hair surface from further damages.

Coefficient of friction values are largest on the macroscale, followed by microscale and then nanoscale values. In general, coefficient of friction increases with an increase in the AFM tip radius. Nanoscale friction data is taken with a sharp AFM tip, while the macro- and microscale tests have contacts which range from nanoasperities to much larger asperities which may be responsible for larger values of friction force on these scales. The combination of higher normal loads with a larger contact area (due to contact with multiple fibers at the same time) may also be responsible for increased coefficient of friction on the macroscale as well.

On all scales, coefficient of friction decreases for chemically damaged treated hair compared to untreated. The same trend occurs for virgin treated hair on the macro- and microscales, but not on the nanoscale. On the larger scales, the thin layer of conditioner acts as a lubricant over the hair fiber across multiple cuticle contacts. On the nanoscale, the hydrophobicity of the virgin hair causes different deposition of the conditioner which increases the adhesive force contribution and results in an increased coefficient of friction. For chemically damaged hair, there is higher negative charge and a hydrophilic surface, which results in more uniform deposition and better smearing of the conditioner layer, which serves to lower coefficient of friction between the tip and the cuticle surface.

7. Conditioner thickness distribution and binding interactions on hair surface

How common hair care products, such as conditioner, deposit onto and change hair properties are of interest in beauty care science, since these properties are closely tied to product performance. Conditioner is one of hair care products which most people use on a daily basis. Conditioner thinly coats hair and can cause drastic changes in the surface properties of hair. Among all the components of conditioner, silicones are the main source of lubrication in the conditioner formulation. Silicone molecules remain as droplets surrounded by water, and their high molecular weight causes them to remain liquid and drain off of hair surface gradually, which creates a long-lasting, soft, and smooth feel for conditioner treated hair. The binding interaction between these molecules and hair surface is one of important factors in determining the conditioner thickness distribution, and consequently the proper functions of conditioner.

Some important issues, such as the thickness and distribution of conditioner on the hair surface which is important in determining the proper functions of conditioner, have been
struggled to answer by cosmetic scientist for decades. In order to determine the thickness and distribution of thin liquid film on a substrate, several possible techniques can be applied: Fourier transform infrared spectroscopy (FTIR), ellipsometry, angle-resolved X-ray photon spectroscopy (XPS), and AFM [7,9]. Ellipsometry and angle-resolved XPS have excellent vertical resolution on the order of 0.1 nm, but their lateral resolutions are on the order of 1 and 0.2 mm, respectively. Therefore, these techniques cannot be used for hair since the diameter of a hair fiber is only 50–100 μm. AFM on the other hand is a versatile tool and has a lateral resolution on the order of the tip radius (few nm), which is difficult to achieve by other techniques. In the study reported here, force calibration plot measurements using an AFM are conducted to obtain the local conditioner thickness distribution on various hair surfaces. The conditioner thickness is extracted by measuring the forces on the AFM tip as it approaches, contacts, and pushes through the conditioner layer. The conditioner thickness distribution on hair is effectively measured using an AFM. The effective Young’s moduli of various hair surfaces are also calculated from the force distance curves using Hertz analysis. The binding interactions of different silicones on the hair surface, as well as the effect on their effective Young’s modulus of the hair are also discussed.

It has been reported earlier that, based on surface imaging using TR mode and friction force mapping on couple of cuticles, the conditioner is unevenly distributed across the hair surface, and thicker conditioner layer can be found near cuticle edges.

7.1. Conditioner thickness and adhesive force mapping

In typical force calibration plots shown in Fig. 63b and Fig. 70 (to be presented later), conceptually, the distance that the sample moves after the tip snaps in until it contacts the hair surface should be a measure of the thickness of the conditioner film. Here we define it as snap-in distance $H_s$. This snap-in distance $H_s$ is not the real conditioner thickness $h$ and it tends to be thicker than the actual film thickness. In previous studies on determination of lubricant-film thickness on a particulate disk surface by AFM [10], it has been realized that as the ellipsometry thickness of the lubricant film increases, the thickness as measured by AFM also increases, however, AFM tends to measure a thicker film than measured by ellipsometry. There is a few nm offset between the snap-in distance $H_s$ determined by AFM and film thickness $h$ determined by ellipsometry. The most likely origin of the offset of the AFM thickness was attributed to a thin coating of the lubricant on the surface of the AFM tip that results from the tip being previously in contact with the lubricant film. This might account for part of the offset, but main reason for this offset should be attributed to the deformation of the liquid film due to its interaction with the AFM tip as the liquid film approaches to the tip [21,22,47]. The liquid film can only approach the AFM tip to a finite minimal distance, below which the liquid surface is no longer stable due to the van der Waals attractive force between the liquid film and the AFM tip. For smaller distances, surface tension and adhesion to the substrate cannot keep the liquid surface from bulging and jumping into contact with the tip. Forcada et al. [29] theoretically analyzed the hydrostatics of the liquid film in the force fields originated by the tip and solid substrate, and indicated that the offset between the snap-in distance and the film thickness measured by ellipsometry arises from the bulging and posterior instability of the liquid film.

A number of theoretical publications [1,5] have addressed the issue of liquid coalescence in terms of the ‘effective stiffness’ of a liquid surface or interface, and have concluded that a
liquid surface behaves like a Hookian spring with an effective spring constant \( K_{\text{eff}} \) equal to its surface or interfacial tension \( \gamma \), viz:

\[ K_{\text{eff}} \approx \gamma. \]  

Therefore, for one of the main components of conditioner silicone (PDMS) in air an effective spring constant of only 20 mN/m is expected, as the surface tension of PDMS is about 20 mN/m [20] and water film has an effective spring constant of 72 mN/m. These are extremely low values compared to the cantilever spring constant of 5 N/m. It suggests that liquid surfaces can deform even by a very weak force. When the hair surface approaches the AFM tip, the weak van der Waals attractive force between the liquid conditioner film and the tip will cause the liquid film to deform and jump-in the tip at a finite distance. The theoretically expected van der Waals force \( F_{\text{vdw}} \) between a sphere and a flat surface is given by

\[ F_{\text{vdw}} = HR/6D^2, \]  

where \( H \) is the Hamaker constant which can be estimated based on the Lifshitz theory [34], \( R \) is the radius of the AFM tip, and \( D \) is the distance between the AFM tip and the liquid conditioner film. Therefore, the jump-in distance \( D_j \) (the minimal distance between a stable liquid film and the AFM tip) can be theoretically calculated based on the criterion for a jump instability:

\[ dF_{\text{vdw}}/dD = HR/3D^3 = K, \]  

where \( K \) is the spring constant. For conditioner treated hair surface, \( K \) is the effective spring constant of the liquid film \( K_{\text{eff}} \) since it’s much weaker than that of the cantilever.

From Eq. (6), one obtains [22],

\[ D_j = (HR/3K_{\text{eff}}^2)^{1/3}. \]  

For a silicon tip covered by SiO\(_2\) (the sphere) interacting with a liquid conditioner film (the flat surface) in air, the Hamaker constant \( H \) is estimated to be in the order of \( 10^{-20} \) J, \( R \) is about 100 nm and \( K_{\text{eff}} \) is in the range of 20–72 mN/m (the surface tension of PDMS and water are 20 mN/m and 72 mN/m, respectively). Then a jump-in distance \( D_j \) about 2 nm can be obtained based on Eq. (7). This jump-in distance is basically the offset between the snap-in distance \( H_s \) and the actual film thickness \( h \). This 2 nm offset (jump-in distance) is surprisingly close to previous measurements on the localized lubricant-film thickness on a particulate type magnetic rigid disk, which indicated that the measured thickness using an AFM is about 2 nm larger than the actual thickness based on the ellipsometry measurements [10]. Note that the offset (jump-in distance \( D_j \)) only depends on the radius of the tip and the intrinsic properties of the film (surface tension and Hamaker constant), but is independent of the film thickness. Recent surface forces apparatus (SFA) experiments indicated that for two 25 nm thick liquid PDMS films interacting in air at quasi-equilibrium state (very slow approach rate of about 0.3 nm/s), the jump-in distance is about 200 nm [23]. SFA measurements gave much large jump-in distance is because of the much larger value of radius (in SFA experiments, the radius \( R \) is about 20 mm). Therefore, although the snap-in distance \( H_s \) in force calibration plot overestimates the actual film thickness (approximately 2 nm thicker), it still provides a very good measurement for the actual thickness of thin conditioner film.
Fig. 64 shows typical film thickness (snap-in distance $H_s$) and adhesive force mappings of virgin, chemically damaged, chemically damaged treated (1 cycle and 3 cycles) hair. The snap-in distance $H_s$ of virgin hair is $2.0 \pm 0.6$ nm with a very narrow distribution, indicating that virgin hair surface is relative uniform and lacks of damages. Virgin hair surface is covered with a saturated fatty acid lipid layer called 18-methyleicosanoic acid (18-MEA) [62], which makes the hair surface hydrophobic (see Table 5 for contact angle data). Therefore, virgin hair surface is absent continuous water film. Instead of the deformation of the liquid film, the AFM tip will jump into contact with the hair surface at a finite tip–sample distant because of the van der Waals attractive force.

The snap-in distance of chemically damaged hair is larger than that of virgin hair, and increases to $3.1 \pm 0.7$ nm. The outermost surface of hair is cuticle which consists of large amount of cystine. Chemical treatment will partially remove the fatty acid lipid layer (18-MEA) covering the hair surface and break the disulfide bonds in cystine to form new ionic groups (such as cysteic acid residues by oxidation of cystine acids). The hair surface becomes hydrophilic and the contact angle with water decreases [55], consequently, the amount of water adsorbed on the hair surface increases. As the sample approaches the tip, the AFM tip will jump into contact with the hair surface at a finite distance because of van der Waals attractive force, as well as small meniscus bridge formation between the tip and the adsorbed water layer. The adhesive force of chemically damaged hair surface is $47 \pm 8$ nN, less than that of virgin hair ($58 \pm 4$ nN). The existence of thin adsorbed water layer tends to decrease van der Waals force attractive force which is now mediated by adsorbed water layer but increase the meniscus force. Note that the tip and the hair surface are not as smooth (rough on the molecular scale) and the adsorbed water layer is very thin, therefore, no single large meniscus but many small menisci form between the tip and the hair surface. The total attractive force of chemically damaged hair therefore is smaller than that of virgin hair.

After conditioner treatment, the snap-in distance $H_s$ increases with the number of cycle of treatment. The snap-in distances $H_s$ for 1 cycle treatment and 3 cycle treatments are $4.6 \pm 1.0$ nm and $5.5 \pm 1.7$ nm, respectively. Thicker liquid film unevenly presents on conditioner treated hair surface, and the thickness tends to have a broader distribution than that of chemically damaged hair. It is more obvious for 3 cycles damaged treated hair, in which the thickness distribution is much broader and tends to have a long tail to larger thickness. The measured mean thickness varies from 5 nm up to 25 nm (data not shown). Excluding the 2 nm offset due to the jump-in deformation of the liquid conditioner film, the actual film thickness should be around 3–23 nm. These values are consistent with the previous estimated conditioner thickness based on the amount of material deposition [42]. The adhesive forces for 1 cycle and 3 cycles are $80 \pm 19$ nN and $84 \pm 23$ nN, respectively. The larger adhesive force is attributed to the formation of large meniscus between the tip and the conditioner layer on the hair surface.

7.1.1. Effect of humidity and temperature on film thickness and adhesion

Fig. 65 shows typical film thickness mapping, histogram of film thickness, and adhesive force mappings of damaged treated hair at different humidities [12]. At different humidities, the film thickness and adhesive force of hair are distinctly different. At low humidity, the treated hair surface has only a very thin layer of film ($2.6 \pm 0.7$ nm). At high humidity, a much thicker film is present on hair surface ($4.7 \pm 1.8$ nm). This film tends to extend a much longer tail into the thicker film regime. At high humidity, hair surface
Fig. 64. Film thickness maps, histograms, and adhesive force maps of Caucasian virgin, chemically damaged, and damaged treated hair samples. The dotted lines in histograms are the Gaussian fits for film thickness [12].
has higher adhesive force comparing to that at low humidity. The conditioner treated hair surface will be covered with a gel network. This gel network can adsorb or desorb water depending on the environmental condition. The conditioner treated hair surface tends to

Fig. 65. Typical film thickness and adhesive force maps of damaged treated hair at different humidities [12].
adsorb more water as the humidity increases, which will increase the film thickness on hair surface and consequently increases the adhesive force.

Fig. 66 summarizes the conditioner thickness and adhesive force of various hair surfaces at different humidities [12]. Film thickness on virgin hair remains relatively constant at different humidities and it only increases slightly at high humidity. The outer layer of the hair is covered with hydrophobic 18-MEA and remains intact in virgin hair. Therefore, water is hardly adsorbed (or desorbed) and penetrated into hair surface and humidity has little effect on film thickness of virgin hair. On the other hand, the hydrophobic lipid layer of damaged hair surface may be depleted or damaged, therefore, inner cellular structures of hair, which consist of many hydrophilic molecules are now exposed to water. Damaged hair surface is partially hydrophilic and will be more sensitive to the humidity. It tends to adsorb more water at high humidity; therefore, film thickness of damaged hair
increases gradually as the humidity increases. Damaged treated hair is covered with a conditioner film; therefore, it has a thicker film thickness. Film thicknesses of treated hair surface typically show large deviations compared to those of virgin and damaged hair, indicating uneven distribution and adsorption of conditioner layer on hair surface. The film thickness increases as the humidity increases because the conditioner gel network layer can easily adsorb more water at high humidity. However, this conditioner gel network layer fails to retain water content at low humidity. As shown in Fig. 66, virgin hair usually has higher adhesive force than damaged hair. Adhesive force includes the van der Waals attraction and meniscus force. Virgin hair has larger van der Waals force than damaged hair because of the hydrophobic nature of the virgin hair surface. Treated hair has higher adhesive force due to conditioner meniscus formation.

The film thickness and adhesive force were also measured at different temperatures [12]. Fig. 67 summarizes the data for virgin, damaged, and conditioner treated hair at those temperatures.

![Fig. 67. Film thickness and adhesive forces of Caucasian virgin, chemically damaged, and damaged treated hair samples at different temperatures [12].](image-url)
temperatures. Temperature has little effect on the film thickness of virgin or damaged hair in the temperature range studied. Conditioner treated hair has thicker film compared to virgin or damaged hair. As temperature increases, the thickness of conditioner layer starts to decrease. At high temperature, conditioner layer will eventually lose all water content. In the studied temperature range, there is little effect on adhesive force of various hair surfaces.

7.2. Effective Young’s modulus mapping

The adhesive force as well as the total force acting on the tip at each measurement point can be accurately measured from the force calibration plot. If the zero tip–sample separation is defined to be the position where the force on the tip is zero when in contact with the sample, the force calibration plot can be converted to a force vs. tip–sample separation curve [22]. Fig. 68a shows the forces acting on the tip as a function of tip–sample separation for virgin, commercial conditioner (PDMS blend silicone) treated, and experimental conditioner (with amino silicone) treated hair. The lowest point on the approach curve is assumed to be the point that the tip contacts the hair surface. Afterward, the hair surface deforms elastically under the load, from which the deformation (indentation Δz) of the surface can be extracted. Plotting the obtained deformation (indentation Δz) against the total force (on approach curve) acting on surface, gives force vs. indentation (deformation) curves. Fig. 68b shows the force vs. indentation curves for virgin, commercial conditioner treated and experimental conditioner (amino silicone) treated hair surface which are extracted from the force vs. tip–sample separation curves shown in Fig. 68a, and the effective Young’s modulus of various hair surfaces can be determined from these curves (12). The effective Young’s modulus of virgin, commercial conditioner treated and experimental conditioner treated hair surface are 5.3 ± 0.9 GPa, 0.60 ± 0.03 GPa, and 0.032 ± 0.002 GPa respectively for these three specific curves. For these calculations, the radius of the tip is measured to be approximately 100 nm. The effective Young’s modulus of conditioner treated hair surface can be one to two orders of magnitude less than that of virgin hair.

Repeating these calculations over the whole surface on various hair samples, the maps of the effective Young’s modulus of various hair surfaces are obtained as shown in Fig. 67. Virgin hair surface has the effective Young’s modulus of about 7.1 ± 2.9 GPa, which is the most stiff among all the samples and is consistent with previous nanoindentation measurement results [81]. The rich in the disulfide crosslinks on the outermost layer of the hair surface accounts for this stiffness; the effective Young’s modulus of chemically damaged hair surface (6.6 ± 3.3 GPa) is slightly smaller than that of virgin hair surface. The chemical treatment partially breaks the disulfide crosslinks in the outermost layer of the hair surface, and weakens the hair surface. Commercial conditioner treated hair surface tends to have much smaller effective Young’s modulus than that of chemically damaged hair surface (5.5 ± 4.6 GPa for 1 cycle treatment, and 3.3 ± 3.2 GPa for 3 cycles treatment). The effective Young’s modulus decreases as the number of cycle of treatment increases. Large deviations of the effective Young’s modulus of conditioner treated hair surfaces are seen, indicating the uneven distribution and adsorption of conditioner on hair surface. This large deviation of the effective Young’s modulus of conditioner treated hair surface is due to a large area of the hair surface has low effective Young’s modulus (dark region). Comparing the conditioner thickness map (see Fig. 67) and the effective Young’s modulus
map (see Fig. 59) of 3 cycles treated sample, it is clear that the region with small effective Young’s modulus (dark region) is closely correlated to the region with thick conditioner layer (bright region) on the hair surface. The effective Young’s modulus decreases as conditioner thickness increases. Therefore, although the average value of the effective Young’s modulus decreases as conditioner thickness increases. Therefore, although the average value of the effective Young’s modulus decreases as conditioner thickness increases. Therefore, although the average value of the effective Young’s modulus decreases as conditioner thickness increases. Therefore, although the average value of the effective Young’s modulus decreases as conditioner thickness increases.

Fig. 68. (a) The force acting on the tip as a function of tip sample separation for various hair samples. The sample is moved with a velocity of 200–400 nm/s, and the zero tip sample separation is defined to be the position where the force on the tip is zero when in contact with the sample. The arrows show the direction of motion of the sample relative to the tip. A negative force indicates an attractive force; (b) surface effective Young’s modulus extracted from the force distance curves. The solid lines show the best fits for the data points of various hair samples [22].

modulus of 3 cycles treated hair surface is 3.3 GPa, some part of the surface can have very low effective Young’s modulus value (as low as the 0.60 GPa value shown in Fig. 68b). Experimental conditioner (amino silicone) treated hair surface has extremely low effective Young’s modulus (0.047 ± 0.045 GPa) compared to the value of chemically damaged hair surface. The film thickness, adhesive force and effective Young’s modulus of various hair samples are summarized in Table 12 [22].

7.3. Binding interactions between conditioner and hair surface

Small molecules in conditioner, such as water and surfactant, may diffuse into the outermost layers of the hair surface and swell the disulfide crosslink network within these layers, which in a way weakens these layers, consequently, a smaller effectively Young’s modulus for conditioner treated hair surfaces. Even more significantly, although silicones in conditioner cannot diffuse into the hair surface layers because of the size of the molecules, they can physically adsorb via van der Waals interaction or bind (chemically or electrostatically) on the hair surface, which will significantly affect the physical properties of the hair surface. Although the AFM cannot give an absolute distance as the surface forces apparatus (SFA) [34], the force distance curves obtained using an AFM still can show the interactions between the surface and the tip, and consequently reveal the essence of various surfaces. As shown in Fig. 68a, virgin hair and conditioner treated hair behave differently as the tip approaches, compresses and retracts from the surface. Virgin hair surface behaves like a stiff elastic solid surface. As the virgin hair surface approaches to the tip, the tip will jump into contact with the hair surface at a small separation around 4 nm because of the van der Waals attractive interaction between the hair surface and the tip. Then the force quickly goes to repulsive and the tip reaches the hard wall contact (tip hair solid–solid contact) with very small deformation. When the virgin hair surface is withdrawn, the tip will simply jump out and no large liquid deformations occur because of the lack of liquid layer. Conditioner treated hair surfaces show much longer range of interactions than virgin hair because of the presence of liquid conditioner layer. The tip will snap in at large separation because of the van der Waals force as well as meniscus formation between tip and conditioner liquid layer. When the sample is pulled away from the tip, the forces on the tip will slowly decrease to zero as a long meniscus bridge of liquid is drawn out from the surface and eventually breaks at a large separation. Another important feature is that before the tip reaches the tip-hair solid–solid contact, commercial conditioner treated hair surface shows larger deformation than virgin hair surface, indicating a thin physically adsorbed layer presents on the hair surface. Experimental conditioner treated hair surface shows very large deformation and no tip-hair solid–solid contact is reached under the given

<table>
<thead>
<tr>
<th>Samples</th>
<th>Film thickness (nm)</th>
<th>Adhesion (nN)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>2.0 ± 0.6</td>
<td>58 ± 4</td>
<td>7.1 ± 2.9</td>
</tr>
<tr>
<td>Chemically damaged</td>
<td>3.1 ± 0.7</td>
<td>47 ± 8</td>
<td>6.6 ± 3.1</td>
</tr>
<tr>
<td>Chemically damaged treated</td>
<td>4.9 ± 1.0</td>
<td>80 ± 19</td>
<td>5.8 ± 4.6</td>
</tr>
<tr>
<td>1 cycle</td>
<td>5.5 ± 1.7</td>
<td>84 ± 23</td>
<td>3.3 ± 3.2</td>
</tr>
<tr>
<td>Amino silicone</td>
<td>n/a</td>
<td>n/a</td>
<td>0.047 ± 0.046</td>
</tr>
</tbody>
</table>
experimental conditions, indicating there is a strongly bound conditioner layer. Large hysteresis between approaching and retracting curves indicates that this bound layer deforms viscoelastically under the load. The adhesive force (on the approach curve) of experimental conditioner treated hair surface is smaller than that of commercial conditioner treated hair surface. The meniscus forces in both cases would be similar, and the extra repulsive force on the tip for experimental conditioner treated surface comes from the compression of the molecules underneath the tip. The tip has to overcome the intermolecular polar or hydrogen bonding and strong binding between amino silicones and the hair surface so as to squeeze out silicones molecules from between the tip and the hair surface.

Fig. 70 illustrates the difference between physisorbed conditioner and bound conditioner. Chemical treatments breaks the disulfide bonds of cystine crosslink network in cuticle and form new ionic groups on the hair surface, therefore, chemically damaged hair surface is negatively charged. Silicones in commercial conditioner are non-polar and do not contain any functional groups, therefore, most of silicone molecules are free and mobile except that the last layer of molecules adjacent to the hair surface may be physically adsorbed via van der Waals interactions. As the tip starts to touch and compress the conditioner film, free conditioner molecules can easily escape from the contact region. The last layer of adsorbed molecules may sustain some load before they are squeezed out eventually at higher load. Then the tip penetrates the conditioner layer and reaches tip hair solid–solid contact and compresses directly on the hair surface. The last layer of physisorbed conditioner molecules is very thin but effectively lowers the Young’s modulus of the hair surface by one order of magnitude (see Fig. 68b and Fig. 69).

On the other hand, experimental conditioner consists of amino silicones, which are positively charged in an aqueous condition and can strongly bind with the anionic groups presenting on chemically damaged hair surface. The bindings between amino silicone molecules and the hair surface, which are much stronger than van der Waals attractions in commercial conditioner treated hair surface, make bound conditioner molecules difficult to escape from the contact region even at high load. Therefore, after the tip touches the conditioner, instead of penetrating the conditioner layer and compressing directly on the hair surface, it compresses on a soft bound conditioner layer. The effective Young’s modulus of this layer (silicones) is about 0.047 ± 0.045 GPa. Although it is much softer than hair, it is still much stiffer than bulk PDMS whose Young’s modulus is only 680 kPa [52]. Two reasons are attributed to this increase of effective Young’s modulus of silicones (PDMS): the bound silicone layer is very thin (a few nm) and it is in a confined geometry during the measurements. It is well known that thin films can exhibit extremely different physical properties compared to bulk materials. Thin liquid film can behave like a solid under confinement [34]. On the other hand, underneath of this thin bound silicones layer is the stiff hair surface whose Young’s modulus is much higher (chemically damaged hair surface 6.6 ± 3.3 GPa, see Fig. 69). Since the bound layer is very thin, the measured Young’s modulus therefore has the contributions from both the soft bound silicone layer and stiff hair surface.

Amino silicones are substantive to the hair surface and work as a cushion protecting the hair surface. Although this strong affinity to the hair surface can dramatically increase the load or contact pressure that a conditioner film can support before solid–solid contact, recent AFM study on hair [42] indicated that treated hair with excess amino silicone has higher coefficient of friction than commercial conditioner (physisorbed) treated hair. It is well known that in general, lubricant film with mobile and immobile fractions
(partially bonded lubricant film) is desirable for low friction and high durability [6,8]. Biolubrication studies using SFA [3] also indicated that a low coefficient of friction is
not necessarily a measure of good wear protection. A conditioner layer strongly bound on the hair surface is good for preventing hair from further damage, but it may be not good from the lubrication point of view. A balance between good lubrication and good protection has to be reached for a good conditioner product.

7.4. Summary

The snap-in distance $H_s$ in the force calibration measurement provides a good estimate for the conditioner film thickness on hair. The conditioner unevenly distributes on hair surface. Conditioner thickness increases with the number of the cycles of treatment. The mean conditioner thickness is on the order of 5 nm. The adhesive force of damaged hair was smaller than that of virgin hair because of different surface hydrophobicities. The treated hair showed a much higher adhesive force because of meniscus formation at the interface. Humidity had little effect on film thickness and adhesive force for virgin hair, however it had a larger effect on damaged and treated hair. Temperature effect was little on all hair. The effective Young’s modulus of virgin hair surface was the highest and damaged hair was slightly smaller and treated hairs had the smallest. Amino silicone conditioner showed strong affinity to hair and strengthened the hair fiber and is expected to work as a cushion for protecting the hair surface from further damage.

8. Surface potential studies of human hair using Kelvin probe microscopy

It is obvious that during combing and running the hands through one’s hair that physical damage is likely to occur. These actions also tend to create an electrostatic charge on the hair, and it is of interest whether or not the physical wear and the electrostatic charge are related, or if charge by other mechanism has been created, as has been shown in previous studies as mentioned above. It is therefore the aim to observe the effects of physical wear on surface potential for both conducting and insulating samples to clarify the mechanism behind the behavior. Further, electrostatic charging of hair is studied by charging the hair with latex, a material that is known to create a static charge on hair. The presence of this static charge in the real world is a major problem concerning hair manageability, flyaway behavior, feel and appearance so understanding the mechanisms behind charge buildup, and how to control it, is thus a focal point in designing effective hair care products such as conditioner. Conditioner is known to affect the surface potential characteristics of hair, and understanding this behavior on the small scale is of great interest. Because surface potential of human hair is of such interest, Kelvin probe may provide great insight into the mechanisms behind the electrostatic behavior of hair. For this reason, Kelvin probe is used in to characterize hairs with varying types and degrees of damage as well as varying types and degrees of conditioner treatments.

8.1. Effect of physical wear and rubbing with latex on surface potential

Lodge and Bhushan [49] measured surface potential change after performing wear experiments in an AFM on hair fiber using a diamond tip with a tip radius of 60 nm at a load of 5 µN. The wear scars were created at 2 µm × 2 µm size for one pass. After samples were worn with the diamond tip, the AFM tip was changed to conductive tip, and the surface potential was mapped in the wear area. All samples were mounted on a sample
puck in conductive silver paint. They found that physical wear alone does not cause a measurable electrostatic charge on hair because hair is non-conductive.

The electrostatic charge build up on hair was caused by rubbing with a natural latex finger cot and surface potential change was measured after rubbing [49]. First, a surface potential map of the hair sample, which was electrically isolated from ground to prevent quick discharging was obtained for “before rubbing” data. Then samples were wiped lightly with the finger cot five times along the hair shaft in the direction from root to tip. Surface potential was then mapped immediately, for “after rubbing” data. Fig. 71a and b show AFM images for virgin, virgin treated, chemically damaged, chemically damaged treated (1 cycle), and chemically damaged treated (3 cycles) hair samples. These images are presented in three columns. The first is the surface height of the sample and the second is the absolute surface potential. The final column shows the same surface potential data as the second column, but the average surface potential (which is presented in the subsequent bar charts) is subtracted out and the scale is reduced to show more contrast. Before rubbing data was taken as a baseline in order to report a change in potential due to rubbing, and will not be discussed or analyzed further. Absolute quantitative values of surface potential were not reliable for this experiment because the samples were not grounded, thus the necessity to report a potential change. It should be noted that some samples became highly charged as a result of the rubbing, beyond the capability of the microscope (10 V). These samples were not used in this study. However, it is important to note that all of the samples tested are capable of developing high amounts of charge. A method where the force of contact is more accurately controlled may provide better insight into this behavior. Some samples, especially the chemically damaged one (Fig. 71a), show a significant amount of change in surface potential during measurement. This is illustrated as a higher potential at the bottom of the image than at the top, as the measurement was started at the bottom. This indicates that the charge dissipates relatively rapidly, and seems to reach a constant value by the time the measurement is finished. The fact that the virgin and treated samples (Fig. 71a) seem to have a more constant potential during measurement indicates that these samples dissipate charge faster, and by the time the measurement is taken a constant potential is more or less achieved. The average surface potential change is shown in Fig. 71c. This bar chart indicates that conditioner treatment greatly reduces the amount of charge present on the hair surface. It also shows that chemical damage increases the amount of charge built on the hair surface.

Fig. 72 shows chemically damaged hair that has been treated with an experimental conditioner containing amino silicone, which is believed to chemically attach to the hair surface. Very little difference is seen between the amino silicone conditioner and the commercial PDMS silicone conditioner. Commercial PDMS silicone treated hair data was shown in Fig. 71b. This is likely because the latex rubbing occurs over a very large area of the hair, and any difference in conditioner distribution is occurring on a much smaller scale. PDMS silicone conditioner is believed to only physically attach to the hair surface, and it remains mobile. Therefore, rubbing with the finger cot is likely to redistribute the conditioner, effectively spreading it evenly over the hair. However, amino silicone conditioner chemically attached to the surface, and distributes evenly to begin with. Moreover, amino silicone conditioner remains evenly distributed due to the chemical attachment. A method to rub the hair over a smaller area may provide more insight into this behavior, and may elucidate the effect of conditioner distribution on surface potential.
properties. However, the amino silicone conditioner still shows a significant decrease in charge from the untreated chemically damaged sample.

Fig. 73 shows mechanically damaged hair samples. This figure shows results more similar to virgin hair than to chemically damaged hair. This is likely due to the fact that the top lipid layer of hair is not removed and that most of the mechanical damage occurs at scale edges. Chemical damage occurs over the entire surface of the hair. For this reason it is likely that mechanically damaged hair will behave more like virgin hair than chemically damaged hair. Because the rubbing procedure is not strictly controlled in terms of location of contact, it is difficult to distinguish a difference between the topmost layer of the hair, and the portions which have been mechanically damaged. However, this indifference between these regions (which generally occur on the surface away from scale edges, and
Fig. 71 (continued)
near scale edges, respectively) may also be due to the fact that physical wear does not affect surface potential in insulating samples, as discussed previously.

8.2. Effect of external voltage and humidity on surface potential

Samples were mounted in conductive silver paint and an external power supply was used to develop charge [50]. To determine environmental effects on surface charge, relative humidity was controlled and varied.

To study the effects of external voltage and humidity, virgin, virgin treated, chemically damaged, chemically damaged treated (1 cycle), and chemically damaged treated (3 cycles) were studied at an external voltage of 0, 1, and 2 V at 50% and 10% relative humidities. Representative AFM images for chemically damaged and chemically damaged treated (1 cycle of conditioner) hair samples are shown in Fig. 74a. It should be noted that the
contrast seen around cuticle scale edges is likely a result of the topography effect [50]. A key point shown by these images is the existence of areas of trapped charge in the low humidity samples. This is not seen in the samples measured in ambient. These areas of trapped charge are seen as bright areas on the sample in the “averaged surface potential” images. In other words, there is more contrast in the averaged surface potential maps under low humidity (neglecting any contrast seen around the scale edge) than is seen for the same samples under ambient humidity. It is important to clarify that the ‘bright areas’ are only in reference to the increase in contrast in the surface potential map (averaged surface potential) away from the scale edges. This is only considered for the “0 V” samples, where added external charge does not affect the surface potential of the sample. This observation indicates that water vapor in the air contributes significantly to the mobility of surface charges on the hair. This result has been previously reported for macro studies on surface charge of hair [36,51,54]. Trapped charges are most pronounced in the untreated samples. This suggests that conditioner treatment has a similar effect as water

Fig. 73. (a) AFM images of mechanically damaged hair both before and after rubbing with latex, (b) bar chart showing average surface potential change after rubbing with latex [49].
Fig. 74. (a) AFM images showing surface height and surface potential of chemically damaged and chemically damaged treated (1 cycle conditioner) at both 50% and 10% relative humidities. (b) Bar charts showing average surface potential change at both 50% and 10% relative humidities for virgin, virgin treated, chemically damaged, chemically damaged treated (1 cycle conditioner), and chemically damaged treated (3 cycles conditioner) hair samples [50].
vapor. Even under very low humidity conditions, conditioner treatment increases the mobility of surface charges, dissipating trapped charges. Fig. 74b shows bar charts of the average surface potential change. Error bars indicate ± one standard deviation. It can be observed in these figures that all samples exhibit very similar values in the 50% relative humidity scenario. This again indicates that the water vapor in the air plays a significant role on the surface charge of the hair, and also on the mobility of charge. For the 50% case it is shown that the potential changes nearly 1 V for every 1 V change in applied potential. However, this is not the case for the 10% relative humidity situation. In this case, a higher 0–1 V value indicates more charge mobility and the ability to dissipate charge, whereas a lower value indicates less charge mobility. This being the case, it is evident that conditioner treatment greatly increases the mobility of surface charges. It is also shown that virgin hair has a better charge mobility and can therefore dissipate charge more readily than chemically damaged hair. This is likely due to the lipid layer that is intact in virgin hair, but has been removed in damaged hair.

Fig. 75a shows AFM images of chemically damaged hair treated with amino silicone conditioner. Here it is observed that the surface of the hair is more or less an equipotential
surface, similar to the chemically damaged treated (3 cycles) sample. This suggests that the amino silicone conditioner coats the surface fully with 1 cycle, where commercial conditioner does not coat fully until several cycles. Fig. 75 shows this behavior as well. Amino silicone conditioner shows potential change in 10% relative humidity that are almost identical to those measured in 50% relative humidity. This indicates that the conditioner is evenly spread over the surface of the hair, which has been previously reported [42,47]. It also indicates that amino silicone conditioner greatly increases charge mobility. Because commercial conditioner is unevenly distributed on the hair surface, the data for the commercially treated samples exhibit relatively high standard deviations in most cases. Consequently, different areas on the hair surface may contain vastly different amounts of conditioner on the surface. For the amino silicone case, however, different areas of the hair seem to have similar amounts of conditioner as evidenced by the lower standard deviation. The data then suggests that amino silicone conditioner is the superior conditioner in terms of charge dissipation.

8.3. Summary

Kelvin probe microscopy is a powerful tool when used to study electrostatic properties of hair. Physical wear alone does not cause a measurable electrostatic charge on hair because hair is non-conductive. Rubbing with a latex finger cot can build up electrostatic
charge on hair. Any electrostatic charge on hair can dissipate rapidly. The natural lipid layer on virgin hair and conditioner treatment may increase the rate of dissipation. Untreated chemically damaged hair, which has no lipid layer, seems to retain charge the longest. Conditioner treatment significantly decreases the charge built on the hair surface. Amino silicone conditioner coats the hair surface uniformly and provides higher charge mobility and less likelihood of trapped charges than the commercial conditioner. Relative humidity plays a significant role in the behavior of surface charges on hair. A low relative humidity decreases charge mobility thereby increasing the likelihood of charges trapped on the surface.

9. Closure

A comprehensive nanoscale characterization of human hair and skin has been performed. 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. Asian hair seems to be the thickest (nearly round), followed by African hair (oval-flat) and Caucasian hair (nearly oval).
The cross section and longitudinal section of virgin Caucasian human hair have been investigated using TR mode II. The cortex and the cuticle, the macrofibril and the matrix of human Caucasian hair were readily revealed. The fine granular structure of the outer β-layer, which has not previously been seen by SEM, TEM, and other AFM studies, is a result of the fine domain formation of lipid layer. Chemically damaged hair surfaces show much more damage; larger areas of the endocuticle were exposed. Conditioner unevenly distributes on damaged treated hair surface; thicker conditioner films are found near the cuticle edges. At high humidity, the cortex and cuticle can absorb water, which will consequently weaken the hydrogen bonds and salt bonds between the protein molecules in hair cellular structure. The effect is more significant in chemically damaged and treated hair.

Nanoindenter has been used to perform nanomechanical studies on human hair. 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. Humidity and temperature have an effect on mechanical properties. The Young’s modulus of damaged treated hair decreases dramatically at high humidity. Little temperature effect was observed on the Young’s modulus. Nanoscratch tests show that coefficient of friction of virgin treated hair is lower than virgin hair for Caucasian and Asian hair in both cases of single cuticle scratch and multiple cuticle scratch. This thin conditioner layer acts as a layer lubricant, reducing the coefficient of friction during scratching. In-situ displacement (30–200 nm) increased greatly at very low initial load and then increased gradually, indicating that the first approximately 200 nm of the hair surface should be softer than the underlying layer. For a hair with hard cuticle, the cuticle cells tend to be fractured during scratching. For a hair with soft cuticle, the scratch tip usually plows and wears away the cuticle cells continuously until it reaches the cortex. The coefficient of friction of virgin and chemo-mechanically damaged Caucasian hair increases after soaking because of the swelling of the water, which softens the hair surface.

Human hair shows a stress–strain curve typical of keratinous fibers. Transition of alpha keratin to beta keratin in yield region is the reason for the unique shape of the curves. Chemical damage, mechanical damage and conditioner treatment have no obvious effect on the stress strain curve or tensile properties. This is because such treatments affect the cuticle predominantly and tensile properties of human hair in dry state are governed by the cortex. Tensile stress in general causes lift off of the outer cuticle. The lift off is sudden and occurs consistently at around 20% strain. Fracture occurs sooner (about 10% strain) in mechanically damaged hair than chemically damaged hair (about 20% strain).

A flat-on-flat tribometer has been used to measure macroscale friction and wear of the polyurethane film (synthetic skin) vs. hair and hair vs. hair. In the case of polyurethane film vs. hair, the chemo-mechanically damaged hair shows highest coefficient of friction, followed by virgin and virgin treated hair. After 24 h skin vs. hair wear test, the coefficient of friction did not change, while some of the cuticles were damaged.

AFM contact mode has been used to perform nanotribological studies on various hair and skin. Friction force and the resulting coefficient of friction are seen to be higher on chemo-mechanically damaged hair than on virgin hair. In virgin treated hair there is a slight increase in friction forces around the cuticle edges and surrounding area. It is currently believed that the increase in friction force is due in part to an increase in meniscus effects which increase the adhesive force contribution to friction at sites where conditioner
is deposited or accumulated on the surface, namely around the cuticle scale edges. Adhesive force studies showed a decrease in adhesive force with chemo-mechanically damaged hair, and significantly higher adhesive force for virgin treated hair, most likely due to meniscus force contributions from the conditioner layer.

Chemically damaged treated hair shows a much stronger affinity to conditioner than virgin hair. With the application of three conditioner cycles on chemically damaged treated hair, friction force increases all over the cuticle surface, showing a more uniform placement of the conditioner. Contrary to the virgin and virgin treated hair results, coefficient of friction for chemically damaged hair decreased with application of commercial conditioner treatment (both 1 and 3 cycles), possibly because the stronger negative charge on damaged hair results in better attraction of conditioner (and lower shear strength), which leads to an overall effect of lubrication and ultimately lower coefficient of friction.

Environmental studies show that coefficient of friction generally decreases with increasing temperature. After soaking hair in de-ionized water, virgin hair exhibits a decrease in coefficient of friction after soaking while chemically damaged hair exhibits an increase. Virgin hair is more hydrophobic so more of the water is present on the surface and results in a lubrication effect after soaking. Chemically damaged hair tends to be hydrophilic due to the chemical degradation of the cuticle surface, and results in absorption of water after soaking which softens the hair, leading to high nanoscale friction even with conditioner treatment. Durability tests show that once conditioner is applied to virgin hair, wear does not show up as an increase in friction force. Thus, conditioner serves as a protective covering to the virgin hair and helps protect the tribological properties when wear ensues.

In most cases, a decrease in coefficient of friction was observed on chemically damaged hair with the addition of the PDMS blend or amino silicones. The silicones are typically used as a major source of lubrication and thus give the conditioner more mobility on the hair surface compared to just surfactants and fatty alcohols. The inverse trend was seen only for the amino silicone group, due to the dampened mobility of the amino silicone. Commercial conditioner physically adsorbed on hair surface via van der Waals attractions can be easily squeezed out from the contact region under the load; on the other hand, amino silicones in experimental conditioner are substantive to the hair surface and cannot escape from the contact region under the load because of the strong electrostatic binding between the polar amino groups of silicone molecules and hair surface. Amino silicones provides much better load-bearing capacity and works as a cushion preventing hair surface from further damages.

Coefficient of friction values are largest on the macroscale, followed by microscale and then nanoscale values. In general, coefficient of friction increases with an increase in the AFM tip radius. On all scales, coefficient of friction decreases for chemically damaged treated hair compared to untreated. The same trend occurs for virgin treated hair on the macro- and microscales, but not on the nanoscale. On the larger scales, the thin layer of conditioner acts as a lubricant over the hair fiber across multiple cuticle contacts. On the nanoscale, the hydrophobicity of the virgin hair causes different deposition of the conditioner which increases the adhesive force contribution and results in an increased coefficient of friction. For chemically damaged hair, there is higher negative charge and a hydrophilic surface, which results in more uniform deposition and better smearing of the conditioner layer, which serves to lower coefficient of friction between the tip and the cuticle surface.
The snap-in distance $H_s$ in the force calibration measurement provides a good estimate for the conditioner film thickness on hair. The mean conditioner thickness is on the order of 5 nm. The adhesive force of damaged hair was smaller than that of virgin hair because of different surface hydrophobicities. The treated hair showed a much higher adhesive force because of meniscus formation at the interface. Humidity has same effect on film thickness and adhesive force, dependent upon hair type. Temperature has little effect. Amino silicones showed strong affinity to hair and are expected to work as a cushion for protecting the hair surface from further damage.

Kelvin probe microscopy is a powerful tool when used to study electrostatic properties of hair. Physical wear alone does not cause a measureable electrostatic charge on human hair because hair is non-conductive. Rubbing with a latex finger cot can build up electrostatic charge on hair. Any electrostatic charge on hair can dissipate rapidly. The natural lipid layer on virgin hair and conditioner treatment may increase the rate of dissipation. Untreated chemically damaged hair, which has no lipid layer, seems to retain charge the longest. Conditioner treatment significantly decreases the charge built on the hair surface. Amino silicone conditioner coats the hair surface uniformly and provides higher charge mobility and less likelihood of trapped charges than the commercial conditioner. Relative humidity plays a significant role in the behavior of surface charges on hair. A low relative humidity decreases charge mobility thereby increasing the likelihood of charges trapped on the surface.

References

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