J. Cosmet. Sci., 72, 687–696 (November/December 2021)

Moisture in the Cuticle Sheath: Effects on Hair Mechanical and Cosmetic Properties

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Synopsis

The role of moisture in the cuticle sheath has not been properly explored so far. In this paper, analysis and experiments indicate that moisture variations in the cuticle sheath have a significant impact on its shear and tensile modulus and, therefore, on the overall hair mechanical and cosmetic properties. Analysis shows that if there is an imbalance in the required moisture content in the cuticle cell inter- and intralayers, steep layer moduli mismatches and stress concentrations are generated across interfaces. Imbalances of this type often arise when the hair has very low levels of moisture or when it is transiently subjected to high temperatures, becoming more severe with tensile extensions. For instance, at high elongations and near the yield point, the intermediate filaments in the cortex undergo an alpha to beta transformation. This keratin phase transition occurs at both low- and high-moisture conditions and causes the cortex tensile modulus to decrease, allowing for higher deformations without severe stress buildup. In contrast, at high elongations, the cuticle sheath has no such stress dissipation mechanism, and high-stress concentrations appear across the cuticle cells. Therefore, moisture loss in the cuticle cells accompanied by extensions aggravate stress concentrations resulting in damage at the cuticle cell cement boundaries.

INTRODUCTION

When studying the physical and cosmetic behavior of hair, more effort should be placed on analyzing both cortex and cuticle sheath properties. Unfortunately, too often, more attention is given to the properties of the cortex, and those of the cuticle sheath are ignored. Such a biased approach can lead to the wrong conclusions. A typical example of this can be found in studies on hair moisturization. Very often, we tend to consider that the effects of moisture on the overall hair cosmetic properties depend solely on the moisture content of the cortex. In doing so, we neglect the role that moisture in the cuticle sheath may play in this endeavor. Incidentally, it should be mentioned that recently, the hair cosmetic community has started to realize that moisture in the cortex may have little or no correlation at all with the sensorial and subjective properties of moisturized hair (1).

It is quite possible that the sensorial properties associated to hair moisturization depend less on the cortex moisture and more on the effects of moisture in the cuticle sheath. This is because of the cuticle sheath's position at the hair surface. At this point, it is difficult to make a definitive assertion in this direction until more data and research elucidate this question. We can be certain that, in the future, studies in this direction will include

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analysis of moisture in the cuticle sheath. This paper reports preliminary observations on this subject. However, before describing the experimental details of this report, it seems appropriate to review one of the most common patterns of hair damage that appears in most individuals, cuticle cell decementation, lifting, and buckling. These patterns are relevant because they are a form of cuticle cell delamination, and, as will be shown later, they are strongly dependent on moisture. Cuticle cell decementation and buckling usually appears in hair fibers at distances larger than 10 or 20 cm from the scalp, depending on the type of care the hair has received.

In fact, this type of damage is so prevalent that it can be considered the initial indication of hair damage. It appears way before hair breakage or before the appearance of any other type of hair cortex physical trauma. Its ubiquitous nature and its relation to moisture demands a clear understanding, first, of how grooming practices lead to its formation, and, second, of its effects on hair sensorial properties. In this paper, experimental results associated to the former will show that cuticle cell decementation, delamination, and buckling are strongly related to the state of moisture in the cuticle cell layers. It will also be shown that this type of damage is usually associated to conditions involving any of the following repetitive processes: (1) cyclic tensile stresses involving elongations higher than 12% and (2) applications of thermal stresses accompanied by elongations lower than 5%.

The first process will be frequently encountered by hair fibers during combing and tangling, especially when the hair is totally or partially wet and when poorly conditioned. The second process will result from blow drying or combing or when using hot irons; both involve rapid dehydration of cortex and cuticle sheath. In this respect, it is worth mentioning the well-known fact that moisture loss in hair has a strong impact on its mechanical modulus. Water loss in hair usually is associated with dehydration of proteins in the matrix since the intermediate filaments (IFs) do not absorb water (2). Water loss from the cuticle cells also occurs, although it has not been studied as much and most certainly stems from the endocuticle, the cell membrane complex (CMC), and to a lesser extent from the exocuticle (2,3). As will be shown later, as the exocuticle, endocuticle, and CMC lose moisture at high temperatures, they become stiffer and change their mechanical moduli, compromising their response to mechanical stresses.

METHODOLOGY

The hair used in the experiments was Virgin Premium Grade Brown Caucasian from International Hair Importers. Two sets of hair fiber samples were subjected each to different thermal stress conditions. In the first set, a tensile deformation of 5% was applied to the hair fibers while they were simultaneously subjected to blow drying within a temperature range between 40 and 80°C; a Diastron Tensile Tester was used to deform the fibers. In the second set, the hair fibers were hot ironed using temperatures between 160 and 220°C. Before thermal stress application, the hair fibers were equilibrated at different relative humidity conditions for 24 hours. Moisture equilibration was made in a glass bowl with a tray containing water saturated with various salts, depending on the moisture value required.

When needed, cuticle cell lifting was produced by applying cyclic elongations using the method described elsewhere (3). The presence of delaminated, lifted, and buckled cuticle cells was readily detected by SEM and optical microscopy. A Hi-Scope KH-3000 from Hirox was employed to detect and analyze buckled cuticle cells via the colorful patterns of light interference that they produce. In the literature, it has already been shown that colorful patterns of light interference are produced when cuticle cells delaminate and buckle, creating micron-size air gaps that lead to the conditions for light interference (4–6).

RESULTS AND DISCUSSION

CUTICLE CELL LIFTING OR BUCKLING AT HIGH ELONGATIONS

In the past, it has been shown that cyclical elongations with deformation values higher than 12% and in the moisture range between 40% and 65% relative humidity (RH) lead to patterns of cuticle cell buckling, forming parabolic shapes (3). Fig. 1a shows a hair fiber displaying cuticle cell buckling after being subjected to similar conditions. Unlike other types of cuticle cell buckling, which will be reviewed later, this type of damage is not caused by transient losses of moisture but rather by high elongations. Its formation, however, depends strongly on the equilibrium moisture content of the cuticle cells. The mechanism is as follows: when hair fibers are equilibrated at moisture conditions between 30% and 65% RH, and then subjected to elongations ranging between 5% and 17%, mechanical energy appears across the hair fiber in the form of tensile, shear, and Poisson stresses. In this range of deformation, the keratin intermediate filaments in the cortex undergo an alpha to beta transformation (7). This protein phase transition enables the cortex to unfold and relax, thereby allowing for higher elongations while partially dissipating high concentrations of mechanical stresses.

In contrast, for similar elongations and humidity conditions, the cuticle sheath does not have such a phase transition mechanism to dissipate stresses. Thus, while the cortex can undergo high extensions without building up high levels of stresses, the cuticle sheath elongates in parallel but develops stress concentrations across its layers. The result is lifting and buckling of cuticle cells, as shown in Fig. 1a. Furthermore, Fig. 1b shows a magnified version of the fiber shown in Fig. 1a. In this picture, it can be seen that when cuticle cells lift under these conditions, there are no endocuticular remnants left on the cuticle cell

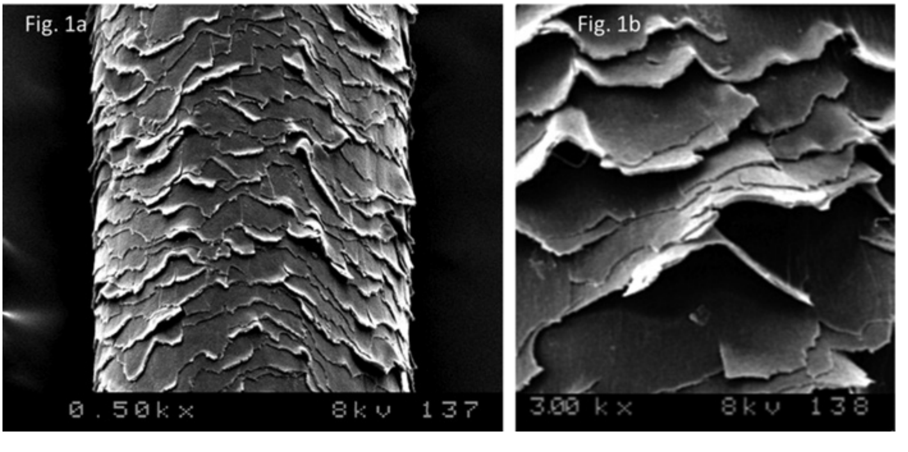

Figure 1. SEM pictures of a hair fiber showing cuticle cell lifting and buckling at different magnifications Fig. 1a (×500), Fig. 2 (×3000). Lifting was produced by applying 10 cycles of 15% elongation at 50% RH.

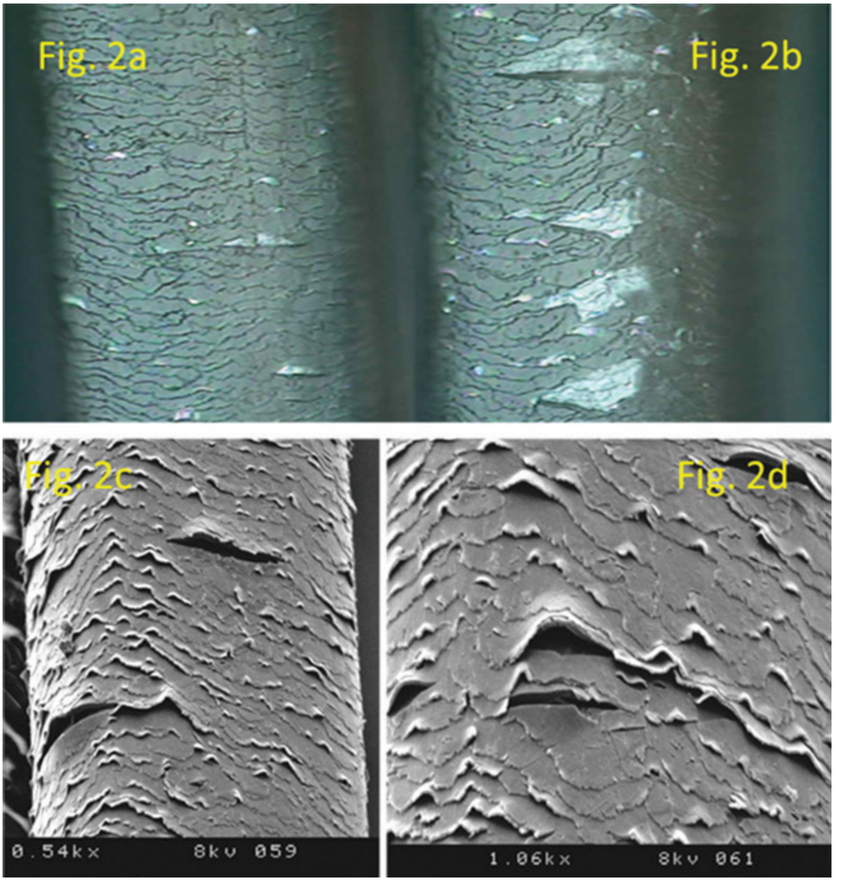

Figure 2. Optical Microscopy (2a and 2b) and SEM (2c and 2d) pictures of hair fibers after subjected to 10 cycles of 15% elongation at 75% RH. Note the appearance of deep transversal cracks accompanied by small area size cuticle cell buckling patterns in all four pictures.

immediately below. This observation suggests that because of its multilayer composition, the top cuticle cells resist shear and tensile stresses produced by elongation. However, they fail at the CMC under the action of hoop or Poisson contraction stresses (3), which force them to lift upward.

Cuticle cell failure by lifting and buckling is, thus, how the composite structure of the cuticle sheath dissipates stresses at high elongations. Cement breakage occurs at the CMC because at such elongations and moisture conditions, the CMC is still rigid and does not allow a compliant transfer of hoop stresses to neighboring cuticle cells underneath. By the same token, this analysis also indicates that the moduli of epicuticles, exocuticles, and endocuticles are stress hoop compliant, and, therefore, there is no damage across their boundaries. Yet the mechanism of stress dissipation changes from cuticle cell lifting or buckling to transversal crack formation and cuticle sheath detachment when the hair fibers are equilibrated at higher moisture contents (see Figs. 2a, 2b, 3a, and 3b).

For instance, as the equilibrium moisture content increases between 65% and 80% RH, the number and area size of buckling patterns decreases, while the number of transversal

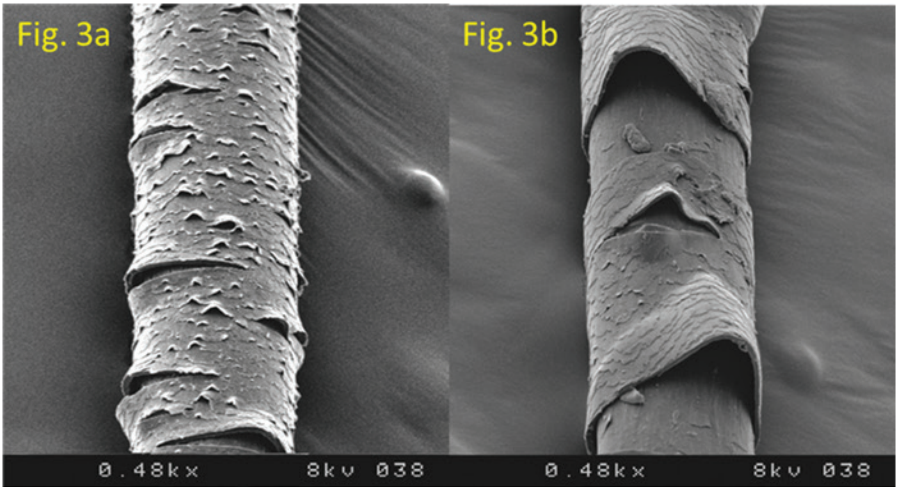

Figure 3. SEM pictures of hair fibers subjected to 15 cycles of 25% elongation, at different moisture conditions. Note the presence of deep transversal circular cracks accompanied by small area size cuticle cell buckling patterns at approximately 90% RH (Fig. 3a). Note also the absence of these patterns, the presence of long transversal circular cracks, and the occurrence of cuticle sheath detachment when the fiber is cyclically elongated while swollen in water.

cracks increases (see Fig. 2a to 2d). Between 90% and 95% RH, the small buckling patterns are accompanied by large transversal circular cracks that form around the whole cuticle sheath (see Fig. 3a). At 100% RH, or when the fiber is immersed in water, no cuticle cell lifting can be observed. Instead, only deep transversal circular cracks and the detachment of the whole cuticle sheath from the cortex is observed (see Fig. 3b). It should be mentioned, however, that the latter phenomena only occurred with cyclical elongations higher than 25%. This means that at 100% RH, most of the hoop or Poisson contraction stresses are dissipated by moisture plasticization and no interlayer failure or cuticle cell lifting occurs.

Thus, it becomes clear that, when the individual cuticle cell layers (i.e., the epicuticle, exocuticle, endocuticle, and CMC) have high levels of moisture, their moduli are such that they have a higher degree of interlayer mechanical compliance. This means that at 100% RH and elongations higher than 20%, there is no build-up of shear, tensile, or hoop stress concentrations across the individual junctions of the cuticle cell intra layers. Rather the assembly of cuticle cells behaves as a single pipe-shaped body. As a result, under these conditions, stress dissipation does not occur by cuticle cell delamination of individual cuticle cell intra- or interlayers. Instead, the cuticle sheath behaves as a solid pipe that undergoes tensile cracking and detaches from the cortex. The latter phenomenon indicates that at high elongations when the fiber is water swollen, the cement between cuticle sheath and cortex breaks because of a mismatch in extensibility between the water plasticized cortex and cuticle sheath (see Fig. 3b).

CUTICLE CELL LIFTING OR BUCKLING BY THERMAL AND MECHANICAL STRESSES

During the experiment's development, it was found that lifting and buckling of cuticle cells could also be produced by elongations lower than 5%, provided that thermal stresses

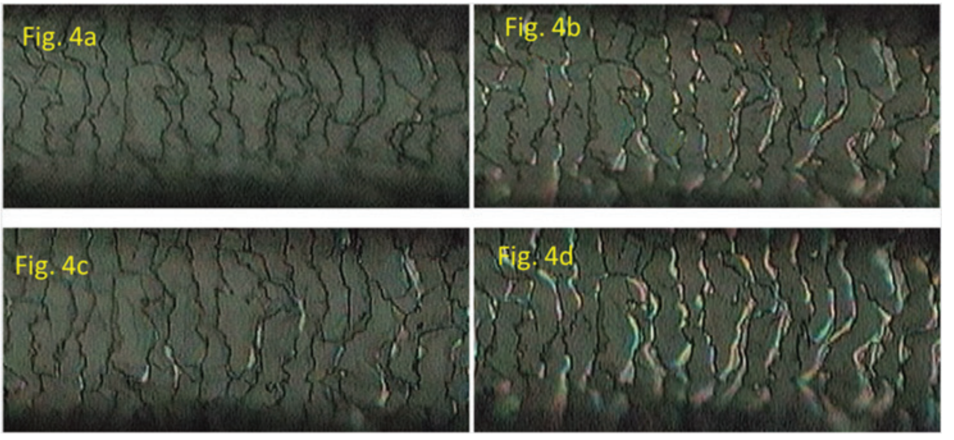

Figure 4. Sequential images of a hair surface taken at different time intervals from a videorecording strip showing gradual increase in cuticle cell lifting with blow drying time at 80°C: Figure 4a (10 s), Figure 4b (20 s), Figure 4c (40 s), and Figure 4d (50 s).

are applied simultaneously to hair. Because of the combined stresses required to produce lifting, we will refer to this phenomenon as thermomechanical cuticle cell lifting. The characteristics of this type of lifting had many differences with respect to those previously discussed and produced by high elongations. Their features varied depending on the range of temperatures accompanying the low mechanical deformations. For instance, blow-drying hair in the range of 70 to 80°C while applying low levels of mechanical elongation in the range of 2% to 5% instantly produced cuticle cell delamination or lifting. Video recording techniques showed that the degree of delamination and number of lifted cuticle cells increased gradually with blow drying time (see Figs. 4a to 4c).

One of the important characteristics of thermomechanical lifting, such as the one shown in Figs. 4a to 4c, is that it only occurs when the hair had been equilibrated to humidity conditions ranging between 65% and 90% RH (i.e., when the cuticle sheath had absorbed high levels of water, and when the fibers were blow dried above 70°C). Moisture conditions lower than 70% RH, or blow-drying temperatures lower than 75°C, did not produce thermal delamination. In fact, hair that had been equilibrated at 30% RH, subjected to 5% elongation, and blow dried at 90°C did not lead to thermal lifting even when the blow-drying periods were extended for 5 minutes. Conversely, hair equilibrated at high moisture contents (i.e., 90% RH) did not produce delamination when blow dried at or below 50°C. These observations clearly indicate that for thermomechanical lifting to occur, the presence of water and its rapid evaporation are necessary in the cuticle cell.

The experiments showed that this type of cuticle cell delamination also occurred by breakage at the cement that joins the endocuticle of top cuticle cells and the surfaces of cuticle cells below (i.e., at the CMC; see Fig. 5a). This can be deduced from the fact that when these lifted cuticle cells are broken and chipped away by friction, they do not leave endocuticular remnants on the surface below (see Fig. 5b). For this reason, we will refer to this type of cuticle cell lifting as endocuticular delamination. The mechanism for its formation is straightforward, namely, the transient and rapid water evaporation from the endocuticle causes its contraction and alters its mechanical moduli. The combined action of both processes, along with the additional hoop stresses produced by low elongations, induces a concentration of stresses across the endocuticle or CMC, causing breakage of the CMC.

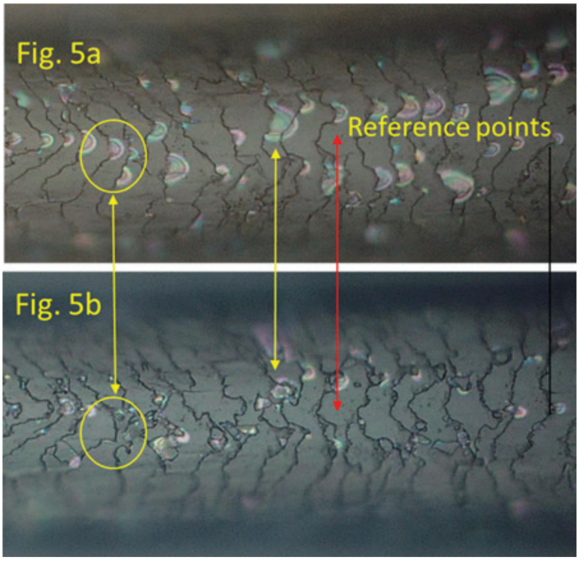

Figure 5. Optical microscopy images of the same hair fiber, immediately after being blow-dried at 80°C for 50 s while subjected to 5% elongation (Figure 5a) and after the same surface was slightly rubbed with a comb (Figure 5b). Note the broken patterns of cuticle cells in Figure 5b.

Cuticle cell delamination was also observed to occur at higher temperatures between the range of 150 and 220°C and with levels of elongation less than 5%. These temperature and elongation ranges are typical during hot ironing processes. The characteristics of thermal lifting produced under these high temperature conditions were similar to those already described for low temperatures. However, in many cases, a new form of delamination was observed. In this new form of thermal delamination, the cuticle cells did not lift forming parabolic shapes but stayed attached to the hair surface, forming rather blister patterns (see Fig. 6a). Furthermore, blister formation was not detected when the hair had been equilibrated at low moisture conditions, thus indicating the need of moisture for their occurrence. When these blistered cuticle cells were broken by friction, they left visible endocuticular remnants on the surface (see Fig. 6b), indicating that lifting occurred by breakage at the junction between exocuticle and endocuticle.

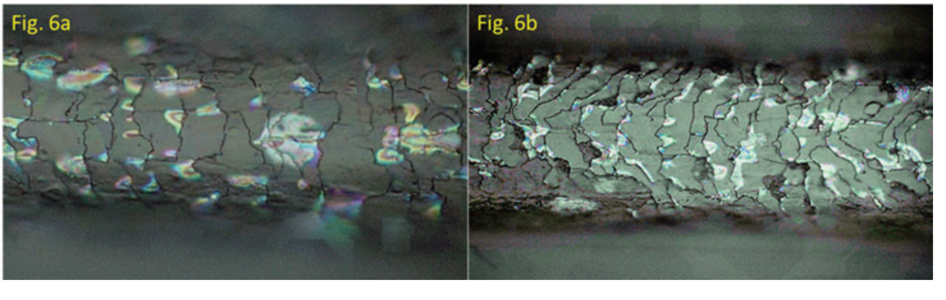

Figure 6. Optical microscopy images of cuticle cell blister patterns, immediately after hot ironing (Fig. 6a) and after the cuticle cell blisters were broken by friction (Figure 6b); the blisters were produced by gently applying two cycles of hot ironing at 220°C to the fiber.

Since in blister formation, the portion of cuticle cells that is lifted consists of the epicuticle and exocuticle joined together, leaving behind endocuticular remnants, we will refer to this type of lifting as exocuticular delamination. This contrasts with what was observed before for endocuticular lifting, in which the solid portion of cuticle cell that was lifted consisted of the epicuticle, exocuticle, and endocuticle glued together. Its mechanism of formation can again be explained by changes occurring in the interlayer moduli as the exocuticle, endocuticle, and CMC lose moisture. When the hot iron surface enters transiently in contact with the hair surface, it rapidly dehydrates and hardens the epicuticle and exocuticle, while contracting the endocuticle. The contracting and hardening of these layers cause stress concentrations across the exocuticle and endocuticle causing their junction to break with a slight lifting leading to blister formation.

SHAPE RECOVERY OF LIFTED OR BUCKLED CUTICLE CELLS BY HYDRATION

It is well known that water acts as the main plasticizer of keratin fibers (7), and water plasticization effects on hair have been mainly ascribed to hydration effects in the amorphous proteins of the cortex. However, moisturizing video experiments carried out with hair fibers presenting lifted and buckled cuticle cells showed that the cuticle cells also sense changes of moisture in the environment. In these experiments, the cuticle cells were seen to respond almost immediately, particularly when exposed to high levels of moisture. This rapid response occurs as long as their endocuticle is not damaged and therefore indicates that the cuticle cells undergo plasticization as they absorb moisture from the environment. The video experiments showed that the light interference patterns (LIPs) corresponding to lifted cuticle cells disappear almost instantaneously as the hair is exposed to small puffs of air containing high levels of moisture (i.e., $>$90% RH). The LIPs disappear when the endocuticle of the lifted or buckled cuticle cells is plasticized by water and allows them to recover their normal shape. This recovery process closes the air gap between lifted cuticle cells and those immediately below. Furthermore, when puffs of moisturized air containing lower levels of moisture (i.e., $<$70% RH) were applied to hair there was no plasticization and shape recovery.

The above experiments indicate that for cuticle cell shape recovery to occur, the endocuticle requires high levels of water absorption. This contrasts with other observations showing that thermal delamination only occurs when the endocuticle loses high levels of moisture, strongly suggesting that the endocuticular protein structure has the characteristics of a hydrogel in its native state. Such structure will allow it to absorb high levels of water when exposed to the environment. Furthermore, the experiments suggest that not only the endocuticle but also other cuticle cell layers exchange moisture with the environment. Unfortunately, currently, there is no available technique by which one can obtain the thermal water absorption isotherm of the cuticle sheath separately from the cortex. Thus, the inference is that moisturization effects on the cuticle sheath must rely on indirect observations such as the one described in this paper.

BUCKLING AND LIFTING CUTICLE CELLS BY IMMERSION IN ISOPROPYL ALCOHOL

As it was shown in the previous section, lifted and buckle-shaped cuticle cells with failure at the CMC can recover their normal shape through rehydration. In fact, the recovery was so efficient that when the hair was analyzed again by microscopy, the previously lifted cuticle cells appeared in a flat position, as if they were cemented like normal cuticle cells. However, as will be discussed later, this is just a superficial change, as the cement had been broken before, and, therefore, the apparent normal cells were readily lifted again by solvent dehydration. For instance, videorecording analysis showed that when these fibers were immersed in isopropyl alcohol (IPA), the apparently normal-looking cuticle cells immediately lifted and buckled again.

It should be mentioned here that real normal cuticle cells (i.e., ones not previously decemented) did not show such lifting behavior upon IPA immersion. The phenomenon of cuticle cell lifting and buckling with IPA can be explained by considering the fact that such a solvent dehydrates the endocuticles of apparently normal looking cuticle cells, causing them to contract, lift, and buckle again. This important observation confirms that the protein structure of the endocuticle behaves like a hydrated gel, which contracts as it loses water, causing cuticle cell buckling once the cement is broken.

CUTICLES CELLS ARE NOT SENSITIVE TO MOISTURE EVAPORATION

So far, enough evidence has been presented indicating that the shape of most cuticle cells in hair fibers is sensitive to moisture. However, during the experimental analysis, it was often found that some cuticle cells do not change shape by either dehydration or rehydration. For instance, the videorecording technique showed that while there are regions of cuticle cells that rapidly undergo lifting and buckling by thermal dehydration during blow drying and elongation, there were also other regions where the cuticle cells did not change shape at all. This observation was true even for long periods of blow drying. Likewise, some cuticle cells that had been de-cemented and buckled either by high elongations or thermal stresses did not recover their shape when hydrated even after long periods of water immersion. Both observations point toward a lack of responsiveness to moisture changes in the cuticle cell. Such a phenomenon indicates the possibility that proteins in the endocuticle of these cuticle cells lost their native structure in a process akin to denaturation. It could also be that other structures in the cuticle cell layers were mechanically denatured or damaged.

CONCLUSION

The experiments discussed above indicate that the mechanical properties and damage patterns of hair cuticle cells are not only sensitive to their moisture content but also to its rate of evaporation. In addition, the results also indicate that in its undamaged form, the endocuticle, exocuticle, and CMC protein structures have a balanced moisture distribution, which allows them to work as an assembly in the transfer of mechanical stresses, providing resistance to damage. The analysis also indicates that cuticle cell buckling can be produced by either only mechanical stresses or by a combination of mechanical and thermal stresses. Two patterns of cuticle cell thermomechanical buckling could be distinguished, namely, endocuticular and exocuticular. Both seem to be driven by transient dehydration of the endocuticle and to a certain extent of the exocuticle. The former is characterized by rupture of the CMC cementing top cuticle cells to those immediately underneath, while the second is characterized by the rupture of the cement between exocuticle and endocuticle. Finally, the results also suggest that the endocuticular protein structure behaves like a hydrogel, which interchanges moisture with the environment.

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