HOW TO ALLEVIATE THE IMPACT OF CALCIUM ON HAIR MECHANICAL PROPERTIES? A NEW SPECIFIC COMBINATION OF ACIDS FOR HAIR CARE

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Introduction

Hair is providing a medium to express personality and group ownership, and salon services like color and texture transformation (permanent wave, relaxers) have multiplied the opportunities for all to dare expressing themselves.

Poorly controlled, these treatments can eventually lead to fragilization of the hair hierarchical structure and integrity. Its repeated exposure to water, washing and grooming routine may bring an important impact upon its mechanical properties and beauty. Moreover, daily mechanical stresses such as combing, brushing or heat drying can even increase the fragility of the fiber. It is therefore important to reduce the tall of hair damages on the aspect of hair and its manageability.

Among all these external aggressors, the quality of the washing and rinsing water and in particular their content in cations, plays a major role in hair quality. It has been long evidenced that exogenous metal ions will accumulate within the hair fiber[1], depending principally on the level of damage of the hair [2]. Chemical damages in keratin (oxidative bond cleavage, formation of cysteic acids increasing coulombic interaction) increase binding sites for metal ions, to which copper, zinc and particularly calcium ions tend to accumulate in the structure. While copper ions are particularly deleterious on the hair integrity during oxidative treatment [3], calcium ions have been linked to the overall mechanical properties (increased young modulus [2], less resistance to breakage [4]) of the fiber and its appearance and shine [4]), although its clear role remains to be better understood.

In our work to improve the quality of damaged hair, we aimed to treat hair fibers with actives able to diminish the impact of calcium ions on the hair fiber and maximize the reinforcement of the protein networks and hair. Hence, a screening of ingredients led to a specific combination of acids which are the most effective.

RESULTS

Actives screening by DSC

To observe the impact of actives on the quality of the hair fiber, we chose to screen a large collection of ingredients by HP-DSC, as this technique allow a large throughput with reasonable preparation. Chemical treatment are known to impact the integrity of keratin, and lower the temperature of denaturation, from 153ºC for Caucasian hair. to 138ºC for Caucasian hair chemically damaged (further reference to damaged hair will relate to this type of treatment) (Figure 1).

Damaged hair was treated five time with solutions of carboxylic acids at similar molar concentration (153mM). In an initial screening: maleic acid, tartaric acid and citric acid were observed as having the largest impact on T_{Den}, with the hair treated with citric acid reaching a T_{Den} in a similar range than natural hair.

We also consider the opportunities to boost the acids by the addition of other ingredients. In a combination with tartaric acid, different carboxylic acids, amino-acids, penetration enhancers, multivalent ions or sugar derivatives were evaluated. We found that the combination of acids with glycine was significantly raising the T_{den} of hair fibers, to a value close to the one of natural fiber. In a final combination, we found that hair treated with citric acid and glycine (further referred as active combination) have the highest value of T_{den} observed for damaged hair.

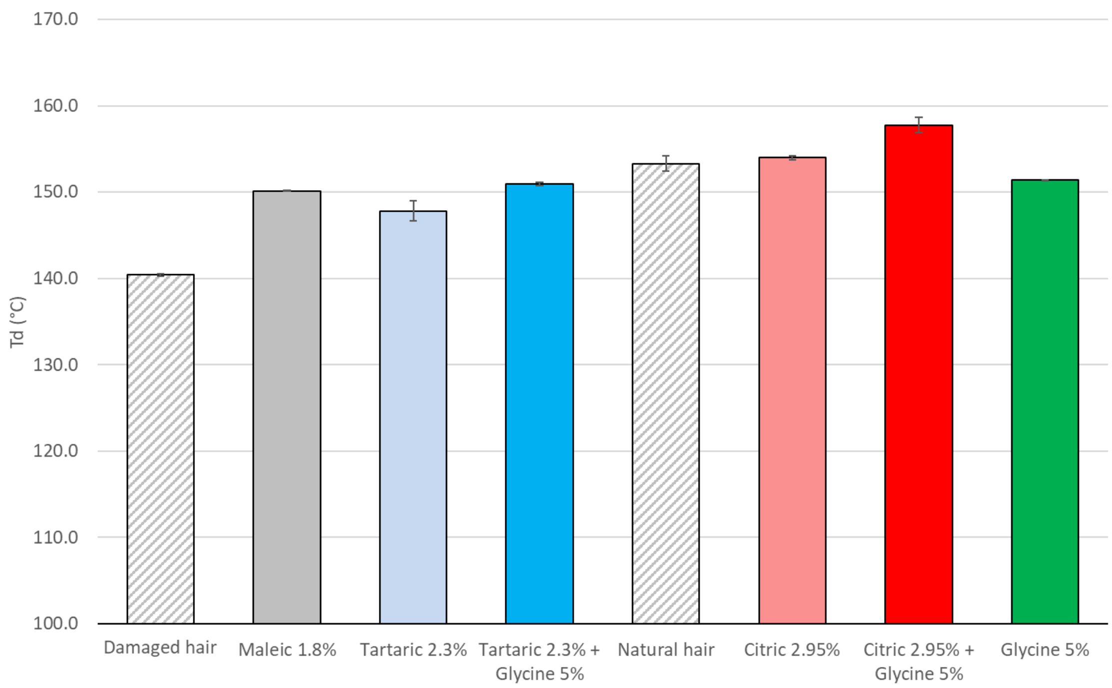


Figure 1. Mean values of denaturation temperature measured by HP-DSC experiment for damaged hair treated with simple aqueous solutions of actives (applied 5 times with shampooing step in between)

Decalcifying effect of Citric and glycine

Given the chelating power of the actives impacting significantly the denaturation temperature (T_{den}), we have evaluated the calcium concentration in different hair samples. In most cases, the application of actives on sensitized hair leads to a decrease in the calcium ion remaining (Figure 2).

In general, the concentration of calcium remaining in the hair fiber follows a similar trend than the DSC experiment. The temperature of the peak T_{den} observed has been related to the degree of cross-linking in the cortex matrix [5], and both calcium ions and small molecules such as the active screened here could impact the T_{den} by forming non-covalent interaction (metallic, ionic or by hydrogen bonding). Still, an apparent correlation could be considered between the removal of calcium ions by the treatment and T_{den}. Our active combination (citric acid 2.95% and glycine 5%) is the most impacting treatment for removing calcium from the damaged hair, in combination to the highed T_{den} observed.

Interestingly, although the hair treated with maleic acid at 3.6% follow the same trend as other treatments, when the maleic concentration is 1.8% (isomolar concentration with other acids), the calcium concentration in the fiber is not significantly impacted. As tap water is used to rinse the swatches after treatment and the damaged fibers are generally prone to capture cations, this could explain the low impact on descaling with maleic acid at low concentration. In this case, isomolar treatments of tartaric acid or citric acid can decrease the re-entry of calcium in the fiber after rinsing.

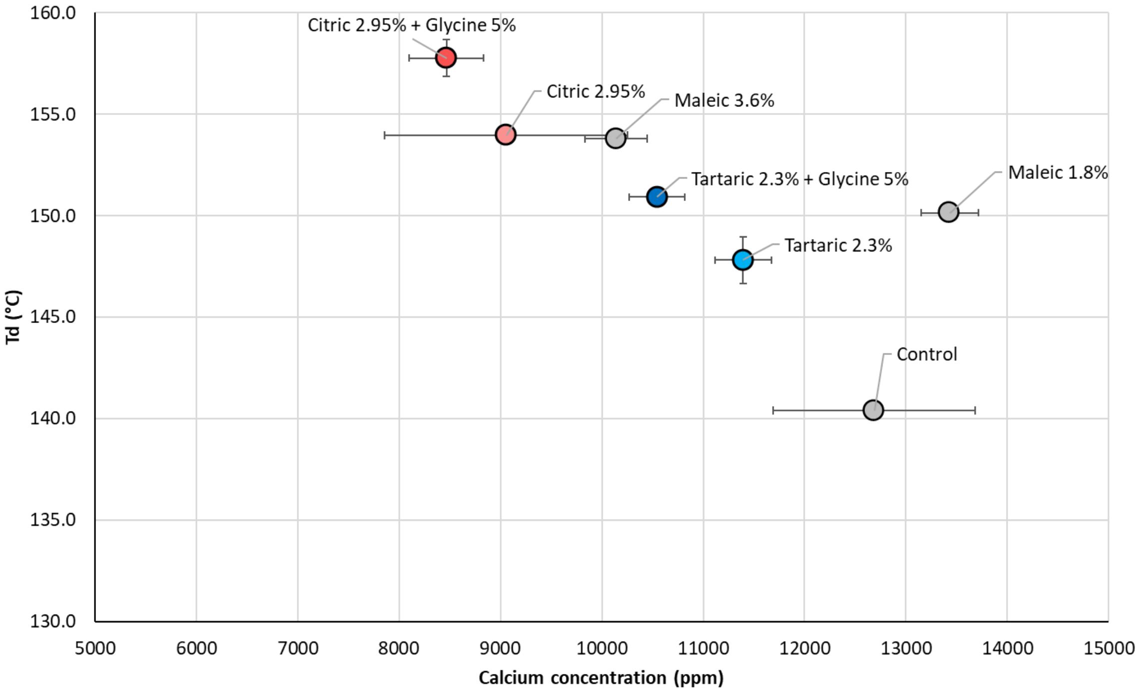


Figure 2. Representation of the Denaturation temperature obtained by HP-DSC and the concentration of Calcium

obtained by ICP-OES analysis for damaged hair treated with simple aqueous solutions of actives (5 applications)

Nano-SIMS observation

Nano-SIMS technique [6] was used to analyze the penetration of our active combination in the hair fiber and also to monitor the presence of the calcium ions in the fiber. Calcium ions are known to accumulate in the outer layer of the fiber, specifically in the less cross-linked endocuticle and the CMC [7]. In the damaged fibers observed, calcium ions are highly concentrated in the cuticle area, but are also reaching deep into the cortex and the cuticle, with specific dense area observed inside the cortex (Figure 3).

When applied with radiolabeled actives (^{13}C-glycine and ^{2}H-Citric acid at 2.95% and 5% respectively), the visible concentration of calcium ions decreases significantly. ^{40}Ca cartography images shows the effect of the active combination on the calcium removal. The concentration in the cuticle region is decreasing. In the cortex, the overall count of atoms is lower than for non-treated hair, and the outer part of the cortex seems even impoverished than the central region of the cortex, suggesting the required penetration and release of the actives chelated to ions.

Additionally, the radiolabeling of the actives allows to see molecules accumulation and remaining at the periphery of the hair fiber. We can see that in the outer region of the hair fiber, a small quantity of active is remaining and can be visualized.

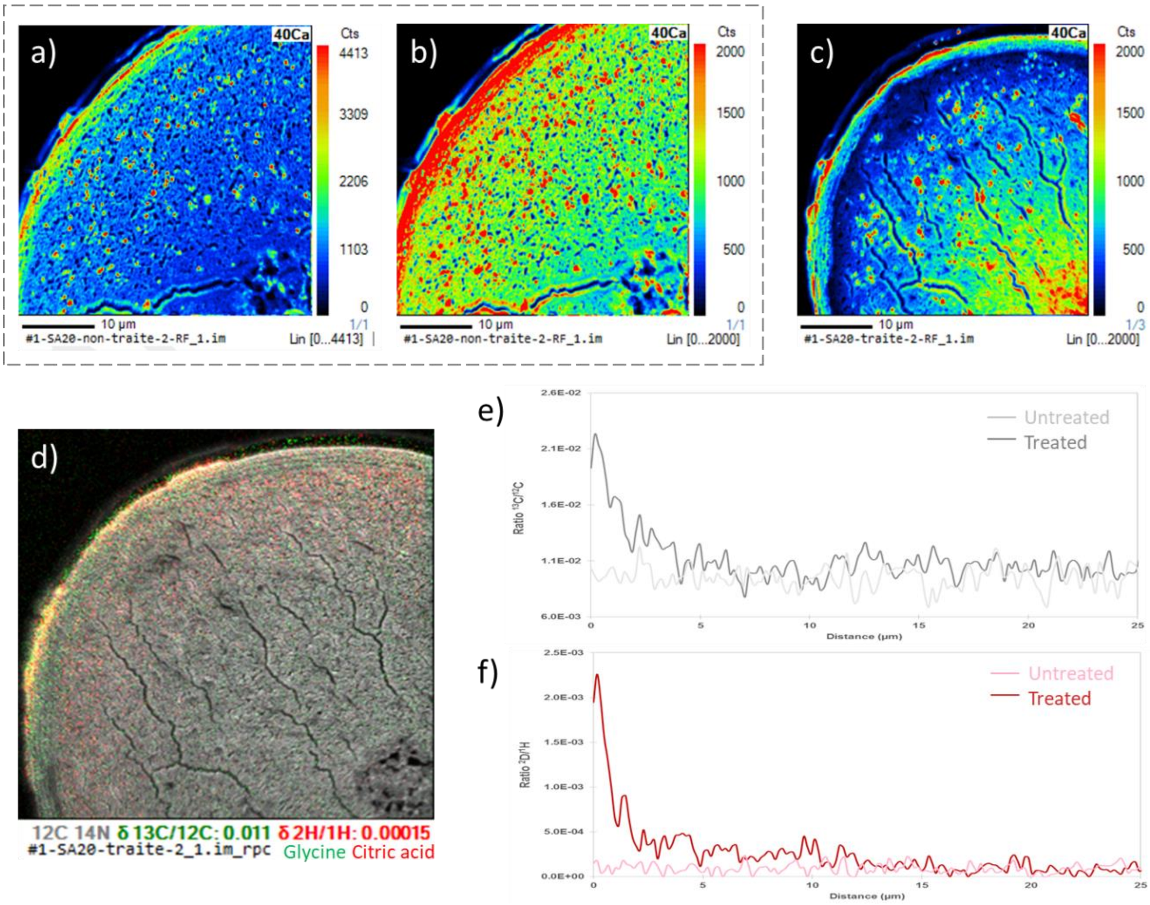


Figure 3. Distribution of 40Ca2+ ions in sections of untreated damaged hair (a & b are the same image at different quantification scale) and treated hair (c). b and c image are equilibrated with the same quantification scale to ease the comparison of calcium removal. d) distribution of 13C-, 2H- ions in treated sample to image the remaining actives after rinse, and the associated line scan e) and f).

Considering the retention of actives in the fiber after treatment, we conducted their quantification. A simple aqueous solution of our active combination was applied on damaged hair fiber in a representative consumer routine (to take into account the desorption of actives due to products application and rinsing). A negligeable amount of citric acid is remaining in the fiber with 0.1ug/g hair after 1 application, this concentration rising to 0.7ug/g hair (Figure 4). At the opposite, the concentration of glycine after 1 application is 607ug/g hair and does not significantly increase with multiple application. We could also observe that the calcium concentration continues to decrease as the application of the treatment are accumulated. The main action of citric acid seems to be the chelation and removal of calcium ions in the hair fiber. Without apparent correlation of the available calcium binding sites, the hair fiber seems to easily accommodate glycine.

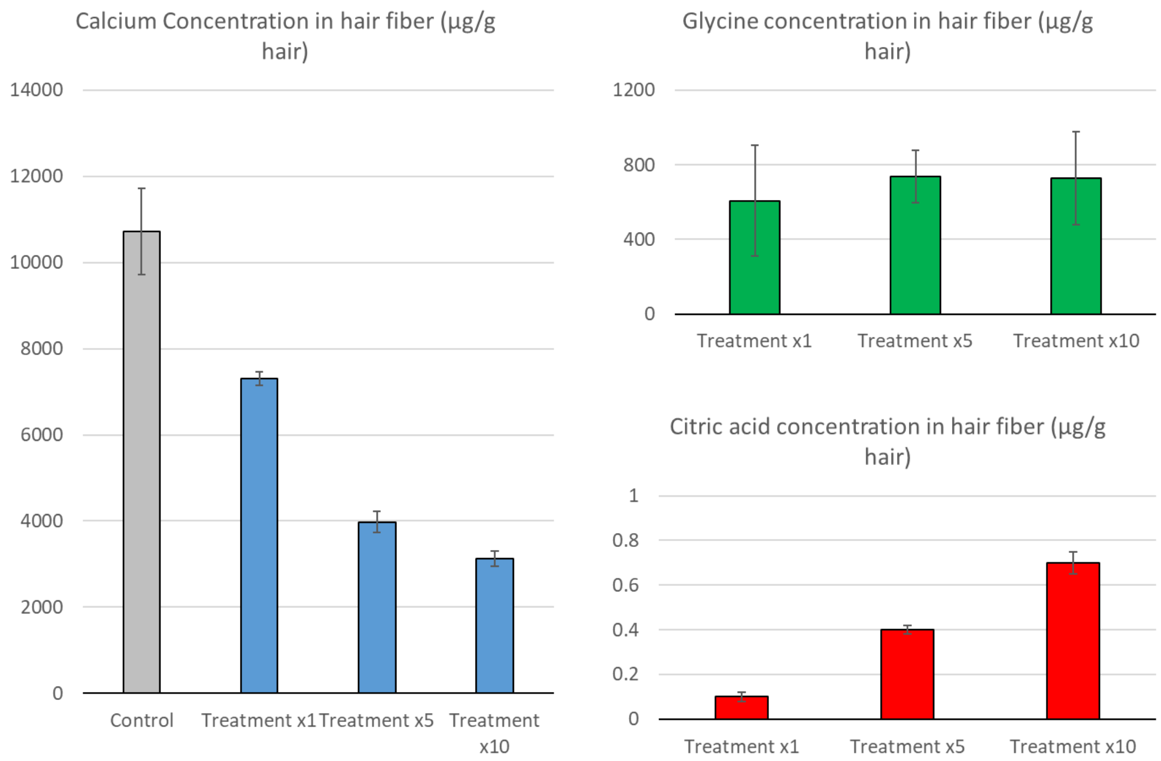


Figure 4. Quantification of calcium ions, glycine and citric acid in damaged hair treated cumulatively with 1, 5 and 10 applications of the simple aqueous solutions of actives (in a representative consumer routine)

Improvement of the mechanical properties of the fiber

The reinforcement of the hair fiber was assessed by instrumental measurement. Cyclic fatigue is the method giving the most consumer representative discrimination of hair integrity, from the repetitive extension stress on the fiber and the failure of the sample, simulating the repeated grooming to which the hair is exposed daily. We evaluated on damaged hair the simple aqueous solution of our actives combination applied 12 times (shampooed in between).

From the survival curve obtained (Figure 5), we determine the area under the curve as an evaluation of the internal reinforcement. The application of active shot shows a statistical improvement of the resistance to breakage compared to untreated hair, highlighting the reinforcement of the fiber from cumulative application of the active combination.

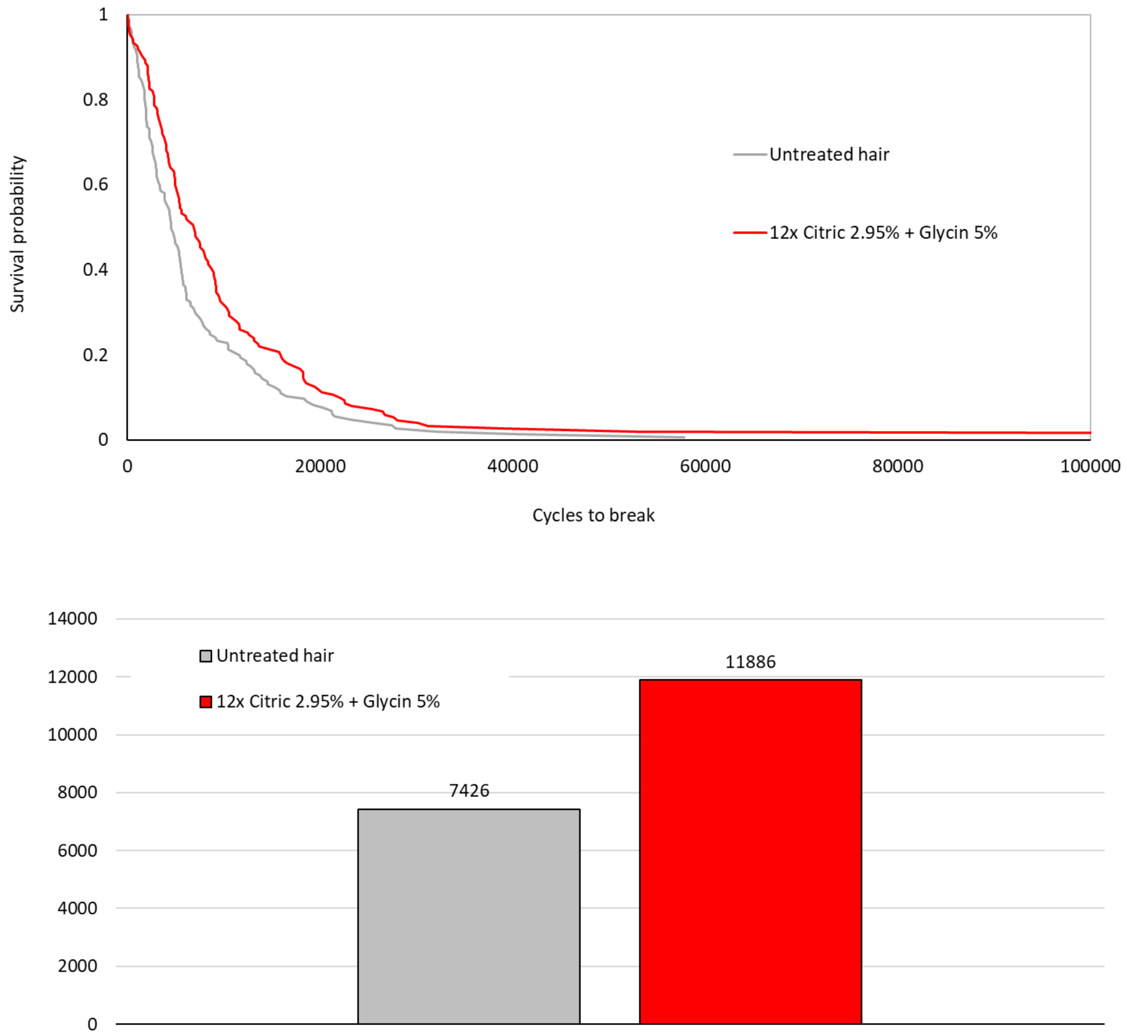


Figure 5. Survival curve (Kaplan-Meyer method) for hair samples subjected to cyclic fatigue measurements. Area measured under the curve for the 2 conditions give discrimination between untreated hair and hair treated with actives.

The tensile properties of the hair were evaluated, and we could observe a decrease of the elastic modulus at dry after 5 applications of the active combination, in comparison to the untreated hair. No difference is observed at wet. This relates to the increased resistance to tension for damaged hair washed in hard water and highlight the action of calcium removal to reduce non-covalent links in the glass state of keratin. [2]

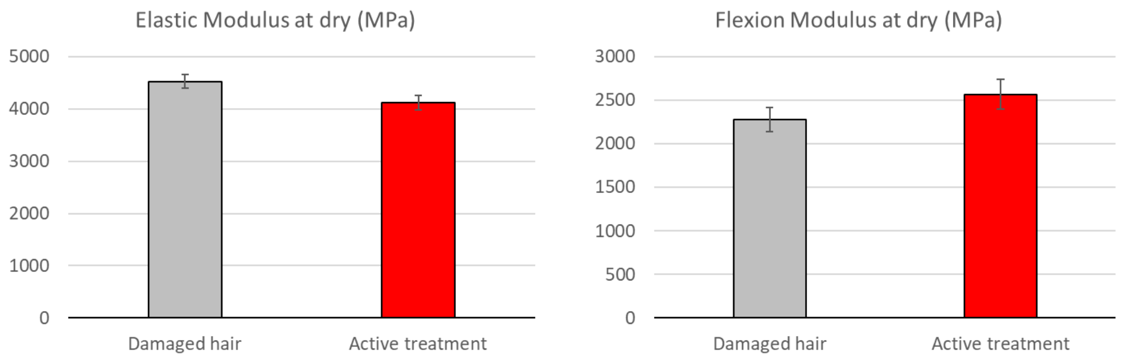


Figure 6. Elastic modulus from tensile test at dry (left) and flexion modulus from bending test at dry (right) for untreated hair and hair treated with simple aqueous solution of actives (5 applications)

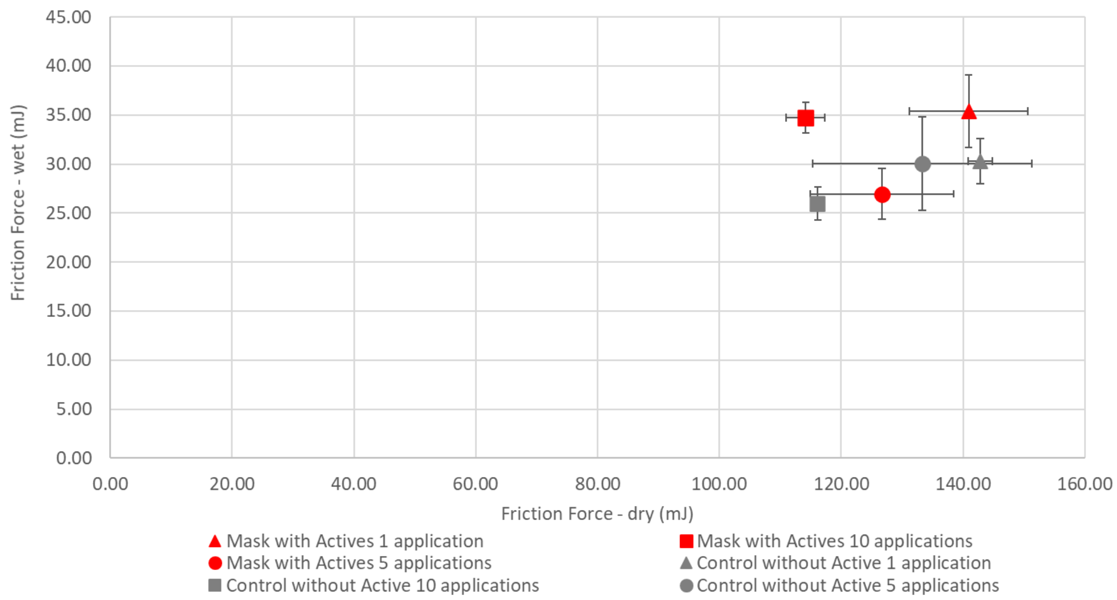
As much as the dry elastic modulus is decreasing, the bending modulus is significantly increasing when damaged hair is treated with our actives. The difference between these mechanical properties could be linked to the contribution of the cuticle layers to the bending properties of the fiber, more prominently that for the tensile properties. Both the calcium ions, remaining in the cuticular region, and the glycine newly anchored there can contribute to increase the bending properties via non-covalent interactions.

Hair repair application of the active combination

We evaluated the repair performances of the actives when used in a rinse-off treatment, considering the ease of application for consumer and leveraging the accepted posing time of masks to boost the penetration of actives.

Citric acid and glycine were incorporated in a rinse-off mask formula, at 2% and 1% respectively. To remove the component of surface cosmeticity in the test, a control formula without active was also evaluated. The two mask formulas were applied as a bundle with a low conditioning shampoo to damaged hair 1, 5, and 10 times, to understand the cumulative effect of the actives on damaged hair.

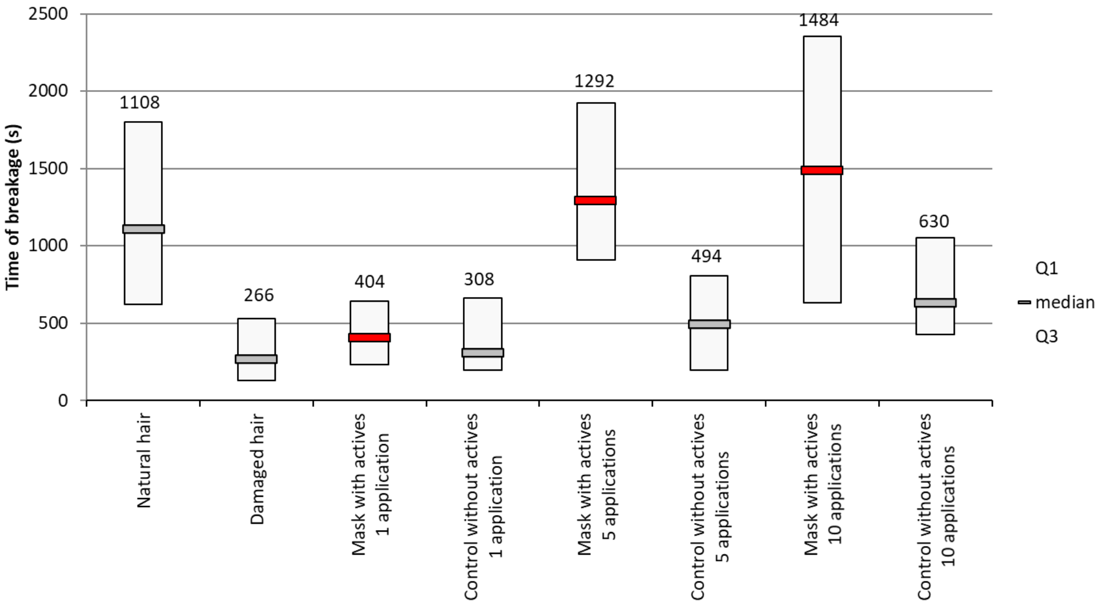
The surface friction of the swatches was evaluated instrumentally by tactile smoothness, at wet and dry. For both formulas, the friction coefficient of damaged hair decreases significantly, regardless the presence of actives. On dry hair, a cumulative effect can also be observed between 1, 5 and 10 repeated applications. This is not the case when the hair swatches are evaluated at wet. Finally, for each series of repeated application, the dry friction coefficient of the formula with active is not significantly different from the control formula.



The same treatment conditions were evaluated by flex abrasion [8]. The methodology principle relies on the resistance to breakage when an extended fiber is subjected to repeated stress of flexion and surface abrasion. The more the fiber is damaged, the more it will break after a short amount of cycle.

After 1 application, the two bundle have comparable resistance to breakage to the untreated hair. Therefore, no significant surface lubrication or internal reinforcement can be deduced to reinforce the fiber.

However, after 5 applications, the time to breakage increases in comparison to untreated hair fiber. The improvement for the control treated fibers can be linked to the surface lubrication, increasing with the cumulative application. For the fibers treated with the active-containing formula, the resistance to breakage is clearly superior. Given the comparable surface friction with the control, a strong internal reinforcement can be concluded.



Consumer evaluation

Two monadic consumer tests were conducted to understand the perception of repair during application, but also as a progressive cumulative repair treatment. The 30 and 20 panelists recruited in Spain and China, respectively, had hair that was brittle, damaged or badly damaged through chemical treatments. We asked them to use the mask containing actives at least twice a week instead of their normal rinse-off treatment.

From the beginning of the test, panelists could perceive a good level of care, talking about shine, smoother hair, less tangling, ease of styling, as well as hydration of softness lasting for 2 days. Although the performances were particularly appreciated compared to their usual products, it would be difficult to associate these instant performances to the mix of actives proposed.

However, we were encouraged to hear panelist express a progressive improvement of the quality of their hair, noticeably in term of strengthening, less breakage, while having hair exceptionally softer. Tips also feel repaired and less dry. The majority of panelists consider the mask with active superior in repair to their traditional care routine.

CONCLUSION

The combination of citric acid and glycine was successfully shown to modify the properties of the damaged hair fibers, from a microscopic level to a more perceived macroscopic evaluation in relation to the improvement of the hair strength. The removal of calcium ions, naturally accumulating in damaged hair, could be the reason of the improvement observed in restoring some mechanical strength of hair. Given the regular exposure of hair fiber to tap water, the repetitive application of the active combination is particularly relevant to protect the hair and cumulate effect on its properties. This simple combination of actives which can be obtained from natural sources present a new opportunity to bring perception of repair and prolonged experience of hair care.

METHOD DESCRIPTION

Sample preparation and swatch application

Simple aqueous solution of actives was prepared by solubilizing the different actives in demineralized water, and the pH equilibrated to pH4 with NaOH. Carboxylic acids were used at equivalent molar concentration, respectively Maleic acid 1.8%, Citric acid 2.95%, and tartaric acid 2.3%.
An active-containing conditioner was formulated using a conventional conditioner architecture with moderate conditioning properties, with 2% citric acid and 1% glycine, equilibrated at pH4. A control formula without active was also prepared.

Straight natural hair native samples of Caucasian origin were use as such (natural state) or damaged by 2 successive chemical treatments (damaged hair). Before treatment, the hair swatches were washed with non-conditioning shampoo.
The protocol for 1 application of active consist of the following steps:

- Hair swatches were washed with low conditioning shampoo (0.4g formula/g hair), pausing for 1 min before rinsing with tap water.
- The test sample is applied (0.4g/g of hair), 5min of posing time, rinsing with tap water (19ºC)
- The swatches are dried in oven with circulating hair at 60ºC for 15min.

DSC

DSC measurements were performed on a differential scanning calorimeter Perkin Elmer DSC8000, in inox high pressure pan, increasing of temperature from 10ºC to 180ºC at 10ºC/min. Each analysis is reproduced three times.

Actives and calcium ions quantification

Calcium ions were quantified in hair fiber samples via ICP/OES after nitric digestion. Glycine was quantified by Amino acid analysis conducted after hair hydrolysis. Citric acid quantification was conducted by HPLC diode array detection after extraction from the fiber.

Nano-SIMS

Samples have been prepared for NanoSIMS according to [Hallegot2006]:

A 300 nm to 500 nm and 20pA Cs+ primary beam has been used for analysis. This beam, scanned onto the sample, slowly erodes its surface. The eroded material is collected and analyzed by mass spectrometry. 40Ca^{2+} ions have been selected to reveal calcium distribution, resolution mass 4000 with screening area from 20×20) μm^2 to (40 × 40) μm^2 obtained and analyzed images of 256 × 256 pixels size. Under these operating conditions, Ni in low concentration can be detected, but we focused on ^{1}H, ^{2}D, ^{12}C, ^{13}C, ^{14}N, ^{32}S, ^{23}Na and ^{40}Ca (K. Smart, SIMS Europe, Munster 2006).

Cyclic fatigue

Cyclic fatigue was performed on a Diastron CYC801 tool in constant stress mode, on a high amount of hair samples per condition. Before testing, samples are equilibrated during a long time in a glove box in which the relative humidity and temperature are controlled, then they are extended to the right constant stress, at a constant speed, in a repeated manner until breakage or reaching a maximum repetitions defined by the operator.

Tensile test

Tensile test was conducted on a miniature Tensile test (MTT680, Diastron, UK) on 50 fibers per condition

Bending test

Bending tests were conducted with a flexion test (FBS 900, Diastron, UK) on 50 fibers per condition

Tactile smoothness

Tactile smoothness was evaluated using a extensometer measurement by compressing a calibrated hair swatch between two surfaces with a constant compression force, and measuring the friction force when the swatch is moved, from root to tip, at constant speed.

Flexabrasion

The equipment Fiberstress DTM-371 from Textechno (Textechno Herbert Stein GmbH & Co. KG, Mönchengladbach, Germany) was used to assess the resistance of the hair fibers. 50 hair shaft samples were analyzed for each condition

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CONFLICT OF INTEREST STATEMENT

L'Oreal funded this study

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