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Impact of acid straightener's pH value in the hair fiber properties

Alessandra Mari Goshiyama MSc | Michelli Ferrera Dario PhD | Cibele Rosana Ribeiro de Castro Lima PhD | Gabriel Lima Barros de Araújo PhD | André Rolim Baby PhD | Maria Valéria Robles Velasco PhD

Faculty of Pharmaceutical Sciences, University of São Paulo, São Paulo, Brazil

Correspondence
Alessandra Mari Goshiyama, Faculty of Pharmaceutical Sciences, University of São Paulo, 580 Prof. Lineu Prestes Avenue, Bl-13/15, 05508-900, São Paulo – SP, Brazil.
Email: alessadra.goshiyama@gmail.com

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Abstract

Background: Acid straightener products are widely used, and it can cause changes in the hair shaft properties. The pH value of these products established by ANVISA (Brazil's National Health Surveillance Agency) as secure is above 2.0. However, the industries are interested in working at lower pH values in order to increase the straightening effect. Unfortunately, there are a lot of products in the market with pH value under the permitted.

Objective: Analyze two different pH values (1.0 and 2.0) of acid straightener formulation and the influence of this difference in the hair shaft properties. In order to provide information to professionals as cosmetologists, dermatologists, and hairdressers.

Methods: Combing and colorimetric analyses, tensile strength, differential scanning calorimetry (DSC), environmental scanning electron microscope (ESEM), and tryptophan content.

Results: The tresses treated at pH 1.0 had a better result in the straightening capacity, improving the combing test in 59.4%, while those at pH 2.0, only in 33.0% compared with virgin hair. However, the tensile strength, at pH 1.0 decreased by 16.0% and 9.0% to the pH 2.0. In addition, the tryptophan content was lower in the tresses treated with formulation at pH 1.0. The DSC analysis showed impairment in the straightened tresses. The images by ESEM, indicated a possible formation of a film around the fiber.

Conclusions: It was possible to conclude that the pH value interferes in the hair shaft properties. Tresses treated with pH 1.0 had more modifications than tresses treated with pH 2.0.

KEYWORDS
acid straightening, differential scanning calorimetry, glyoxylic acid derivative, hair, pH

1 | INTRODUCTION

Hair products are broadly used in order to obtain a good appearance and the possibility to modify instantaneously. Among these products, the chemical acid straighteners are used in many countries, especially in Brazil. Probably, the mechanisms of acid straighteners are similar, because they have the same organic function. It is likely that involves rearrangements within the structure.[1] In addition, a hydrophobic film is formed by heat activation (flat iron) around hair shafts, resulting in biopolymer reaction, this reaction happens when

the hair shaft is treated with formaldehyde[1,2] and it is possible that could occur in other acid straightener. Currently, the glyoxylic acid associated with carbocysteine and amino acids (INCI: *Glyoxyloyl Carbocysteine (and) Glyoxyloyl Keratin Aminoacids (and) Water*) is the only acid straightener allowed by ANVISA. An important discussion regarding this straightener is related to the pH value of the formulation, because as lower the pH value probably higher is the risk of adverse effects, due to the product's intrinsic irritability in contact with the scalp, and possible changes in the hair fiber properties. It is important to consider that a change in one pH unit means a difference of 10 times in the concentration of hydrogen ions (H^+) because the pH scale is logarithmic.[3]

ANVISA recommends that industries keep straightener's pH value higher or equal to 2.0, concerned about the safety of the product. However, there is an interest to reduce the pH value of the product aiming for greater straightening effect. Unfortunately, it is known that exist many products in the market with pH lower than 2.0. Therefore, understanding the effect of a straightener product at pH < 2.0 on the hair fiber becomes essential to establish its potential risk, evaluating parameters as mechanical, physical, and chemical properties of the hair fiber.

2 | MATERIAL AND METHODS

2.1 | Hair sample

It was used curly dark brown virgin tresses from De Meo Brothers® with approximately 3.0 g and 15.0 cm long in triplicate for each group. The tresses were divided into three groups: (1) control, (2) tresses treated with straightening emulsion at pH 1.0, and (3) tresses treated with straightening emulsion at pH 2.0. All tresses were subjected to a standard washing procedure in order to remove any dirt, using 3.0 mL of sodium laureth ether sulfate (10%). Hair tresses were washed for 10.0 seconds with warm water (37.0 ± 5.0°C), then applied the dispersion with gentle movements with thumb and middle fingers from the root to the end for 60.0 seconds, and rinsed for 30.0 seconds, the excess of water was removed with fingers. The tresses were dried naturally for at least 24 hours under (22.0 ± 2.0°C) and 55% of relative humidity (RH).[4]

2.2 | Straightening process

2.2.1 | Formulation

The straightener formulation, prepared as an oil-in-water (O/W) emulsion, presented the following composition according to INCI (International Nomenclature of Cosmetics Ingredients): *Aqua*, *Behentrimonium Methosulfate (and) Cetearyl Alcohol*, *Isopropyl Palmitate*, *PEG-90M*, *Polyquaternium-67*, *Shea Butter Amidopropryl Trimonium Chloride*, *Glyoxyloyl Carbocysteine and Glyoxyloyl Keratin Amino Acids* (15.0%; AQIA®). The pH of the formulation was adjusted to 2.0 and 1.0 with triethanolamine or citric acid, respectively.

2.2.2 | Application

The tresses were treated with the ratio of 1.0 g of formulation/1.0 g of hair, according to their group classification, and it was applied on the tresses with a brush so that could be in contact with all the fibers for 20 minutes. Then, they were brushed and dried with a hairdryer and flatted 10 times with a flat iron (180°C).

2.3 | Hair analysis

2.3.1 | Combing assay

The total work (Joules) for combing was determined by MTT175 Dia-stron®, disposed with UvWin® PC Software at room temperature (22.0 ± 2.0°C) and 55% RH. Five tests were performed in each tress before and after straightening treatment, obtaining an average value of total work for each sample.[5,6]

2.3.2 | Tensile strength

The rupture force for each sample was obtained with MTT175 Dia-stron® at room temperature (22.0 ± 2.0°C), 55% RH and rate of 300 mm/min with the UvWin® PC Software. Ten random fibers were selected and attached to crimps from each tress. The diameter of the hair shaft was measured with a Mitutoyo® micrometer, and the value was used to calculate the cross-sectional area of the hair fiber.[4] The cross-sectional (mm^2) area and rupture force (gmf) were used in the calculation of tensile strength at break (gmf/mm^2).

2.3.3 | Colorimetric analyses

The tresses were analyzed (Group 01 and 02) by Chroma Meter CR-400 Konica Minolta®, the equipment provides three parameters L* (luster), a* (color from green to red) and b* (color from yellow to blue). With all these parameters, it was possible to calculate the total color difference (DE), the color difference between the tresses before and after treatment.[7]

2.3.4 | Differential scanning calorimetry

The hair was cut in snippets and stored under room conditions (22.0 ± 2.0°C, 55% RH) for at least 24 hours to ensure constant water content. The measurements were taken using 2.0 mg of hair snippets for each sample into aluminum capsule, partially closed using a cell DSC model 50, Shimadzu Corporation®, with a heating rate of 10°C/min (25-300°C), under dynamic N_2 atmosphere (flow rate of 100 mL/min).[8]

2.3.5 | Determination of tryptophan

Alkaline hair hydrolysis

All hair samples were cut and weighted (20.0 ± 1.0 mg) into Falcon tubes with 6.0 mL of 4 N sodium hydroxide, 200 μL ascorbic acid

(1 mg/mL) as an oxygen scavenger, and 300 μL of α-methyl-tryptophan (0.16 mg/mL) as the internal standard and then sparged with freshly nitrogen (N_2). The tubes were incubated in a forced-air oven at 100°C for 72 hours. After incubation, the tubes were neutralized with 2.0 mL of 12 N HCl, then made up to 10 mL with deionized water and filtered through a 0.45 μm Millipore® filter prior to HPLC injection.[9]

High-Performance Liquid Chromatography

Tryptophan was quantified in an HPLC system, Shimadzu® 20A separation module equipped with a DGU-20A5R degasser, a SIL-20A HT autosampler, a CTO-20A column oven, an SPD-M20A UV–VIS diode array detector, and an RF-20A fluorescence detector (Kyoto, JP) with a C18 column Luna 5 μm, 250 × 4.6 mm (Phenomenex®). The conditions were a mobile phase with methanol: 10 mmol/L sodium dihydrogen phosphate (pH 2.8; 20:80 v/v) was used a flow rate of 1.1 mL/min at 45°C and ran isocratically. An aliquot (10.0 μL) of each sample was auto-injected into the column and used the fluorimetric detection performed at 277/346 (excitation/emission) for tryptophan and α-methyltryptophan.[9] The liquid chromatographic separation of tryptophan presented in hair samples, followed by fluorimetric, was validated according to the ICH guidelines.[10]

2.3.6 | Environmental scanning electron microscope

Four fibers of each hair tress were coated with platinum and analyzed in the ESEM Quanta 650 FEG, FEI®, with a system of micro analyze Quantax, Bruker® and the image analyzer Mineral Liberation Analyser.

2.3.7 | Statistical analyses

Results were analyzed in the Minitab® 16 Statistical Software using different tests according to the assay (one-way ANOVA, Tukey test and Student's *t* test) with $P = 0{,}05$.

3 | RESULTS

3.1 | Combing test

To evaluate the cuticle, two characteristics are important, combability and friction, both are related with the dry-combing test, as more intact and aligned the cuticle, better the characteristics as smoothness, shine and frizz.[11] These analyses evaluate the state of the cuticle by the Total Work (Joules) necessary to comb the hair tress, how easier or harder is the work.

The analysis showed that the Total Work value decreased 59.4% to tresses treated with straightener formulation at pH 1.0 and 33.0% to pH 2.0 when compared to same virgin tresses (Figure 1).

3.2 | Tensile strength

Hair shaft has three distinct phases until the rupture: Hookean (up to 3.0% of stretch), plastic (3.0%-30.0%) and postplastic regions (above 30.0%).[12] The load value necessary to reach the plastic region and to break depends on the cohesion between keratins.[13]

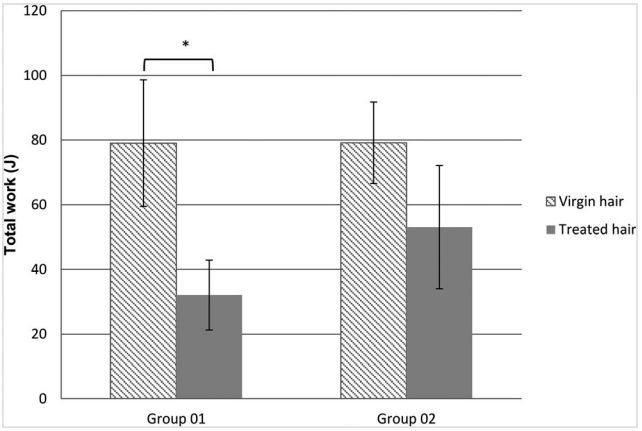


FIGURE 1 Combing analyses comparing virgin hair (before treatment) with treated hair with acid straightener at pH 1.0 (Group 01) and 2.0 (Group 02). * means significantly different ($P \leq 0.05$)

To evaluate the hair strength, it is important to correlate the breaking load and tensile strength graphic profile. In this test, it was possible to analyze the tensile strength and the tensile profile of each hair group. The pH 1.0 tresses presented 15.7% and at pH 2.0, 8.7% less strength when compared with virgin hair (control; Figure 2).

Some hair fibers during this test did not present the typical tensile profile as a healthy hair described in Figure 3A, but an atypical profile (Figure 3B) without the three phases showed by the numbers. For hair tresses from Group 01, 26.6% presented atypical profile and 10.0% of the fibers from Group 02.

3.3 | Colorimetric analyses

The treated tresses (*Group 01 and 02*) had a color variation, the total color difference (DE) was 5.1 and 4.8, respectively. There was no

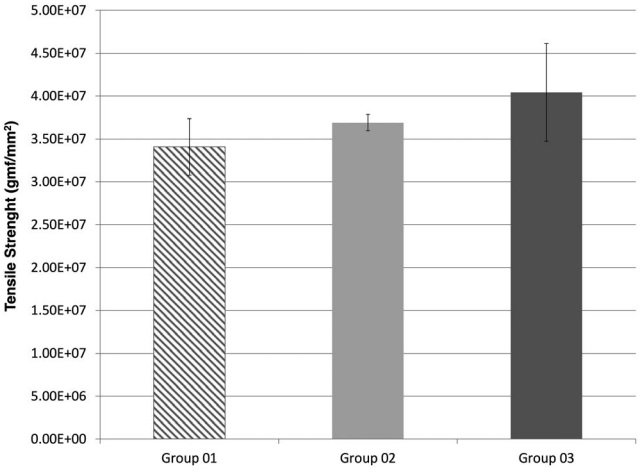


FIGURE 2 Tensile strength analyses of virgin (Group 03) and treated hair with acid straightener at pH 1.0 (*Group 01*) and 2.0 (*Group 02*). There were no statistical differences between the groups

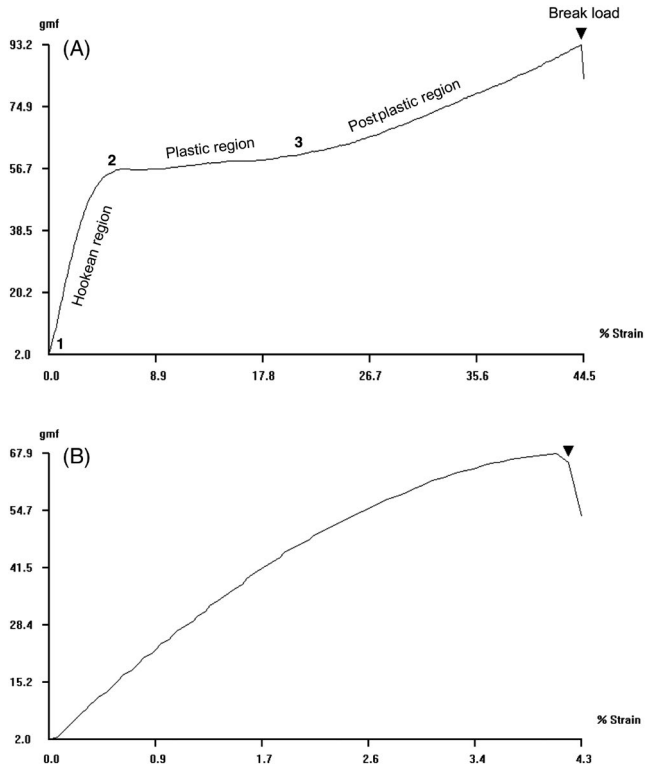


FIGURE 3 A, Virgin hair tensile strength profile with the three distinct phases. B, Straightened hair tensile strength profile of a breakage (inelastic). The numbers represent each phase, Hookean phase (1-2), plastic phase (2-3), postplastic region (3- Break load), and rupture point (Break load)

statistical difference. With this test, it was possible to prove that the straightener procedure changes hair color, once the virgin hair did not have any change.

3.4 | Differential scanning calorimetry

The typical hair dry-DSC curve has two standard peaks: (a) the removal water in the temperature range 25-150°C and (b) the denaturation (melting) of the α-helix in the temperature range 230-240°C denominated as denaturation temperature (T_D)[14,15] and each peak has their enthalpy value (ΔH). Figure 4 shows DSC results (T_D and ΔH_D) and the curves of the hair samples (virgin hair, pH 1.0 and pH 2.0).

The profile of the DSC curves showed a change at T_D in treated hair when compared to virgin hair tresses which imply a impairment in these samples.[16] Both *Groups 01* and *02* (tresses treated with straightening formulation) had their ΔH_D value decreased by 29.1% and 26.8%, respectively, when compared to untreated hair.

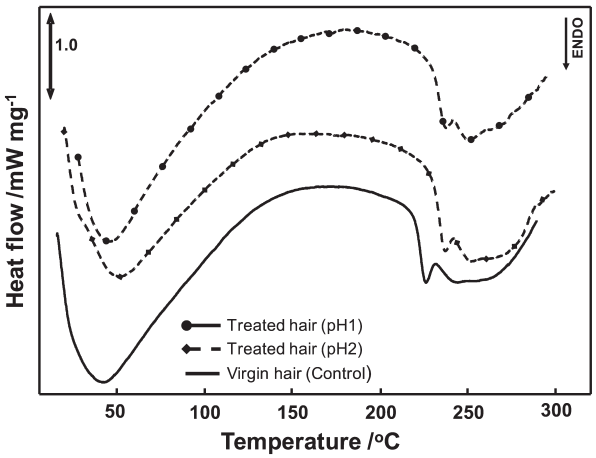
According to Popescu and Gummer,[15] dry-DSC measurements identify the pyrolysis of some components of the hair which occurs simultaneously with the denaturation of the keratin crystalline structure. Thus, the DSC results obtained in the present research indicated that the use of acid straightening caused damages within the hair. Lima et al demonstrated that above 200°C, the hair starts the process of thermal decomposition, with the formation of gases containing sulfur and nitrogen (CO_2, SCO, H_2S, and NH_3). In the study herein reported, the heat contributed to damage the hair structure.

3.5 | Determination of tryptophan

In order to evaluate the composition of all hair layers, the quantification of a specific amino acid is indicated. For this, there are numerous amino acids in hair composition such as cysteine, tryptophan, and tyrosine. To this study, the tryptophan was chosen, the determination of this amino acid showed possible impairment and degradation of hair protein. Hair tresses treated with formulation at pH 1.0 (Group 01) presented 3.00 μg Try/g hair, less tryptophan content than tresses from Group 2.0 with 3.45 μg Try/g hair and Group 03 (virgin hair; Figure 5).

3.6 | Environmental scanning electron microscope

The ESEM images can show hair shaft's properties such as the appearance of the cuticle, deposition of particles on the surface and affinity for substance.[18,19] In the ESEM image analyses, it was possible to observe the formation of a film on the hair because the treated hair (Figure 6B)



Sample	T_D /°C	ΔH_D /J g^{-1}
Group 01	242.3	5.06
Group 02	241.8	5.23
Group 03	235.3	7.14

FIGURE 4 DSC results (T_D and ΔH_D) of the hair samples (22.0 ± 2.0°C; 20.0% ± 2.0% R. H.), *Group 01* (treated hair with formulation at pH 1.0), *Group 02* (treated hair with formulation at pH 2.0), and *Group 03* (virgin hair) and respectively their curves

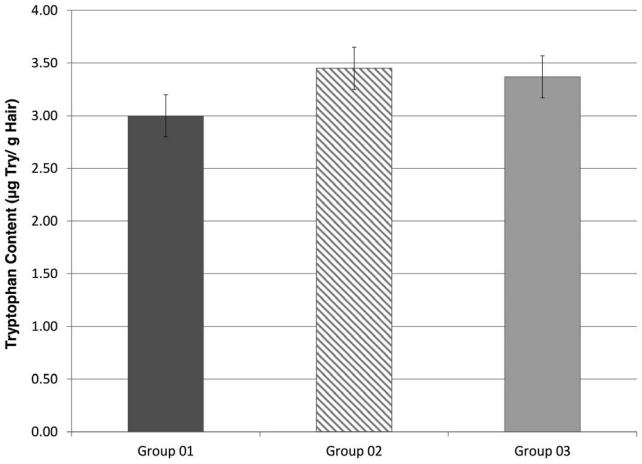


FIGURE 5 Determination of Tryptophan in hair tresses: *Group 01* (formulation at pH 1.0), *Group 02* (formulation at pH 2.0), and *Group 03* (virgin hair). There were no statistical differences between the groups

had the cuticle more sealed than the virgin hair (Figure 6A). It was possible to confirm the formation of the film, because in the sample that the treated tress was washed out (five times) in a standardized way, it was possible to observe the removal of some parts of the film (Figure 6C).

4 | DISCUSSION

According to the results herein reported, it was possible to imply that the tresses treated with formulation at pH 1.0 had a more significant alignment of the cuticle, resulting in a more pronounced straightening effect, when compared to tresses from *Group 02*.

However, tresses treated with formulation at pH 1.0 had the tensile strength value decreased around 55% more than tresses from *Group 02*. This percentage is associated with the quantity of keratin that lost their integrity,[20] affecting the fiber resistance. And also, the tresses from *Group 01* had more atypical tensile strength graphic profile when compared to the other groups, indicating that some impairment occurred regarding the shaft elasticity profile.

Corroborating with these results, the treated tresses dry-DSC curves presented a decrease in the enthalpy value compared to the virgin tresses, these results prove that some impairment occurred, and it could be associated with the mechanism of this acid straightener. The study made in 2014 regarding others acid straightener demonstrated that aldehydes present in formaldehyde and glyoxylic acid interacts with hair's amino acid chain, forming an unusual product in the hair shaft: imine and hemiacetal. The temperature is highly associated with this process, because high-temperature, increase the formation of these products, causing rearrangements in the structure, mainly in the secondary structure.[1]

Thus, it was possible to extend this mechanism to the acid straightener (*Glyoxyloyl Carbocysteine* and *Glyoxyloyl Keratin Amino Acids*) herein studied, and this rearrangement can be highly related with the decrease of denaturation enthalpy value (ΔH_D), showing that

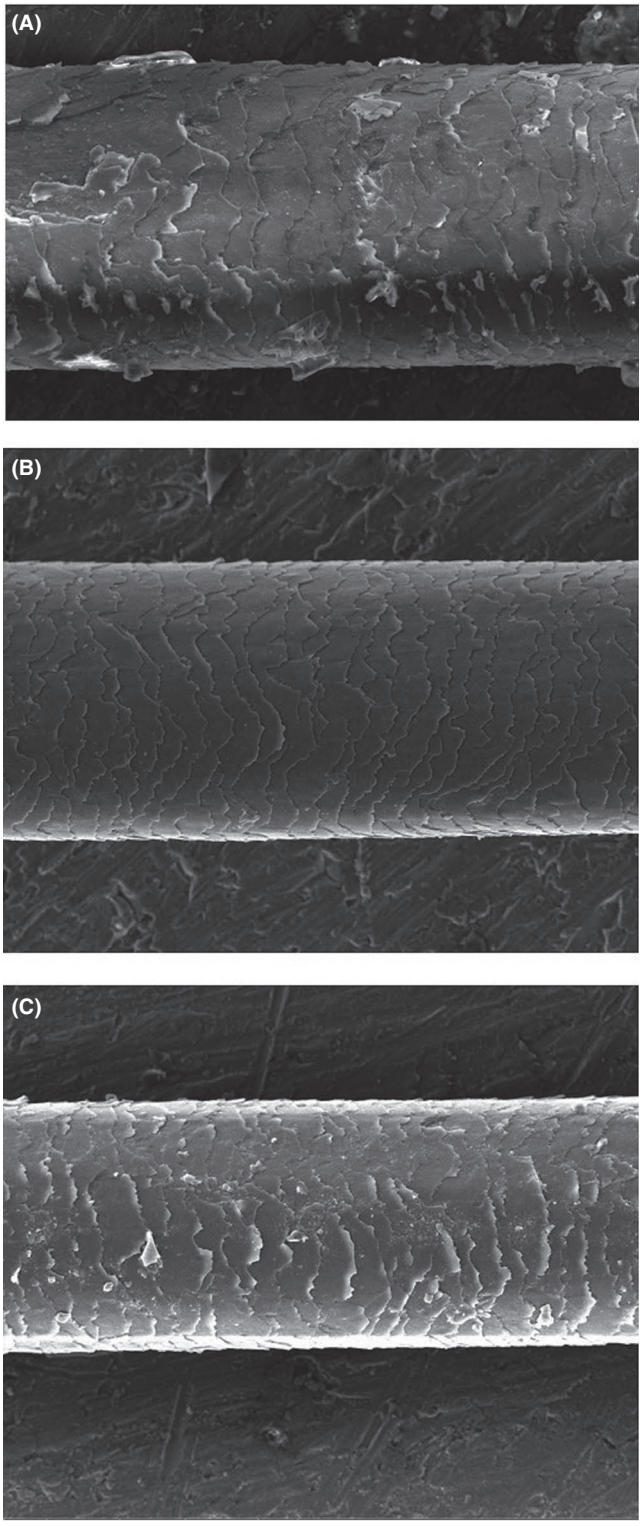


FIGURE 6 SEM image of hair samples: A, Virgin hair (2042×), B, Straightened hair (1800×), and C, Straightened hair washed five times (1800×)

this process weakens the hair. The same was observed in straightened tresses with formaldehyde, as higher the concentration of the product lower the enthalpy value.[21] And also in bleached tresses, besides the different treatment both affect the hair structure[15] and their keratin integrity.

The major decrease of tryptophan content in tresses from *Group 01*, combined with the tensile strength result, represented that the impairment in the structure was higher at pH 1.0. Bleached tresses presented less concentration of tryptophan, compared with the virgin hair,[9] even though the treatment is different from the study herein reported both caused impairment in the cortex.

It was possible to observe a color change in treated tresses, because the product oxidized the melanin present in the cortex. This effect was observed in others acid straightener, as the formaldehyde.[2]

With the ESEM images, it was possible to observe a uniform surface, because of the formation of a hydrophobic film when treated with this acid straightener, the same was observed in tresses treated with formaldehyde.[2]

And the tress treated and washed out (five times) had some parts of the film removed.

5 | CONCLUSION

In conclusion, the results showed that the acid straightener changes hair properties as combing, tensile strength, color, amino acid content and internal structure. And that the straightener's pH value has high influence in these properties. The presence of more hydrogen ions (H^+) as the pH value decrease caused more damage in the hair shaft and affected the elasticity of the fiber. It is important to control the pH value in order to avoid more damage and possible breakage of the shaft.

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CONFLICT OF INTEREST

The authors have no conflict of interest to declare.

ORCID

Alessandra Mari Goshiyama https://orcid.org/0000-0001-8800-7327

Cibele Rosana Ribeiro de Castro Lima https://orcid.org/0000-0002-2352-1007

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