

Evaluation of the performance of cosmetic products on reduction of porosity by measurement of the diffusion of red 80 dye solution.

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Abstract

Hair is a complex polymer that can absorb liquids and small particles through its structure. A complex net of interconnected microvoids formed mainly in the amorphous domain of the polymer. Different types of damage such as chemical treatments, thermal treatments, and others can degrade the amorphous phase increasing the amount of free space. The study of the reduction migration of liquids and small particles is the high interest to the cosmetic industry as the amount of microvoids is related to the hair's mechanical properties. In this study, we presented a methodology to study the effect of cosmetic products on porosity reduction. Indian Hair bleached twice, were treated with commercial cosmetic treatments (3 swatches per treatment) and then, the swatches were held in a straight position with the tip immersed in an aqueous solution of dye red 80 for 30min. After this time, the distance traveled by the dye was measured. All the treatments presented a lower distance of dye permeation in comparison to the control group. Among the products, the one that promises to repair disulfide bonds presents the highest reduction. The statistical analysis shows that the methodology was reproducible, was able to differentiate treatments, and this differentiation was maintained on the 2 experimental days.

Keywords: Hair Permeation, Hair Porosity, Hair Evaluation, Hair Integrity.

Introduction.

Human hair structure is a complex biological matrix characterized by three main layers: the cuticle, cortex, and medulla, cemented by cell membrane complex (CMC) [1][2][3]. The cuticle, comprising overlapping scales, serves as a protective barrier against external stressors. The cortex, the thickest layer, predominantly consists of keratin fibers arranged in a helical pattern, providing structural integrity, strength, and elasticity to the hair shaft. Melanin granules within the cortex determine hair color. The medulla, present primarily in larger hairs, contains a large concentration of lipids and contributes to overall structural integrity, though its precise function remains incompletely understood [1]. This high complexity of the hair structure organization leaves free spaces (microvoids) that allow substances to permeate the hair fiber. The permeation is influenced by different factors including pH of the environment, hair porosity, and quality of the hair.

Hair also plays an important role in the psychological development of humans, that use it as a way of expression of cultural heritage and personality [4][5]. In order to change the color of the hair or format, several chemical treatments can be used. Those chemical treatments, in order

to penetrate the fiber and make their actions, results in breakage of disulfide bonds (S-S), which are the main structural connecting bonds of the hair fiber [6][7], letting the fiber more fragile, damaged and increasing the mobility of the protein chains and consequently hair porosity [1][8].

Porosity can happen in different levels of the hair's macro and microstructure due to the rearrangement of the hair fibrils; the α -keratin helices are more organized while the, β -keratin sheets are dominant in the amorphous phase where there are more free space [4]. The pores are classified by their size in micropores (<20Å), mesopores (20Å – 500Å) and Macropores (>500Å), being the macropores located mainly in the medulla and the micropores and mesopores on the cortex [8]. The application of mechanical loading or chemical treatments (Damage) can induce the transition of the keratin from the α to the β configuration increasing porosity [4].

When hair is more porous, the absorption and desorption of substances is increased [9]; the sorption of water in the interior, plasticizes the fibers and affects all hair properties such as diminishing the resistance to breakage, increasing of frizz, difficulty to combing, shine, between others [7][10]. Thus, the study of the hair porosity is highly important for the cosmetic industry that is always in search for the development of formulations that improve hair's properties. Several formulations have been studied for the reduction of porosity such as, natural oils, treatment creams between others, but the techniques available for the identification of the effect are expensive, making them not suitable for screening of formulations. Taking this into account, this work has the objective to develop and present a practical and fast methodology that permits evaluate the actions of cosmetic products in the reduction of hair porosity, by measuring the extent of the sorption of a solution of water with dye red 80.

Materials and Methods.

Hair and Treatments

18 swatches of pre-cleaned and standardized Caucasian hair, 25cm in length and 1 g, were bleached twice. The mixture was prepared on a chapel using a commercial bleaching powder and 20 vol oxidant (hydrogen peroxide) in a proportion of 1:3 (w/w). It was applied 10g of mixture per 1g of hair and was left to rest for 35 min in a controlled room. In the end, the swatches were rinsed with tap water for 5min. After let the swatches get dry naturally by 24h in a controlled environment (55%RH \pm 5 and 22°C \pm 2), the swatches were divided into groups of three swatches and treated with commercial cosmetic products as shown in Table I.

| Group Name | Treatment |
|--|--|
| SLES 10% | Solution of Sodium laureth sulfate 10% in water. 0,2 ml/g of hair, massage 30s and rinse by 30s |
| Shampoo + Conditioner (SH + CD) | Shampoo: 0,2 ml/g of hair, massage 30s and rinse by 30s + Conditioner: 0,2 ml/g of hair, massage 30s, pause time 2min and rinse by 30s |
| Shampoo Baby | 0,2 ml/g of hair, massage 30s and rinse by 30s |
| Mask | 0,2 ml/g of hair, massage 30s, pause time 3min and rinse by 30s |
| Repairing Treatment | 0,2 ml/g of hair, massage 30s, pause time 5min and rinse by 30s |

Table I. Experimental design, product application list.

Measurements

Right after product application, the hair swatches were placed over a beaker with 1cm of the tip submerged in an aqueous solution of Red 80 (5mg of dye/ 100ml of water), pH \approx 6, as shown in Figure 1, during 30 min. After this time, the swatches were let dry naturally by 24h in a temperature-controlled room (55%RH \pm 5 and 22°C \pm 2) and then, the distance precured by the dye was measured with a scale; the measurements were performed by 3 different observers and the medium values were calculated from all the data collected. This experiment was repeated in 2 different days in order to check the reproducibility of the method.



Figure 1. Experimental array. 3 swatches per treatment group.

Statistics

To verify if there were differences between the measurements, statistical comparisons were performed on the software GraphPad Prism, version 8.3.4, using ANOVA one-way test followed by Tukey's post-test. Statistically significant differences between samples were checked with a p-value \leq 0.05. The comparison between measurements performed in different days was performed using an unpaired t-test with an 95% confidence interval on the same software. Statistically significant differences between samples were checked with a p-value \leq 0.05.

Results.

The results obtained of distance traveled by the colored solution on the hair swatches were tabulated and the graph is presented in the Figure 2.

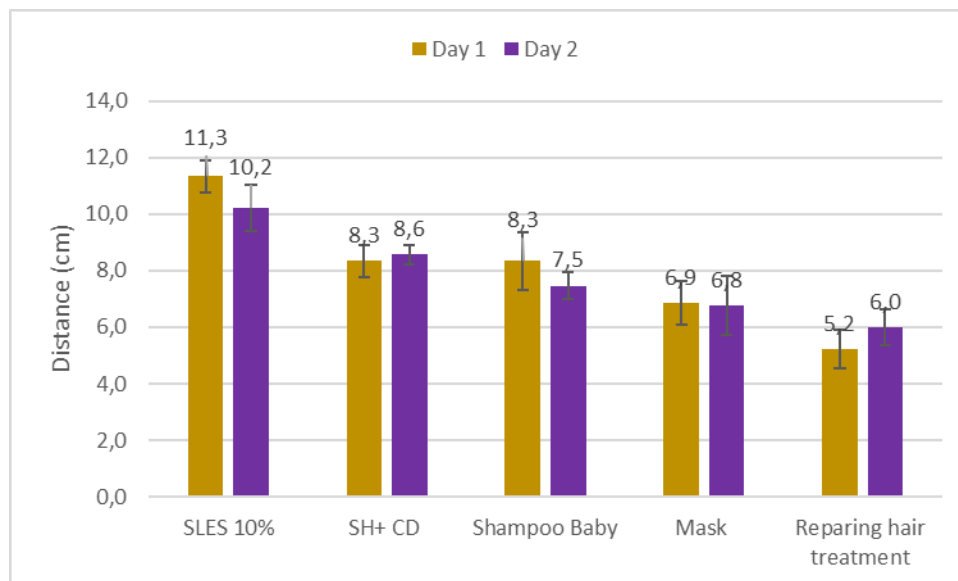


Figure 2. Traveled distance by the dye solution on the hair swatches treated with the different products on 2 different days.

The results shows that the application of cosmetic products change the distance traveled by the dye solution. On day 1, the distance traveled by the dye in the hair swatches treated with the control group (SLES 10%) was statistically significant higher than all the other groups; the distance traveled by the dye on the groups treated with shampoo + conditioner, shampoo Baby and mask presented no statistically significant differences between each other and the distance traveled by the dye on the group treated with the Repairing treatment was statistically significant lower than the distance traveled by the dye on the groups SLES10%, SH+CD, Shampoo Baby, but do not present statistically significant differences with the mask group.

Each group also was compared with the corresponding group on day 2. This statistical analysis shows that the distance traveled by the dye in each group on D1 was no statistically significant different with the distance traveled by the dye on each group on D2. Showing good reproducibility of the method.

Discussion.

Adsorption of substances have been used in the past for estimation of porosity of materials, being the only requirement that the material present a type IV adsorption isotherm (exist a hysteresis between the sorption and desorption curves) [11] [12]. The isotherm curve of water sorption/desorption on hair presented this type of behavior and several models has been developed to describe the shape of the curve [13] [10]. As the environment has high influence on the sorption behavior, the experiment was conducted in a controlled room.

As the keratin is hydrophilic, the porosity of the fiber is also affected by the amount of water, reaching maximum pore sizes when hair is wet [8], for this reason the experiment was performed with the wet hair maximizing the solution sorption and using the colorant as marker of the migration trough the fiber on the longitudinal direction. Direct Red 80 dye was selected for its availability and ease of visualization on bleached hair strands. There is also important to take in account the size of the dye Red 80 is higher than other available dyes on the market

[14][15], then is probable that the use of other dyes results in different migration rates. Further studies are needed to understand the influence of particle size on the migration rate of different substances within the hair; however, the results obtained are sufficient to achieve the project's objective, which is to develop a screening methodology for selecting products with efficacy on the reduction of hair porosity.

Porosity is commonly associated with hair damage. While hair is naturally porous, exposure to external aggressors, such as chemical treatments, can damage the keratin fiber and increase porosity [9]. In this experiment, the hair was subjected to two bleaching treatments to simulate such aggression, since discoloration is considered one of the most aggressive treatments, surpassing straightening and perming [16]. The groups treated with cosmetic products showed a reduction in dye solution migration compared to the control group. This reduction could be attributed to the decreased capillarity of the hair, as the cosmetic products penetrated the hair cortex and acted as a physical barrier, or to an increase in the hair's hydrophobicity, preventing water migration. Another noteworthy observation is that the treatment promising to repair/reconnect bonds showed the lowest migration of the dye solution, likely due to the decrease in hair micro voids related to structural restoration. Associating these results with measurements of the tensile strength of the fiber is recommended to determine if the reduction in porosity is related to a reduction in damage.

Conclusions.

The proposed methodology was able to differentiate treatment and it was reproducible, but as the measurement with 3 hair swatches presented a high variation making difficult to differentiate some of the cosmetic treatments. In order to reduce the variation one option is increase the number of swatches per group used on the study.

Between the tested groups the one that claims bond repair was the one that presented lower migration of the solution, probably due to the reduction of porosity by the combination of 2 factors; physical barrier and by the increase of covalent bonds that decrease the mobility of the hair proteins.

Taking in account all the results it possible to affirm that the presented methodology is a non-expensive option for screening of products that have the proposal of reducing the hair porosity without differentiating the mechanism of action of the product.

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Conflict of Interest Statement.

NONE.

References.

1. Velasco M V R, Dias T C, Freitas A Z, et al (2009). Hair fiber characteristics and methods to evaluate hair physical and mechanical properties. *Braz. J. Pharm. Sci.* 45(1):153-162.
2. Pötsch L and Moeller M R(1996). On pathways for small molecules into and out of human hair fibers. *J. Forensic Sci.* 41(1): 121-125.
3. Wortmann F J, Hardie K, Schellenberg N, et al (2023). pH-equilibration of human hair: Kinetics and pH-dependence of the partition ratios for H^+ - and OH^- -ions based on a Freundlich isotherm. *Biophys. Chem* 297:107010.
4. Müllner A R M, Pahl R, Brandhuber D, et al. (2020). Porosity at different structural levels in human and yak belly hair and its effect on hair dyeing. *Molecules* 25:2143.
5. Sedik H M, Gheida S F, Ibrahim W M, et al. (2020). Effect of hair straightening treatment on porosity and cysteine acid content of hair. *J Adv Med Med Res* 32(18):91-97.
6. Kuzuhara A (2014). Internal structure changes in bleached black human hair resulting from chemical treatments: A Raman spectroscopic investigation. *J. Mol. Struct* 1076:373-381.
7. Sinclair R D (2007). Healthy Hair: What is it?. *J Invest Dermatol. Symposium proceedings* 12:2-5.
8. Kaushik V, Kumar A, Gosvami N N, et al. (2022) Benefit of coconut-based hair oil via hair porosity quantification. *Int. J. Cosmet. Sci.* 00:1-10.
9. Hill V, Loni E, Cairns T, et al. (2014) Identification and analysis of damaged or porous hair. *Drug Test. Anal.* 6:42-54.
10. Evans T, (2012) Adsorption properties of Hair in: *Practical Modern Hair Science*. Allured Books ch 10: 333- 366
11. Brenner A M, Adkins B D, Spooner S and Davis B H. (1994) Porosity by small-angle X-ray scattering (SAXS): comparison with results from mercury penetration and nitrogen adsorption. *J Non-Cryst Solids*.185:73-77.
12. Rahman M M, Muttakin M, Pal A, et al. (2019) A Statistical approach to determine optimal models for IUPAC-classified adsorption isotherms. *Energies*. 12 :4565.
13. Barba C, Martí M, Manich A M, et al. (2010) Water absorption/desorption of human hair and nails. *Thermochim. Acta* 503-504:33-39
14. Oliveira R A G, Zanoni T B, Bessegato G G, et al. (2014) A química e toxicidade dos corantes de cabelo. *Quim. Nova*, 37(6):1037-1046.
15. Ardejani F D, Badii K, Limaee N Y, et al. (2008) Adsorption of direct red 80 dye from aqueous solution onto almond shells: effect of pH, initial concentration and shell type. *J. Hazard. Mater.* 151:730–737.
16. Di Foggia M, Boga C, Michelletti G, et al. (2021) Structural investigation on damaged hair keratin treated with α,β -unsaturated Michael acceptors used as repairing agents. *Int. J. of Biol. Macromol.* 167:620-632.