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Water content of hair and nails

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ABSTRACT

Water content plays an essential role in human keratinized tissues such as hair and nails. However, daily routines impair the keratin structure of hair and nails, inducing a decrease in their water content. A new methodology for the determination of the internal and external water content of keratinized tissues was optimized. The water content of untreated human hair and nails was studied. Results showed differences in the water content between hair fibers and nails. Furthermore, hair and nails were subjected to a number of treatments and the water content was determined. Evaluation of the moisture content in treated hairs showed that chemical treatments damaged hair fibers, resulting in a pronounced decrease in their external water content. However, the chemical treatments of nails impaired their integrity and led to a decrease in the internal water content.

1. Introduction

Human hair is structured in highly organized strata that are very resistant to external stimuli. Its high stability is due to stiffness of the central α-helical core of keratin and to a high number of disulfide crosslinks [1]. Although weather and oxidants (i.e., environmental factors) can give rise to hair damage, morphological changes can result from daily care routines. In particular, permanent wavings, straightening or relaxing and bleaching during hair coloring processes are major causes of hair damage [2,3]. These alterations are attributed to poor manageability, dryness, brittleness, loss of shine and decreased strength (fiber breakage).

Reactive cosmetic treatment of hair often impairs the fiber structure. The resulting damage has an adverse effect on water absorption by hair at ambient humidities and leads to an increase in swelling or to liquid retention on wetting [4]. It is well known that tensile properties are related to the moisture level within the hair fiber. Water molecules are able to penetrate hair and plasticize the components of hair fibers. Moreover, the force required for a given extension length is reduced as the moisture content of the hair is increased [5].

Nails are mainly composed of a hard horny plate known as the nail plate. The nail plate is composed of three histological layers: the dorsal, intermediate and ventral plates. Like hair, the nail plate consists of hard keratin and lipids [6]. The cells of the nails are produced continuously and become keratinized, compacted and cemented together [7]. The nail plate is a hard keratin structure that is recognized as an indicator of overall health [6]. The nail plate contains approximately 10.5% cystine, which is responsible for holding the nail plate together, giving it the structural integrity required for its functions.

Despite being resistant to external influences, the nails change their physical properties when they are soaked in water during hand washing and bathing. They become soft and their flexibility increases [8]. The degree of hydration is thought to be the most important factor influencing the physical properties of the nail [9]. Frequent washing of nails can increase their brittleness [10]. It has been reported that repeated hydration and dehydration of nail plates cause delamination, dryness and brittleness, which is a condition known as lamellar dystrophy [9]. This condition has been attributed to (1) the diminished capacity of the nail plate to hold water as a result of a change in the ability of the protein structure to bind water and (2) a reduced water content between the corneocyte cells. It goes without saying that lamellar dystrophy can be prevented by increasing the hydration of the nail and improving the barrier function.

Several studies have been carried out to determine the hydration of human hair and nails given the crucial role of hydration in keratinized tissues. Moisture sorption isotherm of keratins has been for a long time deeply studied [11]. Many factors were demonstrated to influence the isotherm characteristics. For this, the hair samples must come from a same initial source and the experimental conditions must be well established. A number of techniques such as infrared spectroscopy and transonychial water loss have been performed *in vivo* to determine nail hydration [6,12–14]. Techniques such as Raman spectroscopy [1], gravimetric [15] and differential scanning calorimetric measurements [16] have been used to determine *in vitro* hydration in hair and nails.

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In the recent literature few papers deal with the thermal analysis of hair and the use of these techniques on the study of specific effects of chemical and cosmetic treatments on human hair. Some results are presented using DSC [17,18], properties and interactions of the main morphological components of human hair are considered to be specifically related to various aspects of their thermal stability. TG has been proven to be a very efficient method of studying the evaporation of cosmetics [19]. Furthermore, the investigation of the amino acids by TG–MS was helpful to study the thermal fragmentation of the hair samples [20]. Moreover, in earlier works [21–22] an electric moisture balance has been employed to measure water loss in cosmetic treated hair samples. In a parallel way we studied the internal and external water content of untreated human hair and nails. A simple methodology based on thermogravimetric studies to determine the water content determination was optimized.

2. Materials and methods

2.1. Materials

Acetone, citric acid monohydrated and hydrogen peroxide 30% were supplied by Merck (Darmstadt, Germany), ammonium persulfate by Amresco (Ohio) and sodium hydroxide by Carlo Erba Reagenti (Rodano). Nail plates were obtained from several healthy volunteers after being cut by themselves. Natural red hair tresses (with 20 cm length) were purchased from De Meo Brothers Inc. (New York).

2.2. Hair treatments

Hair was chemically damaged by treatments commonly used in hair dressing such as:

- *Bleaching*: Hair was placed in a *bleaching solution* (9% H_2O_2, 1% ammonium persulfate, pH 8.3,) for 3 h on a rocking table; then it was rinsed with water and dried in air.
- *Relaxing*: Hair was placed in a 2.5% NaOH solution for 30 min on a rocking table and then was rinsed with water for 5 min. Next it was placed in a 9.5% citric acid solution for 5 min and then it was rinsed with water for 10 min. Finally, the hair was separated carefully while wet and it was dried in air.

2.3. Nail treatments

Nail plates collected from eight volunteers (all females) with a mean age of 35 ± 6 were subjected to two different treatments:

- *Hydration/dehydration cycles*: Nail plates were subjected to several cycles of hydration/dehydration to mimic daily wear and tear. The cycles consisted in immersing the nails plates in water for 20 min and then dry them in the heater at 40 °C for 2 h. Eight hydration/dehydration cycles were performed (H/D8).
- *Acetone treatment*: Two treatments were performed: (1) a treatment where the nail plates were ultrasonicated in acetone for 30 min and then air dried (A1) and (2) a treatment where nails were ultrasonicated in acetone for 30 min three times and then air dried (A3).

2.4. Moisture content measurements

To measure the moisture content, a thermogravimetric analysis (TGA) instruments (TG-50, Mettler Toledo) were employed. Before measuring the moisturizing effect, the hair and nails were kept in a humidity controlled box (22 °C, 50%rh) for 24 h. Samples were transferred to an aluminum crucible, weighed and sealed for an elapsed time of 30 s. The crucible was then placed in the TGA balance where it was pierced. Measurements were conducted in an atmosphere of dry a N_2, where a purge at 30 mL min^{-1} was employed.

First, hair and nail samples were heated from 25 °C to 300 °C at 10 °C/min (Procedure A). Next, the hair sample was then heated from 25 °C to 65 °C at 20 °C/min, and a temperature of 65 °C was maintained for 40 min, which is assumed to be the normal temperature used by a hair dryer. Thereafter, the temperature was increased from 65 °C to 180 °C at 20 °C/min, and was kept at 180 °C for 30 min to evaporate all the water contained in hair [21,22]. As regards the nails, the samples were heated from 25 °C to 65 °C at 20 °C/min, and a temperature of 65 °C was maintained for 60 min. The temperature was then increased from 65 °C to 180 °C at 20 °C/min, and kept at 180 °C for 60 min to evaporate all the water contained in the nails (Procedure B).

Nails (taken initially from eight volunteers) have been grouped to form a nail sample. All nails and hair samples TGA measurements have been done three times. Mean values and standard deviations for external, internal and total water content of each sample were calculated.

3. Results and discussion

3.1.1. Thermogravimetric analysis procedure to determine water content of hair and nails

The loss of moisture content of a sample with the increase in temperature can be followed by thermogravimetrical analysis (TGA). Different analyses were performed to optimize the method to determine the water content of hair and nails.

Two decomposition temperatures were obtained in initial experiments, where the hair samples were heated from 25 °C to 300 °C at 10 °C/min (Fig. 1). The first mass loss from 40 °C to 180 °C, corresponded to the water content of the sample and the second, starting at 200–220 °C, corresponded to the decomposition of the keratin structure.

Preliminary experiments concluded that a suitable range of temperature was from 40 °C to 180 °C for the determination of water content in the keratinized tissues of hair samples. These results were supported by other authors who studied the water binding properties of different treated hairs in the same temperature range [21,22]. In order to differentiate between external and internal water of the keratinized tissue, two successive heat treatments were carried out on the hair samples. Water loss was determined

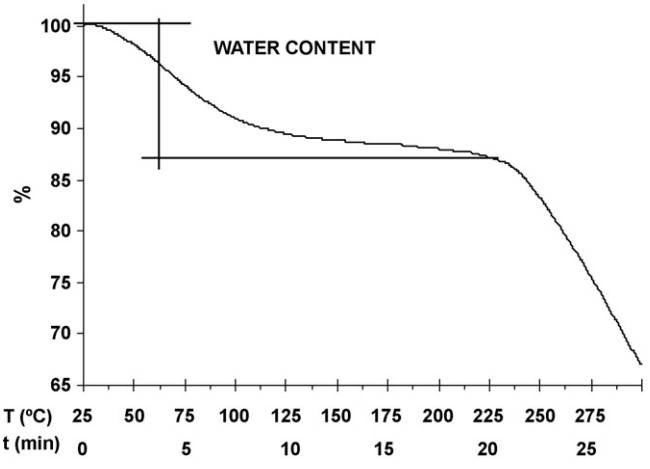

Fig. 1. Decomposition process of a hair sample with temperature (Procedure A).

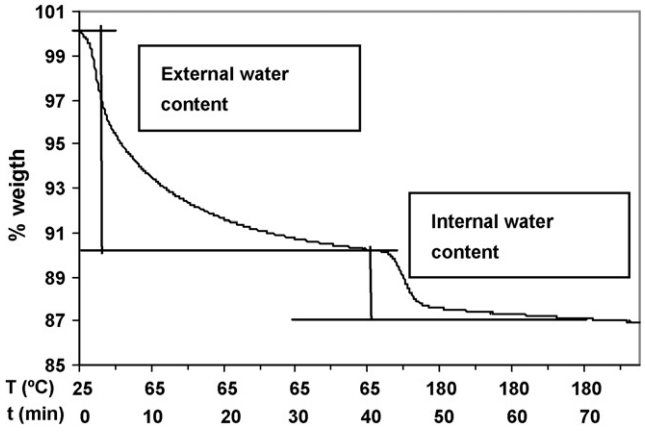

Fig. 2. Determination of water content of the hair sample (Procedure B).

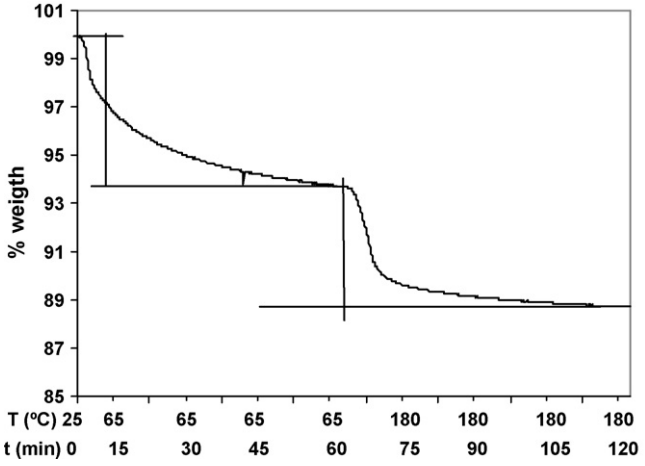

Fig. 4. Determination of water content of the nail sample.

first in the temperature range of 25–65 °C at 20 °C/min, maintaining the temperature at 65 °C for 40 min, and the second from 65 °C to 180 °C at 20 °C/min, keeping the temperature at 180 °C for 30 min. This procedure proved to be suitable for the determination of the external and internal water contents (Fig. 2).

Same studies were performed for the determination of water content of the nail samples. When heating the nails from 25 °C to 300 °C at 10 °C/min two different decomposition temperatures were obtained, as in the case of hair. Results showed (Fig. 3) that the differences between the two processes were less marked. The first process could be considered in the temperature range of 25–200 °C. Beyond this temperature, the slope of the curve changed, indicating the start of the second decomposition.

The preliminary results suggest that water could be more strongly linked to the nails than to the hair fibers. Accordingly, nail samples were studied in the temperature range from 25 °C to 180 °C, as in the case of hair. However, a modification was introduced into the heating procedure. Given the difficulty of water release in nails, the nails were kept longer at the final temperature of each heating process. Therefore, for the determination of water content of nails, the sample was heated from 25 °C to 65 °C, maintaining this temperature for 60 min and then increasing the temperature from 65 °C to 180 °C, while maintaining this final temperature for 60 min (Fig. 4). This methodology enabled us to determine the water content of the nail samples and to differentiate between the external and the internal water contents.

The confidence of the methodology allows us to compare the moisture content of these two keratinized tissues. Table 1 shows

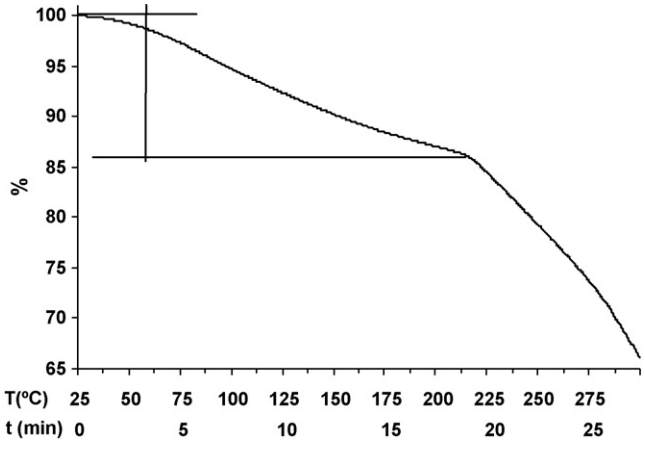

Fig. 3. Decomposition process of a nail sample with temperature (Procedure A).

Table 1
Total moisture content, external and internal water obtained for human hair and nails (mean values ± SD).

	External water (%)	Internal water (%)	Total moisture content (Procedure B, %)
Hair	11.29 ± 0.39	3.68 ± 0.12	14.97 ± 0.37
Nails	5.78 ± 0.86	6.00 ± 0.76	11.78 ± 0.62

that hair fibers have higher values of total moisture content than nails at the same relative humidity. These results are consistent with earlier studies using other methodologies. Studies have shown that as a result of heating clipped nails and recording their prehydration and posthydration weight, the water content was 11.90% [14]. On the other hand, a DSC experiment showed that the water content for human hair was about 15% [23].

Furthermore, a different pattern is observed for the loss of moisture content of hair and nail samples (Figs. 2 and 4). Results show that hair fibers lose 75% of their total moisture content in the first heat treatment whereas nails lose only 50%. Moreover, the internal water content was higher in nails than in hair fibers. This can be explained because of the lower nail permeability related to the hair fibers, resulting in a higher difficulty for the water release through the nail structure. This behavior suggests that water molecules may be more strongly linked in nails than in hair fibers.

Evaluation of moisture content by this methodology could be used to determine fiber modification due to cosmetic treatments or degradation processes.

3.2. Moisture content of treated hair

Hair fibers were chemically modified with treatments such as bleaching and relaxing, which are commonly used for hair care. Some hairs were left untreated. The two hair treatments employed impair the keratin structure of the hair. Bleaching is based on an oxidizing agent whereby melanin and other hair components are oxidized [24]. Relaxing transforms the basic structure of the hair shaft and results in the penetration of the cortex, the breakage of disulfide bonds in the keratin, and in the capping of bonds so that they cannot re-form chemically, thus preventing the hair from curling again [25].

Thermogravimetric analysis (TGA) for untreated (UT), bleached (B) and relaxed (R) hair samples are shown in Fig. 5. Evaluation of the total moisture content of the different hair samples demonstrates that these chemical hair treatments impair the hair fibers, reducing their moisture content with respect to the untreated hair fibers (Table 2). This decrease is much more pronounced in the case

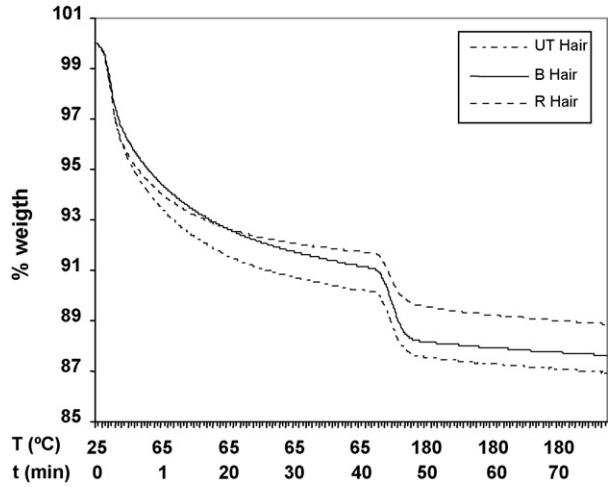

Fig. 5. TGA for untreated (UT), bleached (B) and relaxed (R) hair samples.

of the relaxed hair fibers (a decrease of its total moisture content of 7% when compared with the untreated hair moisture content). Results for the external and internal water contents (Table 2) show that the fiber surface suffers greater damage because of the chemical hair treatment. This is corroborated by the similar internal water content of all fibers and by a marked decrease in the external water content (3.5% for the bleached and 9.5% for the relaxed hair sample with respect to the external water of the untreated hair).

It is well known that tensile properties are related to the moisture level within the hair fiber [5]. An earlier study of strength measurements of untreated, relaxed and bleached hair [26] showed a decrease in the mechanical properties of the treated hairs, especially in the case of the relaxed hair, indicating a deterioration of the treated fibers. In our study, the diminution in the water content of treated hair fibers could result in the deterioration of the hair fibers. The water content would therefore enable us to evaluate the condition of the hair fiber.

3.3. Moisture content of treated nails

The water content of the different nail plate samples was evaluated by a thermogravimetrical analysis with two heat treatments as described in Section 2.

Nails were subjected to two treatments that caused a deterioration of their structure. Hydration/dehydration cycles were prepared to mimic daily wear and tear. Acetone treatments were carried out given the association of this product with nail brittleness and discoloration [27].

TGA for untreated nails (UT), nails subjected to eight hydration/dehydration cycles (H/D8) and nails subjected to 1 and 3 acetone treatments (A1 and A3) are shown in Fig. 6. Results show that nails subjected to acetone treatment and to repeated hydration/dehydration cycles lead to a marked decrease in their total moisture content (Table 3), indicating that these treatments increase nail dehydration and impair nail integrity. Acetone treatment (A1) and hydration/dehydration cycles (H/D8) result in a decrease of about 11% in the total moisture content of the nail. The

Table 2
Total moisture content, external water and internal water for untreated, bleached and relaxed hair samples (mean values ± SD).

	Total moisture content (%)	External water (%)	Internal water (%)
Untreated	14.97 ± 0.37	11.29 ± 0.39	3.68 ± 0.12
Bleached	14.69 ± 0.35	10.88 ± 0.34	3.81 ± 0.14
Relaxed	13.78 ± 0.05	10.22 ± 0.06	3.56 ± 0.09

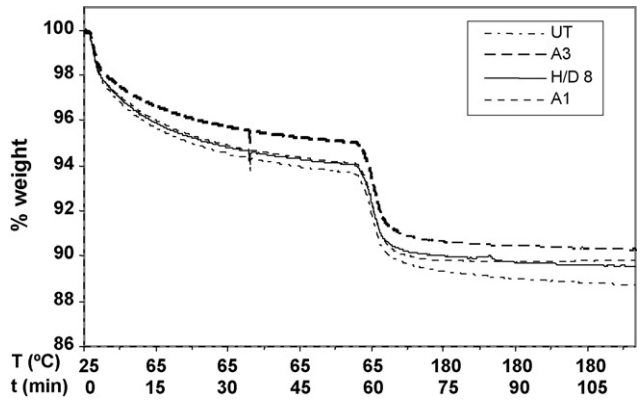

Fig. 6. TGA for untreated (UT), acetone (A1 and A3) and hydration/dehydration cycles (H/D8) nail samples.

Table 3
Total moisture content, external water and internal water for untreated nails and nails subjected to acetone and hydration/dehydration cycles treatments (mean values ± SD).

	Total moisture content (%)	External water (%)	Internal water (%)
Untreated	11.78 ± 0.62	5.78 ± 0.86	6.00 ± 0.76
Acetone (A1)	10.54 ± 0.36	5.67 ± 0.29	4.87 ± 0.57
Acetone 3 (A3)	10.14 ± 042	5.58 ± 0.54	4.56 ± 0.37
Hydration/dehydration (H/D8)	10.44 ± 0.32	5.82 ± 0.36	4.61 ± 0.12

nails that underwent the three acetone treatments (A3) induce a decrease of about 14%.

In the case of nails results show that the most marked reduction occurred in the internal water content.

Given the interest in maintaining nails in good condition, the maintenance of the optimum water level is of paramount importance [6]. Earlier studies showed that the water content of nails varies with ambient conditions such as temperature and relative humidity [28]. Moreover, it has been reported that the nail plate becomes soft and tends to be double layered when its water content exceeds 20% and tends to split when the water content is below 10% [29–31]. Our methodology proves to be suitable for determining the water content of normal and treated nails. Furthermore, the water content, which can be fractionated into external and internal water, may vary due to chemical treatments or disease.

4. Conclusions

The moisture content of keratinized tissues such as human hair and nails was evaluated using a thermogravimetric methodology. This methodology was optimized to determine external and internal water contents of two keratinized tissues. There were differences in the water content between hair fibers and nails. The water content of the hair samples was increased with respect to the nail samples. Furthermore, nails released water with more difficulty.

It is possible to differentiate between external and internal water contents of these keratinized tissues. Although similar amounts of water were found in the external and internal nail fractions, the moisture content was higher in the surface of the hair fibers. Chemical treatments damaged hair fibers, resulting in a decrease in their external water content. Furthermore, nail treatments led to a reduction in the internal water content, impairing nail integrity.

The evaluation of external and internal water contents proves to be a suitable methodology to determine the integrity of these two keratinized tissues.

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