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Water absorption/desorption of human hair and nails

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ABSTRACT

Water produces changes in the properties of human keratin fibers, such as hair and nails, and therefore plays an important role in their cosmetic performance. Reactive cosmetic treatments of hair and nails often impair fiber structure, resulting in an adverse effect on water absorption. The moisture absorption/desorption isotherm curves for untreated hair and nails and the kinetics of these processes are studied in this work. The effects of different chemical cosmetic treatments on hair and nail water absorption are also evaluated. The isotherms for these human keratinized tissues behaved as expected, with a characteristic hysteresis between moisture uptake and desorption. Human nails showed a lower moisture regain and a much lower diffusion coefficient with respect to human hair. Permeability, directly related to the diffusion coefficient, increased with the degradation treatment. The diffusion coefficient was important in determining the integrity of keratin fibers.

1. Introduction

Human hair is a heterogeneously composed natural semi-crystalline polymer of α-keratin. Hair presents three main components: cuticle, cortex and medulla. The cortex is made up of macrofibrils, microfibrils and cell membrane complexes [1]. Reactive cosmetic treatment of hair often impairs fiber structure. The resulting damage has an adverse effect on hair water absorption at ambient humidities and leads to an increase in swelling or to liquid retention on wetting [2].

Nails are mainly composed of a hard horny plate known as the nail plate. Like hair, the nail plate consists of hard keratin and lipids [3]. The nail plate is an indicator of overall health [3]. The degree of hydration is thought to be the most important factor influencing the physical properties of the nail [4]. Frequent washing of nails can increase their brittleness [5]. It has been reported that repeated hydration and dehydration of nail plates causes delamination, dryness and brittleness, which is a condition known as lamellar dystrophy [4]. 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 corneocytes cells. It goes without saying that lamellar dystrophy can be prevented by increasing the hydration of the nail and improving the barrier function.

Water changes a wide variety of properties of human keratin fibers, such as hair and nails, and therefore plays an important role in their cosmetic performance. Water diffusivity in wool, horn, and the corneocyte phase of stratum corneum considerably increases with increased water content in the tissue [6]. However, water sorption of wool is well documented [7] whereas there are few data on human hair and nails.

The amount of water in a sample may be expressed in terms of either regain or moisture content. Regain is the mass of adsorbed water over the mass of dry sample, whereas moisture content is the same mass over the mass of the sample [8].

The determination of water sorption isotherm by isothermally applying discrete, cumulative humidity changes involves dynamic and static aspects from which diffusion coefficients and equilibrium water contents are deduced [9]. Time/absorption isotherms provide a complete description of the absorption phenomenon under particular conditions such as initial regain of the sample, temperature and relative humidity [8]. Moisture sorption isotherm of keratins has been for a long time deeply studied and models specifically developed for describing the shape of the moisture sorption and desorption can be found. The Vrentas and Vrentas model emphasizes the role of the glass transition in generating the sigmoidal shape of the adsorption isotherm [10]. In another work, the uptake of water by polar polymers was described by the Flory–Huggins equation [11].

It is common knowledge that there is a good correlation between the number of water molecules calculated that exist in a monolayer and the number of polar side chains using the classic Brunauer, Emmet and Teller (BET) multilayer sorption equation. This suggests that each polar group initially sorbs one molecule

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of water followed by multimolecular sorption at higher humidity [12]. The BET equation is used because its simplicity and the International Union of the Pure and Applied Chemistry (IUPAC) approval. However, the Guggenheim, Andersen and de Boer (GAB) sorption equation also provides monolayer sorption values and has become more popular because the range of relative vapour pressure interval is much wider than that of the BET equation [13]. The BET and the GAB isotherms are closely related since they are based on the same statistical model. The GAB is an improvement on the BET model and shares with it the two original BET constants: (a) the monolayer capacity Wm, and (b) the energy constant Cg.

The moisture absorption/desorption isotherm curves for untreated hair and nail samples and the kinetics of these processes are discussed in this work. To this end, sorption isotherms were modeled according to the GAB model not used so far for keratins. The effects of different chemical cosmetic treatments on hair and nail water absorption were also evaluated. The apparent diffusion coefficients were calculated.

2. Materials and methods

2.1. Materials

Acetone, hydrogen peroxide 30% and thioglycolic acid were supplied by Merck (Darmstadt, Germany) and ammonium persulfate by Amresco (Ohio, USA). Nail plates were obtained from several healthy volunteers who cut their own nails. Natural red hair tresses (with 20 cm length) were purchased from De Meo Brothers Inc (New York, USA).

2.2. Hair treatments

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

- *Bleaching (B Hair)*: Hair was placed in a *bleaching solution* (9% H_2O_2, 1% ammonium persulfate, pH 8.3,) for 3 h on a rocking table, rinsed with water and dried in air.
- *Perming (P Hair)*: Hair was placed in a *perming solution* (8% thioglycollate, pH 8) for 3 h on a rocking table, rinsed with water and placed in a neutralizing solution (2.5% H_2O_2, pH 3) for 30 min. It was then rinsed again and dried in air.

For comparison, tresses of virgin hair were kept as controls (UT Hair).

2.3. Nail treatments

Nail plates collected from 8 volunteers (all females, 5 never lacquered and 3 occasionally lacquered) with a mean age of 34 ± 7 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 nail plates in water for 20 min and then drying them at 40 °C for 2 h. Eight hydration/dehydration cycles were performed (H/D8 Nail).
- *Acetone treatment*: The nail plates were ultrasonicated in acetone 3 times for 30 min at 40 °C and then air dried (A3 Nail).

For comparison, virgin nails were kept as controls (UT Nail).

2.4. Sorption experiments

Absorption and desorption curves were obtained in a thermogravimetric balance equipped with a controlled humidity chamber, the Q5000SA Sorption Analyzer (TA Instruments, New Castle, USA). The weight of the keratin samples analyzed ranged between 6 and 9 mg. All experiments were conducted at 25 °C with a total gas flow of 200 ml/min and followed the same measuring procedure:

1. *Initial drying*: Temperature 60 °C and 0% relative humidity (RH) overnight. The sample remains in this step until its mass reaches equilibrium (arbitrarily defined by a change in mass of less than 0.02% per minute for 10 min).
2. *Pre-stabilization*: Temperature 25 °C, 0% RH and then initial absorption kinetics at 5% RH.
3. *Absorption curve*: The sample previously stabilized at 5% RH is subjected to absorption tests progressively increasing in steps from 10% up to 95%, the sample being stabilized at 95% RH after the last step. The sample remains in each step until its mass reaches equilibrium (arbitrarily defined by a change in mass of less than 0.02% per minute for 10 min).
4. *Desorption curve*: The sample stabilized at 95% RH after the absorption process kinetics is subjected to desorption tests progressively decreasing in steps from 10% down to 5%, the sample being stabilized at 5% RH after the last step. The sample remains in each stage until its mass reaches equilibrium (arbitrarily defined by a change in mass of less than 0.02% per minute for 10 min).

The high reproducibility of these measurements was established in the validation study of this instrument in which three replicates of a single sample gave essential coincident sorption isotherms. For this reason, and given the long time needed for a measurement (2.5 days), only one measurement was performed for each sample.

Sorption isotherms are generally described by mathematical models based on empirical and/or theoretical criteria which can be found in the literature. One of the most commonly used equations is that of the Guggenheim–Anderson–de Boer (GAB) model. It has a theoretical background and its parameters provide a physical meaning to the sorption process, when compared with empirical models. The GAB model is based on the monolayer moisture concept and gives the value of the monolayer moisture content of the material [14]. The GAB model has proved to be applicable in hydrophilic polymers [15,16] and food [17] systems and has considerable theoretical justification [18]. Thus, in this work, sorption isotherm data were modelled according to the GAB model in line with other authors [19,20]. Table 1 shows the sorption isotherm and

Table 1
GAB model and parameters used to fit the experimental sorption data.

Model	Mathematical equation
GAB [21]	$W = \mathrm{Wm}\,\mathrm{Cg}\,Ka_w/[(1 - Ka_w + \mathrm{Cg}\,Ka_w)]$
Parameter	**Definition**
a_w	Water activity expressed as vapour relative pressure p/p_0, where p_0 is the saturated vapour
W	Equilibrium moisture content at aw in g sorbed/100 g of sorbent on dry basis
Wm	Monolayer moisture content in g sorbed/100 g of sorbent on dry basis d.b.
Cg	Energy constant related to the difference between the free enthalpy of the water molecules in the pure liquid state and in the monolayer. This is proportional to the rate between both the attachment and the escape rate constants of the primary sites.
K	Ratio between the standard vapour pressure of the liquid and the vapour pressure of the sorbate in the secondary (upper) layers. Proportional to the rate between the attachment rate constant and the escape for all higher layers.