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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.

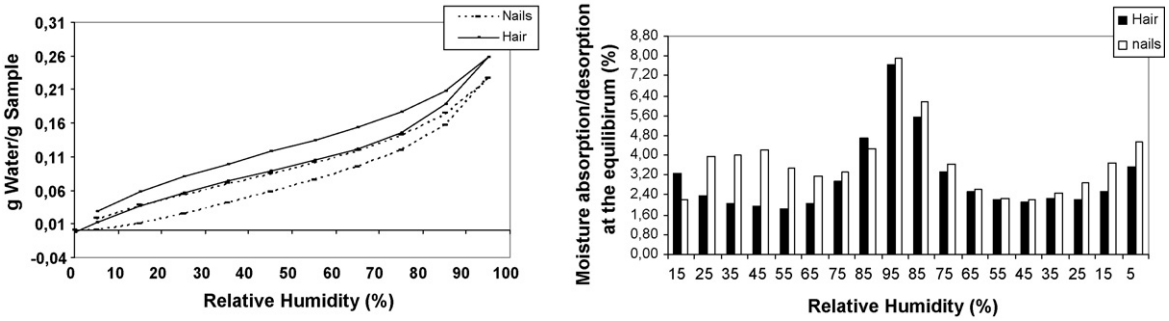

Fig. 1. Water sorption isotherms and moisture absorbed/desorbed at equilibrium in regain (%) for human hair and nails.

the parameters used to fit the experimental sorption/desorption data. The goodness of the fit was evaluated by the determination coefficient (R^2).

Moisture sorption/desorption tests on hygroscopic samples take very long time to reach the equilibrium, although the most important interchange of water is done at the initial steps. Therefore, in order to shorten the testing time some conditions are fixed. Although at this point the regain at the equilibrium has not been reached properly, the regain at the equilibrium R_∞ can be calculated by fitting the appropriated model. Therefore, the absorption/desorption curves of each step have been fitted to the following kinetic model [8]:

$$R(t) = \frac{Bt^C}{A^C + t^C}$$

$R(t)$ is the regain of the sample at time t, B the regain at the equilibrium (R_∞), A coincides with the time of half absorption ($t_{1/2}$) and c is a power coefficient of each step.

The application of the non-linear regression procedures obtains the best estimates of the model parameters yielding B, A and c, which enable us to calculate the asymptotic regain at equilibrium R_∞ and the half absorption time $t_{1/2}$ and rate $v_{1/2}$. The non-linear regression requires unbiased initial estimators of the model parameters that are given by the linear regression between $t/R(t)$ and t through the straight line $t/R(t) = \alpha + \beta t$, where α/β and $1/\beta$ are, respectively, the initial estimators of A and B [8].

The diffusion coefficient was obtained using the method applied by Vickerstaff [22] to study the diffusion of dyes within the fibers. It appears that the diffusion is well fitted by an expression derived from Fick's equation applied to moisture diffusion. This expression gives satisfactory results in the early stages of moisture absorption as in the case of those obtained in dye diffusion. If the fractional absorbed moisture is plotted against the square root of the absorption time, the points should lie on a straight line:

$$\frac{R(t)}{R_\infty} = \sqrt{D_A}\sqrt{t}$$

The slope is considered to be the square root of the apparent diffusion coefficient D_A of the moisture. If the apparent diffusion coefficient is measured over sample mass instead of over sample surface, is measured in min^{-1}.

2.5. Data treatment

The ANOVA variance analyses have been used to determine significant differences between values obtained from different treatments (significance level accepted $^*p < 0.05$) using the Statgraphics® program.

3. Results and discussion

The physical properties of keratinized tissues are closely related to their water content [6]. Water uptake and desorption isotherms for human hair and nails were evaluated by the software provided by TA Instrument and are shown in Fig. 1. The isotherms for these human keratinized tissues behaved as expected with a characteristic hysteresis between uptake and desorption similar to that observed in wool and porcupine quills [23]. The shape of the isotherm reflects the manner which water is bonded to the system. In the field of water vapour sorption by a solid sorbent, moisture sorption hysteresis is the phenomena as a result of which two different paths between sorption and desorption are observed. The extent of hysteresis is related to the nature and state of the components of the sample, reflecting their potential for structural and conformational rearrangements, which alter the accessibility of the water to the energetically favourable polar sites [24,25]. The shape of the equilibrium water sorption isotherms found for hair and nails can be described by a Type II isotherm with a small amount of water persisting at a very low relative humidity and a large increase at a high relative humidity.

A maximum regain of 25.87% for hair and 22.77% for nails occurred at 95% relative humidity (Table 2). These first results showed differences in the moisture content of these human keratinized tissues and are consistent with earlier studies using other methodologies [26,27].

The moisture absorbed and desorbed at the equilibrium in each RH step (Fig. 1) is evaluated fitting the sorption results to a kinetic model which considers that the sample remains at each humidity step until it reaches equilibrium ($t = \infty$). Following this, a different behavior between hair and nails samples is found. Nails take much longer to reach equilibrium than human hair and the moisture absorbed and desorbed at equilibrium achieves higher values for nails than for the hair sample. Even the higher amount of moisture obtained at the equilibrium for nails, the sorption results provided by the TA instrument with a higher moisture for hair can be con-

Table 2
Maximum moisture regain, GAB monolayer capacity (Wm), GAB energy constant (Cg), GAB determination coefficient (R^2), total time to reach equilibrium (t_T) and apparent diffusion coefficient (D_A) (mean value ± SD) for human hair and nails.

	Regain at 95% RH (%)	Wm (%)	Cg	R^2	t_T (min)	Mean D (min^{-1})
Hair	25.87	7.487	6.706	0.9976	3204.22	0.0163 ± 0.007
Nails	22.77	1.611	0.948	0.9981	4925.85	0.0042 ± 0.005

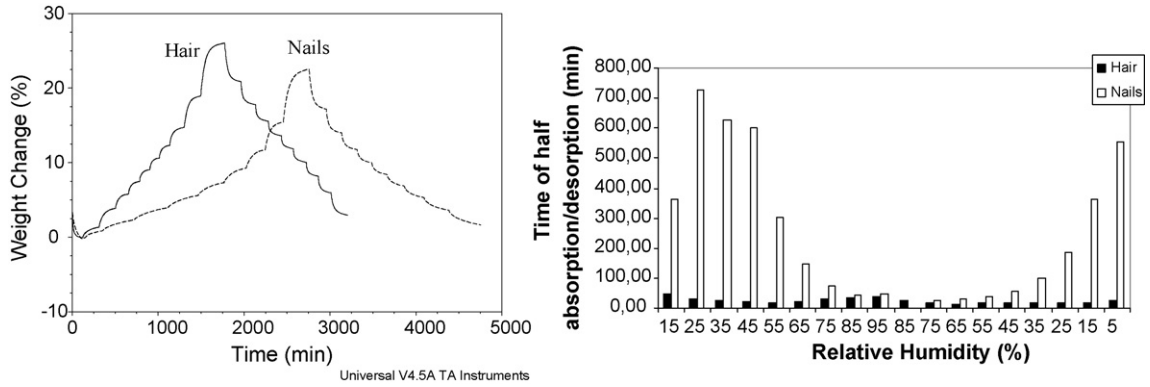

Fig. 2. Moisture uptake as a function of time and time of half absorption/desorption in min for human hair and nails.

sider more realistic because the rapid changes of humidity in real life would not allow to reach equilibrium at $t = \infty$.

The regression of the experimental sorption data by the GAB model yields values of Wm, the monolayer capacity, and Cg, the energy constant [13]. A good fit of the GAB model to the uptake and desorption data was achieved ($R^2 > 0.997$). The values obtained are shown in Table 2. Monolayer capacity values and energy constant, which are much higher for human hair related to human nails, confirm the differences in water sorption between these two human keratinized tissues.

Estimation of the kinetics of the moisture uptake and loss is a good strategy for obtaining more detailed information about the structure integrity of a given sample. There were significant differences in the rate at which human hair and human nails reached equilibrium. Curves are depicted in Fig. 2. Results show that nails take much longer to reach equilibrium, especially in the absorption process, than human hair. The nail plate is composed of highly compacted keratinized cells [28], making it difficult for water to be absorbed and desorbed through the nail structure. This low permeability is more marked at low humidity values.

Differences in the keratinized structure of hair and nails are also confirmed when the apparent diffusion coefficients (D_A) (Table 2) and the time of half absorption/desorption ($t_{1/2}$) (Fig. 2) are evaluated. The lower nail permeability with respect to hair fibers is demonstrated by a considerable decrease in its apparent diffusion coefficient and by significantly higher values of the $t_{1/2}$ in all the RH steps, mainly at low RH values.

3.1. Treated hair sorption measurements

The water sorption isotherms of untreated hair and hair chemically modified with treatments such as bleaching and perming were determined. These two hair treatments impaired the keratin structure of the hair. Bleaching is based on an oxidizing agent whereby melanin and other hair components are oxidized. Perming consists in breaking the disulphide linkages that join the pairs of cysteine units together with a reduction solution and in re-forming them in a new position with an oxidation solution [29].

The absorption and desorption isotherms are summarized in Fig. 3. Differences may be observed between the sorption isotherms of untreated, bleached and permed hair samples. Different values for the maximum regain at 95% RH of chemically treated hair samples were found (Table 3), with a decrease in this parameter for bleached hair and a marked increase for permed hair. The decrease in bleached hair can be attributed to the bleach treatment which mainly affects the fiber surface and decreases its ability to retain water. These results demonstrate, in line with other authors [30,31], that bleaching is more harmful than perming. Furthermore, as stated above, perming consists in a reorganization of the disulfide bonds of the fiber, which may give rise to a fiber with a higher capacity to absorb water [27].

The GAB results (Table 3) show the detrimental effect of bleaching with a diminution of the monolayer capacity for bleached hair fibers; a slight increase in the monolayer water absorption was obtained for permed hair with respect to untreated fibers. The energy constant measurements, which evaluate the binding strength of the water molecules to hair fiber, did not show differences between the hairs studied.

To improve the evaluation of the differences in the sorption process of the different hair samples, the moisture absorbed and desorbed at equilibrium in each RH step of the isotherm was calculated and plotted in Fig. 3. It can be seen that while the bleached hair sample absorbs/desorbs a little less moisture in most steps, permed

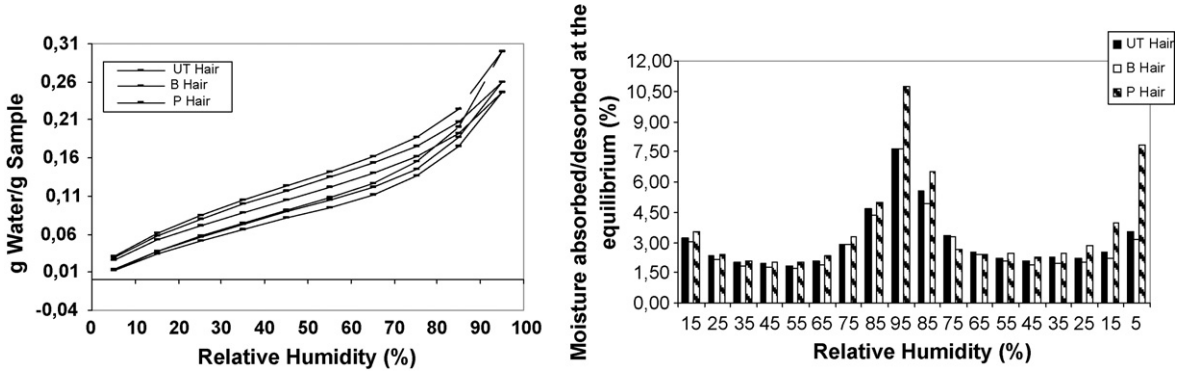

Fig. 3. Water sorption isotherms and moisture absorbed/desorbed at the equilibrium in regain (%) for untreated (UT), bleached (B) and permed (P) hair samples.

Table 3
Maximum moisture regain, GAB monolayer capacity (Wm), GAB energy constant (Cg), GAB determination coefficient (R^2), total time to reach equilibrium (t_T) and apparent diffusion coefficient (D_A) (mean value ± SD) for untreated (UT), bleached (B) and permed (P) hair samples.

	Regain at 95% RH (%)	Wm (%)	Cg	R^2	t_T (min)	D_A (min^{-1})
UT Hair	25.87	7.487	6.706	0.9976	3204.22	0.0163 ± 0.007
B Hair	24.60	6.630	6.803	0.9982	2895.12	0.0203 ± 0.010
P Hair	29.97	7.518	6.597	0.9986	3297.16	0.0175 ± 0.014

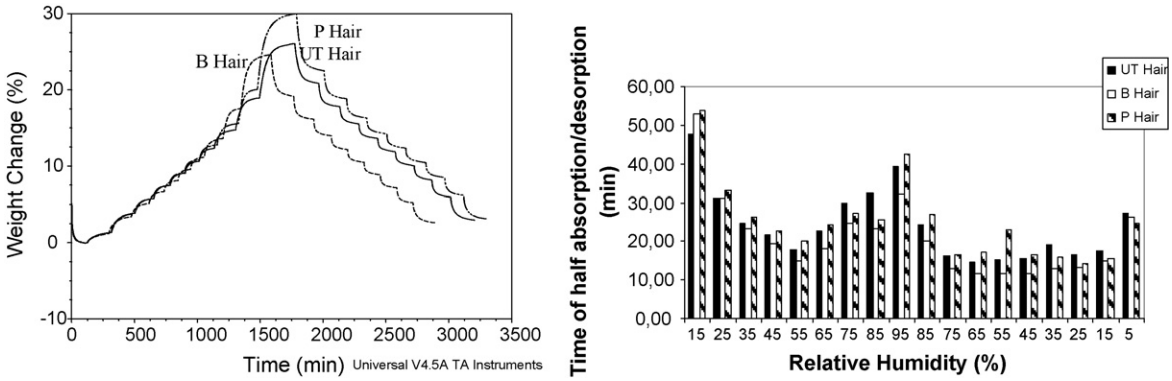

Fig. 4. Moisture uptake as a function of time and time of half absorption/desorption in min for untreated (UT), bleached (B) and permed (P) hair samples.

hair sample presents higher values of moisture absorbed/desorbed at all relative humidities.

The time taken by a sample to reach equilibrium can be used to evaluate the sample state. The shorter the time needed to reach equilibrium, the more deteriorated the sample. The evaluation of the kinetics of moisture uptake and loss in each RH step confirms the role of chemical treatments in altering the rate at which hair reaches equilibrium (Fig. 4). Fig. 4 shows that bleached fibers are the first to reach equilibrium, mainly in the desorption cycle. This is also the case when considering the total time needed to reach equilibrium (Table 3), the shortest time being for bleaching.

The moisture diffusion kinetics through the hair fibers was also evaluated and the apparent diffusion coefficients (D_A) were calculated as detailed in the experimental part. The results are summarized in Table 3. Moreover, the time of half absorption/desorption ($t_{1/2}$) for each RH step was calculated and is plotted in Fig. 4. The relationship between the time parameter and the diffusion coefficient may be observed. Longer times needed to reach equilibrium were recorded for fibers with small diffusion coefficients, which are related to small water permeability. Results demonstrate the damage caused by bleaching, with a diminution in the $t_{1/2}$ in most of the RH steps with respect to untreated hair. Deterioration of hair due to bleaching is characterized by a marked decrease in the time needed to reach equilibrium and by an increase in its water permeability. Permed fibers showed less deterioration with only a diminution of the $t_{1/2}$ in some RH steps, and a lower increase in their water permeability with respect to untreated hair.

3.2. Treated nail sorption measurements

The moisture absorption/desorption isotherm curves for the different nail plate samples, the kinetics of these processes and their diffusion coefficients were also evaluated. 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 [29].

The absorption and desorption isotherms for untreated nails (UT), nails subjected to acetone treatment (A3) and nails subjected to 8 hydration/dehydration cycles (H/D 8) are summarized in Fig. 5. The maximum regain at 95%RH is reported in Table 4. Comparison of the isotherms from untreated and deteriorated nails shows only minor differences, with the main changes for the acetone treated nails. Both nail treatments present higher moisture regain at 95%RH when compared with the untreated nail sample.

Detailed results for the moisture regain are shown in Fig. 5. The tendency of the moisture regain to increase or diminish in the dif-

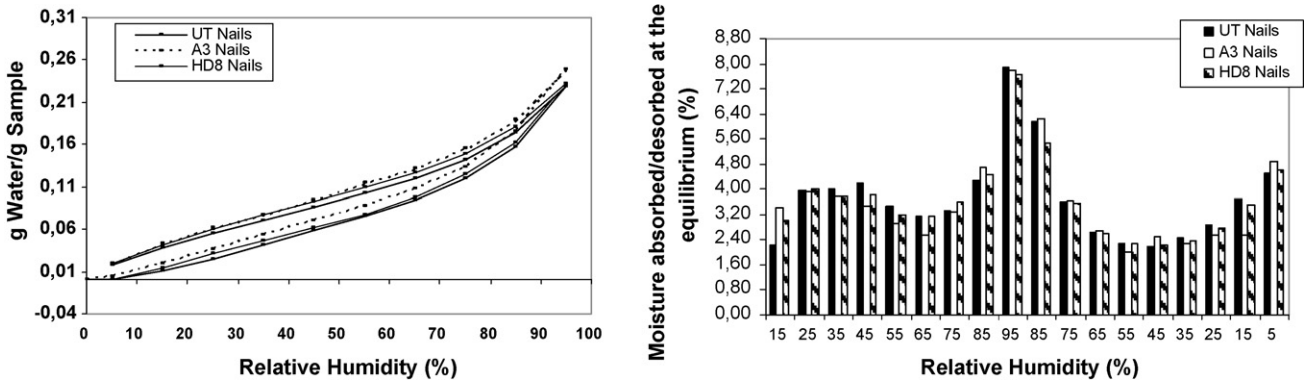

Fig. 5. Water sorption isotherms and moisture absorbed/desorbed at the equilibrium in regain (%) for untreated (UT), acetone (A3) and hydration/dehydration cycles (HD8) nail samples.

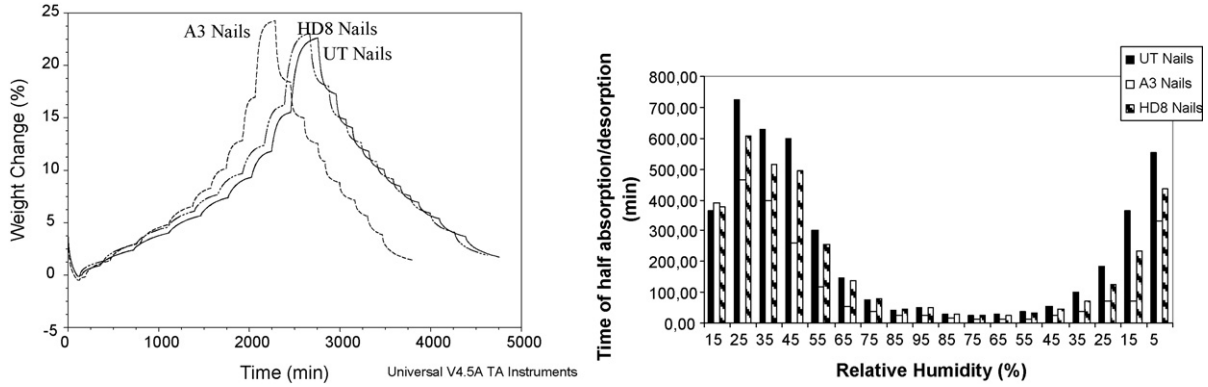

Fig. 6. Moisture uptake as a function of time and time of half absorption/desorption in min for untreated (UT), acetone (A3) and hydration/dehydration cycles (HD8) nail samples.

Table 4
Maximum moisture regain, GAB monolayer capacity (Wm), GAB energy constant (Cg), GAB determination coefficient (R^2), total time to reach equilibrium (t_T) and **a**pparent diffusion coefficient (D_A) (mean value ± SD) for untreated (UT), acetone (A3) and hydration/dehydration cycles (HD8) nail samples.

	Regain at 95% RH (%)	Wm (%)	Cg	R^2	t_T (min)	D_A (min^{-1})
UT Nails	22.77	1.611	0.9480	0.9981	4925.85	0.0042 ± 0.004
A3 Nails	24.87	8.376	2.498	0.9985	3795.32	0.0099 ± 0.010*
HD8 Nails	23.17	8.629	1.889	0.9986	4625.57	0.0052 ± 0.005

* $p < 0.05$.

ferent relative humidity steps due to the different treatments is unclear.

As in the case of hair samples, the experimental sorption data for nails were also subjected to the GAB model, and both parameters, the monolayer capacity (Wm) and the energy constant (Cg), are shown in Table 4. It has been reported that the nail plate becomes soft and tends to be double layered when its water content exceeds 20% [32–34]. In our case, the GAB results demonstrate the damaging effect of both treatments on the nail structure, with a big increase in the amount of water absorbed in the monolayer and with a small increase in the energy constant.

As in the case of hair, possible modifications of the rate at which the nails reach equilibrium are studied (Fig. 6). Evaluation of the rate curves shows that the untreated nail sample takes much longer to reach equilibrium in both the absorption and desorption cycles. These results demonstrate the damaging effect of both treatments on nail plate integrity. This damage was greater in the case of nails treated with acetone where a significant increase in the rate of both cycles was observed.

The apparent diffusion coefficients of the nail samples were also evaluated (Table 4) and the results show an increase in water permeability, hence a deterioration of the keratin structure in the treated nails. This increase is much more marked for the nail samples subjected to acetone treatment. Furthermore, the evaluation of the time of half absorption and desorption in each step of relative humidity for the different nail sample (Fig. 6) confirms the detrimental effect of the treatments on nail integrity with a decrease in this parameter in most of the RH steps. This decrease in the time of half absorption/desorption is much more pronounced for nails subjected to acetone treatment, confirming greater nail deterioration.

4. Conclusions

Water adsorption and desorption of human hair and nails were evaluated. The isotherms for these human keratinized tissues behaved as expected, with a characteristic hysteresis between uptake and desorption as observed in other keratinized tissues. A lower moisture regain and a much lower diffusion coefficient were obtained for human nails with respect to human hair.

Degradation treatments could vary the moisture content of hair and nail samples. Sometimes the water content tends to decrease (bleaching hair) and sometimes it tends to increase (perming hair and both acetone and hydration/dehydration cycles on nails). However, permeability, directly related to the diffusion coefficient, tends to increase with the degradation treatments. The diffusion coefficient was essential for determining the integrity of the keratin fibers.

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