

## Hair Efficacy of Botanical Extracts

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**ABSTRACT:** The great increase of capillary treatments (bleaching, perming, etc.) has created an important demand for hair cosmetics designed to repair and even prevent adverse effects on the capillary structure. In this work, the effect on hair of three botanical actives is investigated. Hair was chemically damaged by bleaching and the efficacy of three botanical actives was demonstrated by evaluation of surface morphology, differential scanning calorimetry, strength/relaxation, and absorption/desorption properties. Bleaching treatments have been demonstrated to modify the hair properties producing an increase in the fiber permeability and detrimental effects on the mechanical properties. Application of the botanical extracts to pretreated hair has improved the mechanical properties, giving rise to a reduction of the fibres' permeability, coating them and increasing the crystalline material of the fibers. Treatments with botanical actives based on either proteins and peptides, sulfated polysaccharides or a combination of polysaccharides could be used to protect and repair the hair fibers. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** botanical actives; hair; efficacy; strength; mechanical properties; dynamic vapour sorption; differential scanning calorimetry; scanning electron microscopy

Received 24 November 2011; accepted 23 June 2012; published online

DOI: 10.1002/app.38244

### INTRODUCTION

Every day hair is exposed to a range of insults, such as sunlight exposure, pollution, cosmetic treatments (bleach and color) grooming practices, and cleansing. This in turn leads to fiber degradation, weakening through compromising the internal structure of the cortex, and roughening of the fiber surface, through damages to the fiber cuticle.<sup>1–6</sup> The great increase of capillary treatments (bleaching, perming, etc.) has created an important demand for hair cosmetics which help to repair and even prevent adverse effects on the capillary structure. In this sense, amino acids, proteins, sugars, vitamins, and a great variety of vegetable extracts have been included in cosmetic formulations especially designed to minimize the negative effects on the skin and hair fibre.<sup>7,8</sup>

In the last 6 months, 3203 hair care products have been launched worldwide (www.gnpd.com). The botanical/herbal concept clearly emerges from the others. Plant derived biopolymers are known to maintain the moisture balance in hair and keep skin soft and moist. They help filling the outer keratin layer of the hair shaft that breaks with age and harsh treatments and also provide protection for the vulnerable inner layers.<sup>4,7–10</sup>

The main aim of this work is to study in depth the efficacy of the different vegetable active/extracts in hair treatments. Three purified extracts were selected to evaluate their efficiency on hair fibers. In the active selection, their components have been carefully chosen; sulfated polysaccharides on the *Cystoseira compressa seaweed extract* (F00), a combination of actives (polysaccharides, proteins, and mineral elements) on the *Lepidium meyenii extract* (F10), and proteins and peptides on the *carob tree extract* (F20). These actives are each trapped into a tridimensional hydrocolloidal matrix that provides sequential release. The matrix is composed of amylopectin, a component obtained from corn (*Zea mays*).

Hair samples were subjected to the most common cosmetic treatment, bleaching<sup>2,3,11</sup> in order to study their chemical and mechanical damage and their possible recovery after treatment with the three different vegetable active formulations. Bleached hair was washed and treated every day with the three different formulations for a period of 10 days.

Strength and relaxation measurements of the untreated and chemically treated hair before and after the three different formulation treatments were performed with 25 fibers randomly

taken from the samples. Fiber fineness was examined by image analysis. Samples in a cardboard were evaluated in an Instron 5500R according to the ASTM Standard D 3822 methodology.<sup>1</sup>

The determination of the water absorption isotherm by isothermally applying discrete, cumulative humidity changes comprises a dynamic and static character from which diffusion coefficients and equilibrium water contents are obtained.<sup>12–19</sup>

In this work, the effect on water absorption of hair treated with three types of plant extracts is investigated. Modifications of hair water absorption due to a bleaching treatment have been demonstrated, with lower values of water sorption capacity and an increase of the fibers permeability.<sup>11,20</sup>

A scanning electron microscopy (SEM) study has been also performed with all hair samples to evaluate the possible changes on the surface morphology of the hair fibers due to the different treatments.<sup>21</sup> Differential Scanning Calorimetry (DSC) of the hair fibers was performed without a thermal medium using a DSC-821, Mettler Toledo. The DSC graphs present four thermal events: vitreous transition, water evaporation, thermal decomposition and denaturation. A decrease of denaturation enthalpy for bleached hair has previously been reported.<sup>22,23</sup>

All these methodologies have been applied to bleached hair and bleached hair treated with the three vegetable extracts to elucidate possible hair properties recovery and their capacity in restoring the hair fibers.

## MATERIALS AND METHODS

### Materials

Hydrogen peroxide 30% was supplied by Merck (Darmstadt, Germany). Natural dark brown hair tresses (20 cm in length) were purchased from De Meo Brothers (New York). Hair tresses were treated with a shampoo base (Table I) and leave-on serum which contained botanical actives (F00 *Cystoseira compressa seaweed extract*, F10 *Lepidium meyenii extract*, F20 *carob tree extract*) (Table II).

Hair was first damaged with a common cosmetic treatment, a bleaching procedure, which is based on an oxidizing agent whereby melanin and other hair components are oxidized. Bleached hair was then treated 10 times with the placebo leave-on serum or one of the three botanical active leave-on serums. Samples of untreated, bleached, and bleached treated with the different formulations were then evaluated.

### Hair Treatment

Hair was chemically damaged by bleaching. Hair was placed in a bleaching solution (9% H<sub>2</sub>O<sub>2</sub>, pH 9) for 30 min on an agitation bath at 30°C; then it was rinsed with water for 1 min. This was repeated 15 times, preparing a new bleaching solution every time. For comparison virgin hair was kept as the control.

Five bleached hair (B) tresses of 8 g were prepared. For comparison, one tress of virgin hair was also prepared as control (UT). All tresses were daily washed with a shampoo base for 2 min and then were rinsed with water. Next, bleached tresses were treated with the leave-on serum: placebo (BP), botanical active F00 (*Cystoseira compressa seaweed extract*), botanical active F10 (*Lepidium meyenii extract*) and botanical active F20 (*carob tree extract*). Tresses of bleached (B) and untreated (UT) hair were kept untreated

**Table I. Shampoo Base Formulation**

Ingredient	% (w/w)
Aqua (water)	73.16
Acrylates/C10-30 alkyl acrylate crosspolymer	1.00
Propanediol	5.00
Sodium laureth sulfate, aqua (water), sodium chloride	12.00
Cocamidopropyl betaine	6.00
Sodium hydroxide, aqua (water)	2.14
Phenoxyethanol, propylparaben, ethylparaben, methylparaben, butylparaben, isobutylparaben	0.60
Maris Sal (sea salt)	0.10

as controls. The treatment of approximately 0.5 g of each formulation was repeated everyday leaving the formulation applied on the hair tress for 24 h. Next all tresses were washed and the formulations were applied again. This was repeated 10 times for a period of 10 days.

### Tensile Properties of the Hair Fibers

A stress–strain test was performed with 25 fibers of each hair sample which were randomly taken from the hair samples previously conditioned for 48 h in a standard atmosphere (20°C and 65% relative humidity [RH]) and centrally attached to a pair of cardboard frames with an internal rectangular cut frame of 50 × 25 mm<sup>2</sup> following the longest direction.<sup>1</sup>

Samples on the cardboard were attached to an Instron 5500R dynamometer with a gage length of 50 mm. The two sides of the cardboard were cut before the beginning of the stress–strain test to enable just the fiber under testing to be stressed. The test was performed according to the ASTM Standard D 3822 methodology. A gage length of 50 mm, a rate of strain of 30 mm/min, and the breaking stress (MPa) and strain (%) were recorded. The multiplication of breaking stress and percentage strain gave rise to the breakage work, which evaluated the fiber conditions.

The test was realized on each hair sample, therefore, 25 measurements were obtained for each kind of sample. Besides, the radius of each fiber of different samples was obtained with image analysis.

### 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.<sup>18</sup>

1. Initial drying: temperature 60°C and 0% RH overnight. The sample remains in this step until its mass reaches equilibrium (arbitrarily defined as a change in mass of less than 0.02% per minute for 10 minutes).
2. Prestabilization: temperature 25°C, 0% RH and then initial absorption kinetics at 5% RH.

**Table II.** Leave-On Serum Formulations

Ingredient	F00(Sw E) (%w/w)	F10 (Lm E) (%w/w)	F20(Ct E) (%w/w)	Placebo (%w/w)
Aqua (water)	76.90	76.90	76.90	81.90
Glycerin	2.00	2.00	2.00	2.00
Tetrasodium glutamate diacetate, sodium hydroxide, aqua (Water)	0.20	0.20	0.20	0.20
Hydroxypropyl starch phosphate	5.50	5.50	5.50	5.50
Sucrose laurate, aqua (water), alcohol denat. (Sisterna L70C emulsifying)	5.00	5.00	5.00	5.00
Prunus amygdalus dulcis (sweet almond) oil	4.00	4.00	4.00	4.00
Phenoxyethanol, methylparaben, butylparaben, isbutylparaben, ethylparaben, propylparaben (phenonip preservative of clariant)	0.60	0.60	0.60	0.60
Parfum (fragrance)	0.30	0.30	0.30	0.30
Botanical active	5.00	5.00	5.00	0.00
Aqua (water), lactic acid	0.50	0.50	0.50	0.50

- Absorption curve: the sample previously stabilized at 5% RH is subjected to absorption tests progressively increasing the RH in steps of 10% up to 95% RH, the sample being stabilized at 95% RH after the last step. The sample remains in each step until its mass reaches equilibrium (arbitrarily defined as a change in mass of less than 0.02% per min for 10 min).
- Desorption curve: the sample stabilized at 95% RH after the absorption experiment is subjected to desorption tests progressively decreasing the RH in steps of 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 as a change in mass of less than 0.02% per min for 10 min).

The high reproducibility of these measurements was established during the validation study for this instrument in which three replicates of a single sample gave essentially 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.<sup>24</sup>

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.<sup>12</sup> The GAB model has proved to be applicable in hydrophilic polymers<sup>13,14</sup> and food<sup>15</sup> systems and has considerable theoretical justification.<sup>16</sup> Thus, in this work, sorption isotherm data were modeled according to the GAB model in line with other authors.<sup>17,18</sup> Table III shows the sorption isotherm and the parameters used to fit the experimental sorption/desorption data. The goodness of the fit was evaluated by the determination coefficient ( $R^2$ ).

The diffusion coefficient has been obtained using calculations based on the solutions of Fick's diffusion equation applied to

cylindrical geometry.<sup>24</sup> A simplified version of this solution is given in eq. 1.

$$C_t/C_{eq} = 4(D_t/\pi r^2)^{1/2} \quad (1)$$

where  $C_t$  is the concentration of the diffusion at time  $t$ ,  $C_{eq}$  is the concentration at equilibrium,  $D$  is the diffusion coefficient,  $r$  is the fiber radius (previously calculated in the section of tensile properties of hair fibers), and  $t$  is the time.

The numerical data from the sorption (or desorption) experiment can be converted into a plot of  $(C_t/C_{eq})$  vs  $(t/r^2)^{1/2}$ . The initial

**Table III.** GAB Model and Parameters Used to Fit the Experimental Sorption Data

Model	Mathematical equation
GAB (25)	$W = W_m C_g K a_w / [(1 - K a_w + C_g K a_w)]$
Parameter	Definition
$a_w$	Water activity expressed as vapor relative pressure $p/p_0$ , where $p_0$ is the saturated vapor.
$W$	Equilibrium moisture content at $a_w$ in g sorbed/100 g of sorbent on dry basis
$W_m$	Monolayer moisture content in g sorbed/100 g of sorbent on dry basis
$C_g$	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 vapor pressure of the liquid and the vapor 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.

**Table IV.** Breaking Stress, Deformation at Break, and Breakage Work of UT and B Hairs, and Bleached Treated with the BP, and the Three Vegetable Extracts (F00 *Cystoseira compressa* seaweed extract, F10 *Lepidium meyenii* extract, F20 *carob tree* extract) (Mean  $\pm$  SD)

	Breaking stress (MPa)	Deformation at break (%)	Breakage work
UT Hair	237.75 $\pm$ 79.66	45.26 $\pm$ 4.80	10968.35 $\pm$ 5038.63
B Hair	214.51 $\pm$ 63.05	48.29 $\pm$ 24.03	9777.93 $\pm$ 2331.78
BP Hair	216.82 $\pm$ 91.44	48.00 $\pm$ 4.57	10474.51 $\pm$ 4660.86
B F00 Hair (Sw E)	210.03 $\pm$ 64.79	49.00 $\pm$ 6.80 <sup>a</sup>	10413.18 $\pm$ 3882.86
B F10 Hair (Lm E)	225.19 $\pm$ 89.53	51.42 $\pm$ 4.66 <sup>a</sup>	11655.31 $\pm$ 4810.55
B F20 Hair (Ct E)	305.51 $\pm$ 199.67 <sup>a</sup>	48.56 $\pm$ 3.86 <sup>a</sup>	13565.01 $\pm$ 8243.28 <sup>a</sup>

<sup>a</sup> $P < 0.05$ , respect UT.

part of this plot (for  $(C_t/C_{eq}) < \sim 0.5$ ) will be linear and its slope (calculated by linear regression) is related to the diffusion coefficient as

$$D = (\pi/16)\text{slope}^2 \text{ cm}^2 \text{ s}^{-1} \quad (2)$$

### Shine Measurements

Shine measurements were obtained using a micro-TRI-gloss BYK-Gardner GmbH (Geretsried, Germany) with standard geometries of 20°, 60°, or 85°. Hair tresses were aligned by combing and the measurement at the three angles was performed through a plate glass (slide) pressed over the tresses. The measurements were performed under controlled conditions (23°C and 50% RH). Mean values were obtained for the 18 values of each incidence angle for the six strands. The values were measured in shine units (s.u). These are related to a standard black glass with defined refraction index (generally 1.567).

### Differential Scanning Calorimetry

DSC of the hair fibers was performed without a thermal medium using a pan with a hole in the lid. Approximately 6 mg of the hair sample was packed into a 40 mL aluminum DSC pan (sealed with the lid with a 50 mm hole). The heating rate used in this study was 10°C/min, with a temperature range of 20–275°C and a flow rate of nitrogen gas of 50 mL/min.

All investigations were conducted on a heat flux DSC instrument (DSC-821, Mettler Toledo, Barcelona, Spain). The samples consisted of short fiber snippets (approximately 2 mm in length) cut from the different hair swatches. Before the measurement, samples were stored under standard room conditions (20°C, 65% RH) to ensure a constant water content.<sup>23</sup>

### Scanning Electron Microscopy

A SEM study was performed with all of the hair samples to evaluate the possible changes in the surface morphology of the hair fibers due to the different treatments. For this, the samples were studied with a TM-1000 Tabletop scanning electron microscope (Hiatchi). The microscope was operated at 15.0 kV. Several fibers from each hair sample were viewed, and representative images were taken.

### Data Treatment

The Dixon's test has been used for detecting outliers, which were excluded from the data. 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.

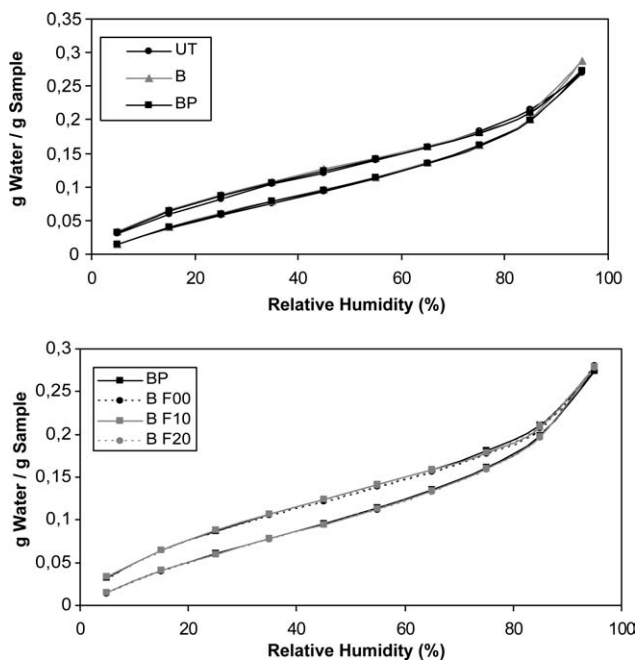
## RESULTS AND DISCUSSION

### Strength Measurements

A stress-strain test was performed on all the different hair samples. Mean values of stress and deformation at break for the different hair samples are given in Table IV. Breaking stress evaluates the fiber integrity. Therefore, higher values of this parameter indicate a larger amount of bonds present in the fiber structure. First results show that the bleaching treatment leads to a modification of the hair fiber integrity with a decrease of the values of stress at break with respect to the untreated hair. As explained in the experimental part, considering stress and deformation at break values the breakage work can be calculated and the results for the different hair fibers are also detailed in Table IV. Values for the breakage work, which evaluates total energy to break, show that the fibers with the greatest change in breakage work are the bleached fibers with an important diminution of this parameter.

When evaluating the different hair treatments (placebo and the three botanical actives) an increase in the breaking stress for the hair fibers treated with F10 (*Lepidium meyenii* extract) and F20 (*carob tree* extract) is observed indicating an improvement of the fibers integrity due to the extracts application. This improvement is more important and statistically significant for the F20 (*carob tree* extract) treatment. Furthermore, a statistically significant increase in the deformation at break for all the hair samples treated with the vegetable extracts has also been found. An increase in the deformation at break indicates an increase of the fibers plasticity. This increase can be explained by: (1) an increase of the water content of the fibers due to the botanical actives. Increased moisture content can increase the fibre's ability to be deformed; (2) binding of some functional groups present in the actives to cystine within the hair fiber, restoring some of the disulfide bonds broken upon chemical treatment. This could also impart greater elasticity to the fiber. When the deformability is increased the resulting hair fibers are softer and more resistant to breakage. The breakage work results indicate that bleached fibers treated with the botanical actives have an improved quality, reaching values for the breakage work higher than the ones obtained for bleached hair fibers. Again, this improvement is more marked for the hair fibers treated with both the F10 (*Lepidium meyenii* extract) and F20 (*carob tree* extract) botanical actives where the breakage work is even higher than the one for untreated, healthy hair fibers.





**Figure 1.** Water sorption isotherms for UT and B hairs, and bleached treated with the BP, and the three vegetable extracts (F00 *Cystoseira compressa* seaweed extract, F10 *Lepidium meyenii* extract, F20 *carob tree* extract).

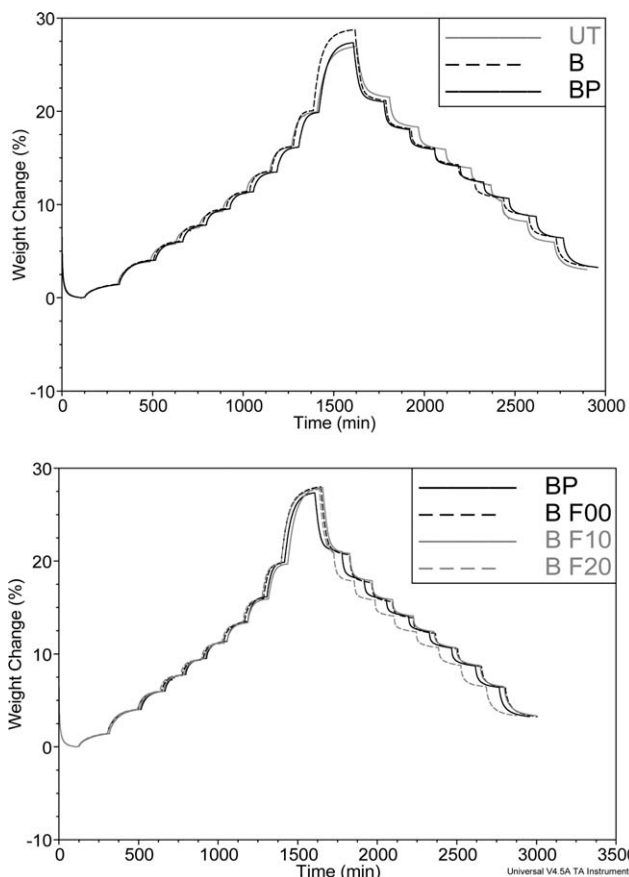
### Sorption Experiments

Sorption isotherms of untreated and bleached hair and bleached submitted to the placebo and the botanical actives treatments were evaluated and are shown in Figure 1. Higher water sorption was found for bleached hair related to UT hair, however, the treatment of bleached fibers with the placebo and with all other three botanical actives formulations showed similar water absorption/desorption profiles to the UT fibers.

The regression of the experimental sorption data by the GAB model gives values of  $W_m$ , the monolayer capacity,  $C_g$ , the

**Table V.** Maximum Moisture Regain, GAB Monolayer Capacity ( $W_m$ ), GAB Energy Constant ( $C_g$ ), GAB K Constant, and GAB Determination Coefficient ( $R^2$ ) for UT and B Hairs, and Bleached Treated with the BP, and the Three Vegetable Extracts (F00 *Cystoseira compressa* seaweed extract, F10 *Lepidium meyenii* extract, F20 *carob tree* extract)

	Regain at 95%RH (%)	$W_m$ (%)	$C_g$	$K$	$R^2$
UT Hair	26.96	8.682	5.464	0.7167	0.9998
B Hair	28.76	8.743	5.999	0.7123	0.9998
BP Hair	27.36	8.813	5.896	0.7059	0.9997
B F00 Hair (Sw E)	28.00	8.505	6.081	0.7163	0.9997
B F10 Hair (Lm E)	27.96	8.664	6.079	0.7071	0.9996
B F20 Hair (Ct E)	27.74	8.568	6.133	0.7105	0.9997



**Figure 2.** Moisture uptake for UT and B hairs, and bleached treated with the BP, and the three vegetable extracts (F00 *Cystoseira compressa* seaweed extract, F10 *Lepidium meyenii* extract, F20) as a function of time.

energy constant and  $K$  the GAB constant.<sup>25</sup> A good fit of the GAB model to the uptake and desorption data was achieved ( $R^2 > 0.999$ ), the values obtained are shown in Table V. Not many differences can be found for the different hair samples studied on the amount of water in the monolayer and the secondary upper sorbed layers, visualized by  $W_m$  and  $K$  values. However, results for the energy constant show that there is an increase of this parameter for all the hair samples treated with the vegetable extracts. The energy constant results, which evaluate the binding strength of the water molecules to the hair fibers, demonstrate that water might be strongly bound to hair due to the damage treatment and moreover, due to the presence of the botanical actives on its fibers. Nevertheless, it is important to emphasize that the modifications on total water absorption and energy of water bonding are minimal and not significant to reach reliable conclusions.

The rate at which equilibrium is achieved is a good indicator of the sample condition. The kinetics of moisture sorption was evaluated for all hair samples studied and curves are shown in Figure 2. The moisture diffusion kinetics for the hair fibers has also been evaluated. Hair radius has been calculated in the strength test with 25 hair fibers of each sample, and then, the mean value of these 25 measurements was obtained (Table VI). The diffusion coefficients ( $D$ ) have been calculated as detailed

**Table VI.** Fiber Radius, Diffusion Coefficient (D), and Total Time to Reach Equilibrium ( $t_T$ ) for UT and B Hairs, and Bleached Treated with the BP, and the Three Vegetable Extracts (F00 *Cystoseira compressa* seaweed extract, F10 *Lepidium meyenii* extract, F20 carob tree extract)

	Radius (cm)	D (cm <sup>2</sup> s <sup>-1</sup> )	$t_T$ (min)
UT Hair	0.00368 ± 0.00074	5.22E-07	2896.95
B Hair	0.00394 ± 0.00081	8.65E-07	2916.62
BP Hair	0.00392 ± 0.00099	6.18E-07	2956.59
B F00 Hair (Sw E)	0.00390 ± 0.00089	6.44E-07	3005.07
B F10 Hair (Lm E)	0.00391 ± 0.00088	6.29E-07	2996.97
B F20 Hair (Ct E)	0.00369 ± 0.00094	5.98E-07	2874.86

in the experimental section for each humidity step. The mean values of fiber radius, diffusion coefficients, and total time to reach equilibrium are summarized in Table VI. In general, for the same amount of water absorption, there is an inverse relationship between the time parameter and the diffusion coefficient, i.e., a higher time is needed to reach equilibrium for fibers with small water permeability and, therefore, a small diffusion coefficient.

In this study, the total time of absorption/desorption is very similar for all samples ranging between 2900 and 3000 min. However, the diffusion coefficient showed a clear increase for the bleached fiber which diminishes both with the placebo treatment and the vegetable formulations, being this effect more marked for the F20 (*carob tree extract*) treated hair. These results demonstrate first, the damaging effect of the bleaching treatment, with an important increase of its diffusion coefficient thus indicating an important increase of the fiber permeability due to the chemical treatment. Furthermore, the application of the placebo and the vegetable extracts on the bleached fibers clearly leads to a decrease of the diffusion coefficients, demonstrating an improvement on the fibers integrity with a clear diminution of their permeability, this effect being more important for the vegetable extract F20 (*carob tree extract*).

### Shine Measurements

As described in the experimental part, shine measurements were performed on three different incident angles: 20°, 60° and 85°. Although a previous study established that hair shine, hair being a “low shine” surface, is better evaluated under an 85° incidence angle,<sup>26</sup> very little variations on shine measurements were found in the present experiment due to the different chemical and cosmetically treatments in the three different incident angle studied. Therefore, not statistical significant differences were found. Mean values are shown in Table VII.

### DSC Experiments

DSC experiments were conducted on untreated, bleached, and bleached hair samples treated with either the placebo or the vegetable extracts without thermal medium. The DSC curves obtained present four thermal events: the vitreous transition,

the water evaporation, the thermal decomposition, and the denaturation. The first event (vitreous transition) occurred between 40°C and 60°C. This step is proportional to the amount of amorphous material present in the sample. The next peak appeared around 120°C and this was attributed to the water content evaporation of the sample. The DSC shows then a denaturation doublet between 230 and 260°C. The two transitions correspond to the denaturation of two fractions of cells that could be identified with the *ortho*-cortex and the *para*-cortex of the fibre.<sup>27</sup>

DSC results for untreated, bleached, and bleached hair sample treated with the different formulations are summarized in Table VIII. It was first observed from the values for the height of the vitreous transition, that bleached hair treated with the different formulations contained the greatest amount of amorphous material. This could be attributed to the presence of the botanical extracts on the hair fibers. The results for the water evaporation process indicated that the bleached hair sample had an increase of its enthalpy ( $\Delta H_W$ ) value, indicating an increase of the water content. This can be attributed to a change of the fiber surface due to the chemical treatment which might result in a more porous fiber with an increase of its hydrophilicity due to the bleaching oxidizing process. Water evaporation results when the bleached hair samples are treated with the different formulations, evaluated with the enthalpy values ( $\Delta H_W$ ), show a trend on decreasing the water content after the application of the botanical extracts F10 (*Lepidium meyenii* extract) and F20 (*carob tree extract*). Furthermore, the last events (denaturation) show that application of the different botanical extracts on bleached hair increased the enthalpy of the denaturation peaks, indicating a possible increase of integrity of the crystalline material due to the botanical extracts application. This integrity improvement is more marked on the first denaturation peak, in which the *ortho*-cortex fraction is evaluated.

### Surface Changes

The SEM results allowed us to visualize some differences in the conditions of the surface morphology of the hair samples due to the treatments of each sample. Several fibers of each hair

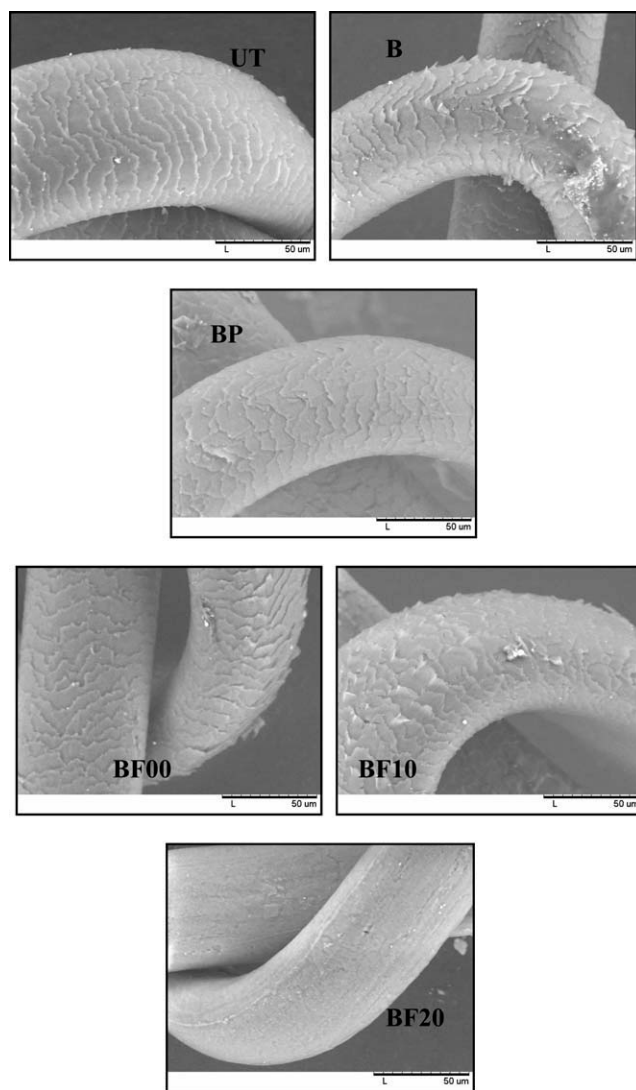
**Table VII.** Mean Values of Shine Measurements on Different Incident Angle for UT and B Hairs, and Bleached Treated with the BP, and the Three Botanical Actives (F00 *Cystoseira compressa* seaweed extract, F10 *Lepidium meyenii* extract, F20 *carob tree extract*) (Mean ± SD)

	20° (s.u)	60°(s.u)	85° (s.u)
UT Hair	130.65 ± 1.9	140.94 ± 1.1	115.00 ± 3.2
B Hair	130.28 ± 2.6	141.89 ± 1.6	115.83 ± 3.0
BP Hair	130.00 ± 2.7	141.29 ± 2.1	114.09 ± 6.0
B F00 Hair (Sw E)	130.61 ± 1.7	142.44 ± 0.6	115.61 ± 3.0
B F10 Hair (Lm E)	128.56 ± 4.5	142.00 ± 1.4	112.43 ± 7.6
B F20 Hair (Ct E)	128.94 ± 2.3	141.61 ± 1.0	115.82 ± 2.4

**Table VIII.** DSC Results for UT and B Hairs, and Bleached Treated with the BP, and the Three Botanical Actives (F00 *Cystoseira compressa seaweed extract*, F10 *Lepidium meyenii extract*, F20 *carob tree extract*)

	Vitreous transition	Water evaporation		1 <sup>st</sup> Denaturation		2 <sup>nd</sup> Denaturation	
	Height (W/g)	$T_w$ (°C)	$\Delta H_w$ (J/g)	$T_D$ (°C)	$\Delta H_D$ (J/g)	$T_D$ (°C)	$\Delta H_D$ (J/g)
UT	0.0641	127.69	148.15	234.19	5.23	244.60	5.48
B	0.0439	125.25	180.30	243.63	3.90	257.10	1.94
BP	0.0850	120.87	193.35	245.83	3.94	254.31	2.95
B F00 ( <i>Sw E</i> )	0.1023	136.47	182.95	240.81	5.58	257.25	1.99
B F10 ( <i>Lm E</i> )	0.0945	125.51	174.58	245.46	4.26	254.97	2.57
BF20 ( <i>Ct E</i> )	0.0877	125.92	167.26	243.41	4.08	256.27	2.42

sample have been evaluated and representative images for bleached hair and bleached treated with the three botanical extracts are shown in Figure 3.



**Figure 3.** Representative SEM micrographs for UT and B hairs, and bleached treated with the BP, and the three botanical actives (F00 *Cystoseira compressa seaweed extract*, F10 *Lepidium meyenii extract*, F20 *carob tree extract*).

Bleached hair showed the greatest modification of the cuticle scale, with the cuticle clearly lifted when compared to the untreated hair sample. The restoring capacities of the different botanical extracts applied on the bleached hair samples were compared. The botanical extracts F00 (*Cystoseira compressa seaweed extract*) and F10 (*Lepidium meyenii extract*) treatments showed a slight improvement of the fibers surface with the presence of some opened cuticles. However, when evaluating the fibers treated with the botanical extract F20 (*carob tree extract*) a considerable coverage residue with a smoothing of the cuticle scale edge is found. This suggested a relatively persistent layer of the botanical extract protecting the cuticle.

## CONCLUSIONS

Bleached hair samples were demonstrated to be chemically and mechanically damaged with an increase in the fiber permeability, a decrease in the enthalpy of denaturation peaks and detrimental effects on the mechanical properties. Treatments with botanical actives based on either proteins and peptides, sulfated polysaccharides or a combination of polysaccharides, proteins, and mineral elements were applied to the bleached hair. These actives were able to induce an improvement of the mechanical properties and a reduction of the permeability, especially in the case of F20 (*carob tree extract*) extract. Furthermore, the decrease of denaturation enthalpy for bleached hair demonstrated damage in the structure of the hair which is reduced in the treated fibers, indicating a possible increase of integrity of the crystalline material. This is more marked in the case of the F00 (*Cystoseira compressa seaweed extract*) botanical active. SEM images indicate that application of the botanical actives to the hair fibers leads to an improvement of the cuticle scale with a smoothing of the scale edge detail. The results obtained for hair efficacy of these three botanical extracts could indicate a higher capacity for F00 (*Cystoseira compressa seaweed extract*) on cystine reformation of the damaged orthocortex, which could be related with the content of sulfate polysaccharides, and a higher coating capacity of F20 (*carob tree extract*) which due to its high protein content could lead to a regain of the hydrophobicity of the hair fibers and a diminution of their permeability. The recovery from the chemical and mechanical damage demonstrates the role of these actives in restoring the hair fiber.

## ACKNOWLEDGMENTS

The authors thank A.M. Manich, J. Carrilla, V. Martínez, and S. Vilchez for their discussions and encouragement of this study. They also thank Provital SL for cooperation and financial support. Thanks are also due to the TRACE Program (TRA2009\_0282) for financial support.

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