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Evaluation of hair fiber hydration by differential scanning calorimetry, gas chromatography, and sensory analysis

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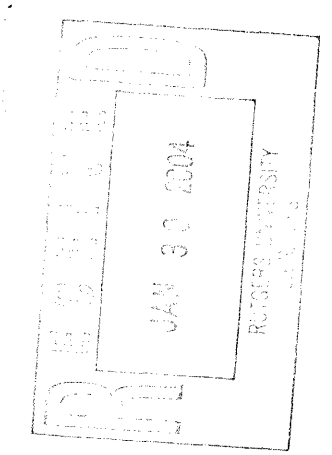

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Synopsis

Hair hydration is one of the effects that consumers most expect when using a cosmetic hair product. The purpose of this study was to combine differential scanning calorimetry (DSC) and gas chromatography (GC) techniques for a precise evaluation of the water content in hair fiber. DSC allowed determination of the bonding strength of water to hair fibers by quantifying the amount of energy required to remove the water. The amount of water thus removed was determined by GC. Post-treatment sensory evaluations of hair tresses were conducted to determine whether the values obtained with these techniques correspond to the moisturizing sensation perceived by consumers.

INTRODUCTION

Moisture content in hair can be detected and quantified by a variety of techniques that include gravimetry (1–3), electric measurements (4,5), and evaporimetry (6).

Microscopy, one of the techniques of reference for evaluating hydration, was used to determine changes in fiber diameter, surface, and volume (7,8). Hair hydration was determined by near infrared spectroscopy (NIR) combined with sensory evaluation (9). Measurements of hair fiber tension-stretch values were used for indirect evaluation of hair hydration (10).

Differential scanning calorimetry (DSC) techniques have been applied by Cao (11) to study thermal behavior of hair. Wortmann *et al.* (12) have used DSC to determine keratin denaturation in bleached hair fibers. Since this technique quantifies the thermal

energy that must be transferred to a material to induce physical changes, it allows measuring the heat of vaporization, melting, and phase transition of different materials. In his studies, Cao (11) identified two characteristic temperature ranges: one, from 0°C to 200°C, for water present in hair, and the other, from 250°C to 280°C, for the crystalline phase transition of α-keratin.

Gas chromatography (GC) techniques using a mass spectrometry detector (GS/MS) have been applied for forensic purposes to detect traces of drugs in hair fibers (13,14). When heated, hair releases a vapor whose components can be identified and quantified by injecting the vapor into a gas chromatograph. The thermal conductivity detector associated with the GC technique is appropriate and sufficiently sensitive for the detection and quantification of water and carbon dioxide in gas mixtures (15).

The objective of this study was threefold: to apply DSC techniques to evaluate the intensity of the bonding energy of water to hair; to apply GC techniques to quantify the amount of water present in hair fibers as a result of a variety of cosmetic treatments; and to determine whether the resulting values correspond to the moisturizing sensation perceived by consumers.

MATERIALS AND METHODS

Two treatments (1 and 2) were evaluated with leave-on products recommended for damaged hair, and two treatments (3 and 4) were evaluated with rinse-off products recommended for normal hair. Standard Caucasian medium-brown hair tresses (De Meo Brothers), measuring 30 cm in length and weighing approximately 2.0 g each, were prepared for this study. For the treatments recommended for damaged hair, the tresses were bleached for 30 minutes in a solution containing hydrogen peroxide (20 vol.), reagent grade ammonium hydroxide, and reagent grade ammonium persulfate in the ratio of 2:1:0.5, respectively. Each tress was previously washed with 10% lauryl ether sodium sulfate to remove impurities.

All tresses were wetted under a constant flow of distilled water (10 ml/s) for 15 seconds and treated with 200 µl of each product; the products were applied along the length of the tresses and massaged over the fibers for 15 seconds. Except for those treated with leave-on products, the tresses were rinsed under a constant flow of distilled water (10 ml/s) for 15 seconds and then dried with a professional hairdryer at room temperature (24°C ± 1). This entire procedure represented one wash. Five washes were carried out for each treatment (Table I). The control tress was treated in the same way as all the others, except for the application of the moisturizing products.

Table I
Hair Tress Treatments

Treatment	Product	Tress condition
1	A (Not rinsed)	Damaged
2	B (Not rinsed)	Damaged
3	C (Rinsed)	Undamaged
4	D (Rinsed)	Undamaged

The tresses were maintained for 36 hours in an environment adjusted to 20°–22°C and a relative humidity of 50–60%. A DSC 204 Netzsch TASC 414/3A was used for the tests, which were performed in duplicate. The samples consisted of approximately 7.5 mg of entire tresses cut into pieces, homogenized, and divided for the DSC and GC tests. Compressed air was used with a flow rate of 10 ml/min and a heating rate of 20°C/min. The tests were conducted within the temperature range of −10°C to 300°C. The pan used in the DSC tests was made of aluminum and sealed under pressure. An empty pan of the same type was employed as a reference and tested under the same experimental conditions used for the samples.

The hair mass used for the chromatographic analysis (GC) was approximately 0.1 g. The oven was maintained in an atmosphere of nitrogen (N_2) and heated at a rate of 2.0°C/min (25° to 300°C). The oven outlet was connected to a semi-automatic injection valve for sampling the gas generated by evaporation and thermal breakdown; the samples were subsequently analyzed to determine the composition of the gas.

The GC used in this study was a Shimadzu GC-8A chromatograph equipped both with a Porapak-Q column for the separation of water and a PM-5A column (molecular sieves) for the separation of CO_2. The carrier gas was He (35 ml/min), with an injector/detector temperature of 140°C and a column temperature of 100°–130°C; the heating rate was 5°C/min. A thermal conductivity detector (TCD) was employed.

Nitrogen served as the internal reference gas for the determination of the percentages of water and carbon dioxide. The correction factor for each sample was determined from the analytical curves provided by the detector response for the different volumes of injected substance (H_2O, CO_2, or N_2).

The sensory evaluation panel was conducted with 41 consumers of hair treatment products. This was an ordination test in which the subjects were asked to assess the hydration levels of two groups of three hair tresses each, which had undergone the same moisturizing treatments as those described above. For the statistical analysis of the results, the score frequencies per product were compared with the Cochran-Mantel-Haenszel (CMH) statistics, using the orders as scores. The description of the general application of CMH statistics for the cases in which an ordinal response is associated with a classificatory variable was cited by Agresti (16). We assumed that the average scores for the reference population were the same across the entire assortment of products used in this study; this hypothesis was tested and proved to be sound. The calculations and preparation of the database were performed with the aid of the SAS system.

RESULTS AND DISCUSSION

Figures 1 and 2 show the DSC curves both for untreated hair and for hair subjected to the four treatments described previously. The peaks correspond to hair degradation. Upward peaks represent endothermic reactions, with the first lowest peak corresponding to the release of water. The second and third peaks denote endothermic fusion reactions of keratin polypeptide chains (11).

Figures 3 and 4 show details of the first lowest endothermic peak corresponding to ΔH values for water vaporization ($\Delta Hvap$). These enthalpy values were collected for each

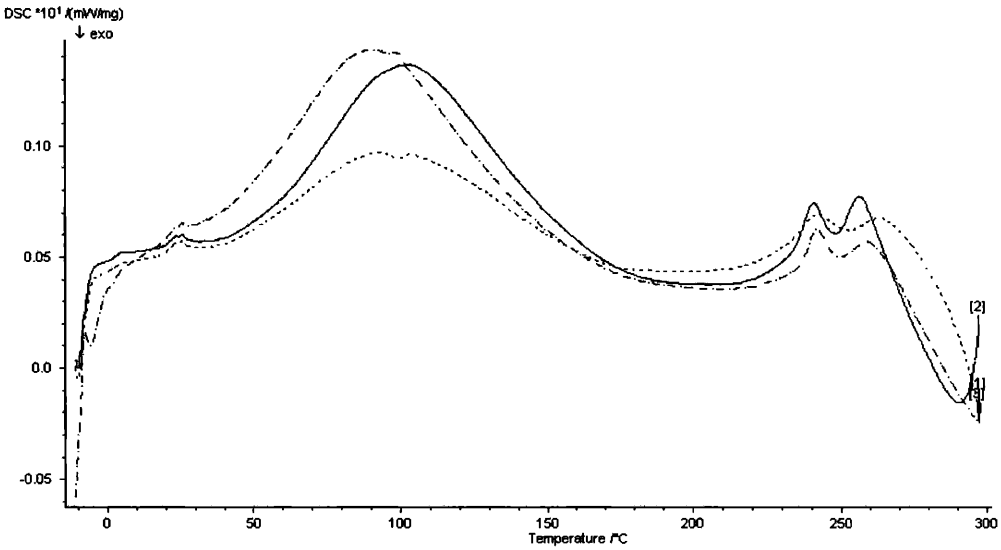

Figure 1. DSC curves for treated hairs and for the hairs without treatment. Bleached without treatment [1] .....; treatment 1 [2] _____; treatment 2 [3] _ _ _.

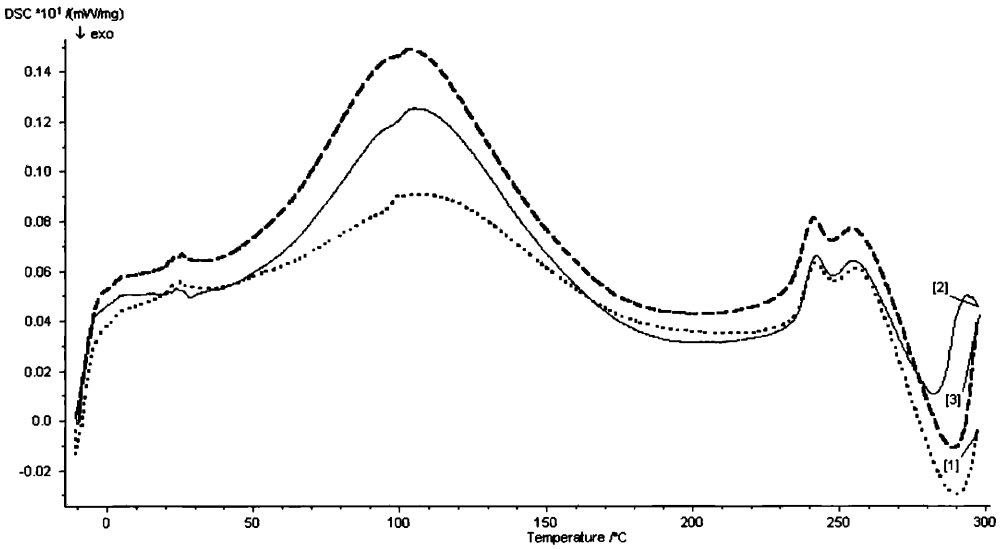

Figure 2. DSC curves for treated hairs and for the hairs without treatment. Without treatment [1] .....; treatment 3 [2] _ _ _ _; treatment 4 [3] _____.

duplicate of the analyses performed within the temperature range of 0°C to 200°C (Table I).

Table II presents the enthalpy values for water vaporization both from untreated (control) and treated hair. It is apparent that more energy is spent to release water from treated hair than from untreated hair. The amounts of energy required to release water after treatments 1 and 2 were, respectively, 44% and 83% higher than for the control.

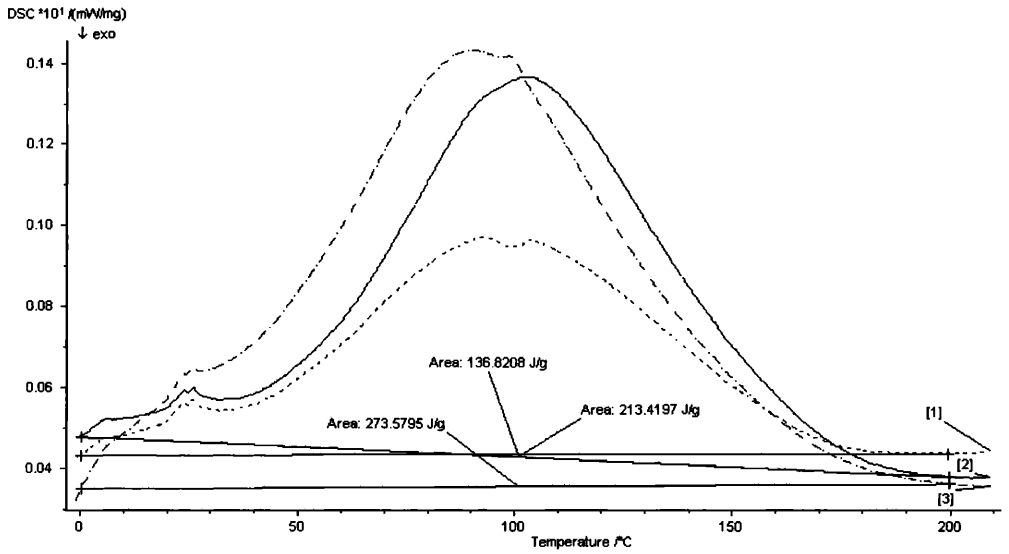

Figure 3. Details of DSC curves for treated and untreated hair. Each curve is an example of the duplicate curves obtained. Bleached without treatment [1] .....; treatment 1 [2] _____; treatment 2 [3] _ _ _.

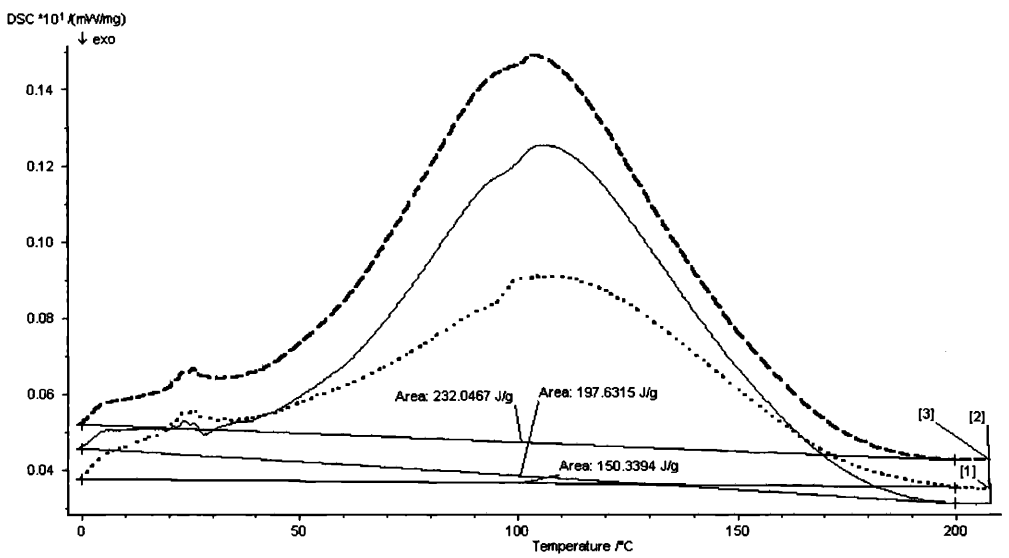

Figure 4. Details of DSC curves for treated and untreated hair. Each curve is an example of the duplicate curves obtained. Without treatment [1] .....; treatment 3 [2] _ _ _ _; treatment 4 [3] _____.

After the rinse-off treatments 3 and 4, these amounts of energy were, respectively, 17% and 41% higher than for the control.

We suggest two hypotheses to explain the increased amounts of energy necessary for the release of water from hair. First, the treatments increase the water content in the fibers. The higher the amount of water attached to the fibers, the more energy will be necessary to release it. Second, the treatments would, in some way, hinder the release of water,

Table II
Water Vaporization ΔH Values Obtained From the DSC Curves for Hair Subjected to Different Treatments

Treatments	ΔHvap, water (average) J/g
Bleached, untreated hair	146 ± 13
Treatment 1, not rinsed	210 ± 5
Treatment 2, not rinsed	268 ± 8
Untreated hair	164 ± 19
Treatment 3, rinsed	192 ± 7
Treatment 4, rinsed	231 ± 2

which would thus require more energy. This interference may be due to the formation of a barrier (film) and/or to the presence of hydrophilic substances.

Dias *et al.* (17) ascribe the retention of moisture in the hair to the formation of a silicone film. Cao (11) argues that the energy spent from 0°C to 200°C in the DSC analysis is associated with the release of water caused by heating the hair fibers.

To ensure that the vapor released from heated hair contained only water, it was necessary to determine the chemical composition of the vapor because other substances, other than water, could volatilize at these temperatures. GC/TCD (gas chromatography/thermal conductivity detector) analysis of this vapor confirmed the presence of water and allowed its quantification. The results are shown in Figures 5 and 6. Water release for all the samples was observed to begin at 25°C and end at approximately 200°C.

Since the GC detector identified nothing but water within this temperature range, the first section of the DSC curves corresponds only to the water present in the test samples. An increase in water content was observed above 200°C. This additional amount of water may result from the constitution of the hair fibers, as well as from the combustion of the entire organic material present in hair.

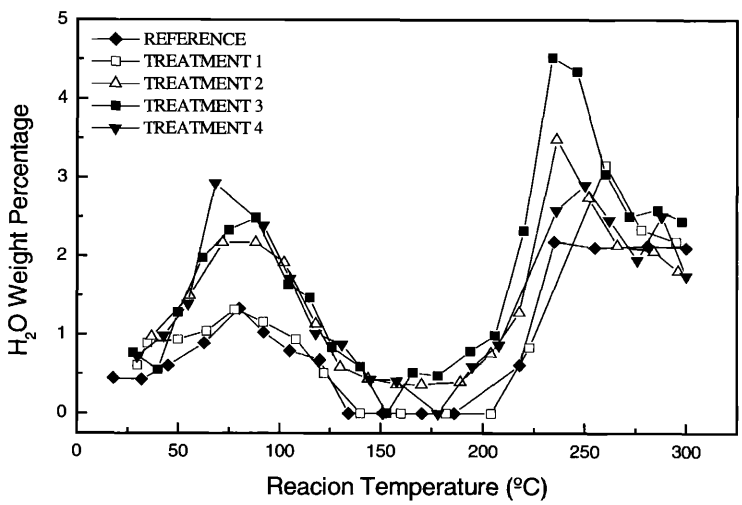

Figure 5. Water weight percentage observed in the vapor from the hair heat treatment.

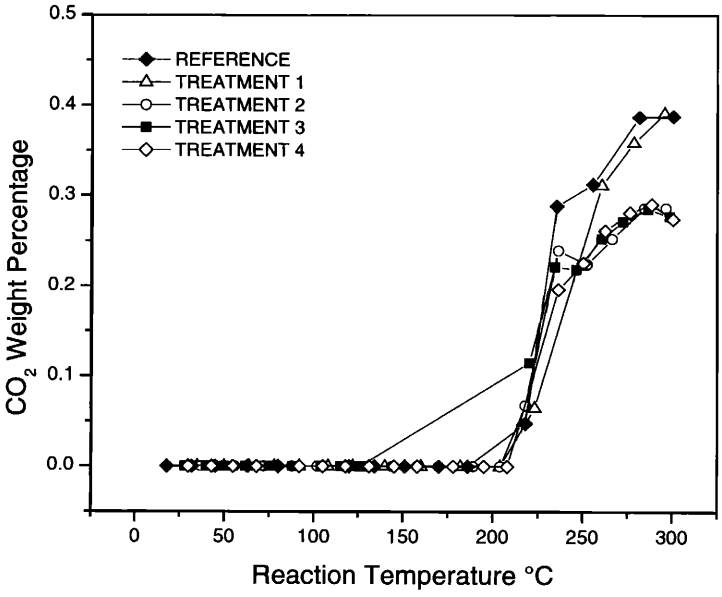

Figure 6. CO_2 weight percentage observed in the vapor from the hair heat treatment.

A comparison of treatments 1 and 2 shows that treatment 2 provides both a higher ΔHvap value (267.79 J/g) and a higher percentage of water (12.82%) than treatment 1 (ΔHvap = 209.96 J/g and 7.43% water). The results for treatments 3 and 4 show that treatment 3 provides a lower ΔHvap value (192.49 J/g), but a higher water percentage (16.73%) than treatment 4 (230.91 J/g and 12.85%, respectively).

The DSC measurements show the extent to which heated hair fibers are protected from water loss, while GC measures the water content in hair fiber. Depending on its composition, the formula may simply add water to the hair fibers and/or protect them from water loss (for example, by forming a film around the fiber), which may or may not result in proportional DSC and GC values.

DSC is an effective technique for evaluating the thermal behavior of water present in hair: it allows the determination of the bonding energy of water in the hair fiber. The amount of water, however, cannot be determined directly by DSC. GC is a reliable technique for the quantification of water present in hair, and was therefore used as a complementary tool to DSC for the purpose of this study. Hair moisturizers can increase the amount of water in the hair fiber and/or form a barrier that hinders water desorption. Therefore, the association of these two analytical techniques proved particularly useful in the evaluation of hair fiber hydration. Because the amount of consumed energy provides an indication of the level of protection, the DSC data also show that this technique can be applied to evaluate the thermal protection properties of hair fibers.

During the consumer research, the following attributes of moisturized hair were most frequently mentioned: softness, gloss, gliding feel, and silkiness. These attributes do not depend exclusively on hydration (7). The panelists did not identify significant differences between treatments 1 and 2 and control (p = 0.1722), nor were they able to identify differences between treatments 3 and 4 and control (p = 0.0643), which indicates that consumer testing is inadequate to evaluate hair hydration. Sensory analysis is

important for the evaluation of other attributes perceived by consumers, such as softness and gloss. Therefore, the results of subjective evaluations, which involve individual psychological and physiological differences (18,19), do not provide the necessary accuracy to determine the level of hydration offered by hair products. Consequently, the assessment and quantification of water in hair by means of DSC and GC techniques become essential for substantiating the moisturizing properties of hair products in their development stage.

CONCLUSIONS

DSC is an effective technique for the evaluation of the thermal behavior of water in hair since it allows for determining the bonding strength of water to hair fibers. GC is a specific, sensitive, and accurate technique for the quantification of the water present in hair fibers. Sensory evaluations are inadequate for the assessment of the hydration levels provided by different cosmetic hair products.

The association of DSC and GC techniques is appropriate, accurate, practical, and readily available, and yields accurate results for water content in hair. Because sensory evaluations have shown that consumer perceptions of moisturized hair are confused with other attributes that do not depend exclusively on hair fiber hydration, obtaining this type of analytical evidence is an essential requirement.

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