

Thermal analysis of hair treated with oxidative hair dye under influence of conditioners agents

Robson Miranda da Gama · Tatiana Santana Balogh · Simone França ·
Tânia Cristina Sá Dias · Valcinir Bedin · André Rolim Baby ·
Jivaldo do Rosário Matos · Maria Valéria Robles Velasco

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Abstract This research aimed the effect on Caucasian hair tresses treated with oxidative hair dye, either incorporated or not with conditioners agents, analyzed by Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TG). The formulations of hair dyes were emulsions oil-in-water with light blond color containing or not the conditioners agents: silanetriol and panthenol; PEG-12 dimethicone; hydrolyzed silk, hydrolyzed milk protein, and lactose. Each dye (1.5 g) was applied in the hair tress (2.0 g/20.0 cm of length of Caucasian light-brown), previously treated, more 1.5 g of hydrogen peroxide 20 vol during 40 min. Evaluation of mass loss of the different hair sample demonstrates that these chemical hair treatments impair the hair fibers, reduced their moisture content with

respect to the untreated hair. The incorporation of conditioners agents (silanetriol and panthenol; PEG-12 dimethicone; hydrolyzed silk, hydrolyzed milk protein, and lactose) in oxidative hair dyes types did not decrease the damage caused on the tresses by the coloring process quantified by TG/DTG. However, the DSC curves demonstrated those conditioners agents (silanetriol and panthenol; PEG-12 dimethicone) dislocated the beginning of the third event in 20 °C and they inhibited the presence of the fourth event, having characterized thermal protection to the hair.

Keywords Oxidative hair dye · Conditioners agents · Hair properties · Thermal analysis

R. M. da Gama (✉) · T. S. Balogh · S. França ·
T. C. S. Dias · A. R. Baby · M. V. R. Velasco
Laboratory of Cosmetology, School of Pharmaceutical Sciences,
University of São Paulo, Avenida Prof. Lineu Prestes, 580,
bl. 15, Conjunto das Químicas, Cidade Universitária,
São Paulo, SP 05508-900, Brazil
e-mail: rmdagama@gmail.com

R. M. da Gama
Laboratory School of Semi Industrial of Pharmacy (LESIFAR),
School of Pharmacy, University of Santo Amaro, Rua Professor
Enéas de Siqueira Neto, 340, Jardim das Imbuías,
São Paulo, SP 04829-300, Brazil

V. Bedin
Healthy Skin Foundation and Hair and Skin Research
and Treatment Institute, Rua Almirante Pereira Guimarães,
150, Pacaembu, São Paulo, SP 01250-000, Brazil

J. do Rosário Matos
Laboratory of Thermal Analysis Ivo Giolito (LATIG), Chemistry
Institute, University of São Paulo, Avenida Prof. Lineu Prestes,
580, bl. 8, Conjunto das Químicas, Cidade Universitária,
São Paulo, SP 05508-900, Brazil

Introduction

The hair thread has a highly organized, cylindrical structure, formed by mostly keratinized inert cells which follow a very precise and pre-defined design [1, 2]. The human hair is composed of about 65–95% protein by weight, and more than 15% of water, lipid pigments, and other components. About 80% of human hair is formed by a protein (α -keratin, with a high grade of sulfur—coming from amino acid cystine). α -Keratin is a laminated complex formed by different structures, which gives the hair strength, flexibility, durability, and functionality [2].

The human hair presents three principal components: cuticle, cortex, and medulla. The cortex is organized in macrofibrils, microfibrils, and cell membrane complexes. Zanh [3] proposed that microfibrils were axially oriented as crystalline filaments, and embedded within an amorphous matrix in the hair cortex.

The cuticle covers the hair thread from the scalp to the in overlapping layers of cells, and it is the most important

component of the human hair, since it may be more or less affected by cosmetic treatments. Cosmetic products, such as conditioners, hair sprays, mousses, and gels are deposited on the cuticle layer. Dyes and straightening and curling products also spread through the cuticle to expand their effects on the hair fiber. There are approximately 8–11 layers of cuticle cells, which overlap in the distal direction of the thread, depending on the type, condition, and length of the hair. Each layer is formed by only one cell. Each cuticle cell has a rectangular shape and they overlap in such way, that only 1/6 of them are exposed [2–5].

The cortex occupies an extensive hair area (75%). In the same way as the cuticle, it has cells filled by cross links of cystine and others cells separated by the cell membrane complex. Each one of the cortex cells has a spindle shape, and measures 50–100 μm in length and a 3 μm in diameter. The distal surface of each cell is rough and irregular, and they tie crossly to each other [2–5]. The cortex is composed of protofibrils, microfibrils (also known as intermediate filaments), macrofibrils, and the intermacrofibrillar matrix. The macrofibrils and the intermacrofibrillar matrix are arranged to form the cells of the cortex. Depending on the arrangement, these cells are classified as either para or orthocortical. These components are organized into cortical cells that form the body of the cortex [4].

The medulla is a thin cylindrical layer at the center of the hair thread containing a high concentration of lipid and little cystine. Its function is not yet completely elucidated, although its cells may become dehydrated and its spaces may be filled with air, which affects both the color and shine of brown and blond hair. The medulla has a small effect on most of the aspects of cosmetic hair treatments and they are only present in terminal hairs [2, 4]. Recently, Wagner et al. [6] studied the medulla using electron microscopy and observed that medulla presents three distinct subunits (globular structures, unorganized cortical cells, and smooth covering layer). Two kinds of medulla were identified namely thin and thick.

The physical proprieties of hair depend mostly on its geometry; the physical and mechanical properties of hair involve characteristics related to: elasticity, smoothness, volume, shine, and softness. These characteristics are related to the adherence of the cuticle scales and the movement control (malleability), as well as the ease of combing, since they reduce the fibers static electricity [2].

Hair coloring is widely used by women and men either to change their natural hair color to delay the onset of gray hair, or to donate new pigments to gray hair [7]. The oxidative dyes are formed by two components that are mixed before use and provide the coloration by means of chemical reactions in the surface and the internal of the hair fiber, in mean strong alkaline and oxidant. Oxidative dyes may

damage the hair, since chemical and physical procedures are involved to alter the hair color [8, 9].

The hair fiber, when exposed with the adverse environmental conditions, can present damages in its structure and, consequently, alterations in its mechanical and of surface properties. Damaged hairs may appear cloudy, dry, rough, fragile, and/or dull, and these conditions may be caused by solar radiation, daily care routines, and/or cosmetic treatments including permanents and dyes among others [9, 10]. The addition of conditioning agents with known protective action on the hair shaft hair into formulations of oxidative hair dyes could decrease the damage caused to hair by the coloring process.

Hydrolyzed proteins, which often contain free amino acids, act as humectants, providing body to damaged hair. The properties are determined by average molecular weight and amino acid composition. Hydrolyzed proteins are used to contribute to conditioning and protection of hair. Because more terminal amino and carboxylic acid groups are available if a lower molecular weight protein is selected, these may confer greater humectants effect on the hair [11, 12].

Different types of silicones are used as conditioning agents in a wide variety of products including conditioners, shampoos, hair sprays, mousses, and gels. Depending on the exact structure and molecular weight, the compounds can be classified as traditional wetting, conditioning, or emulsifying agents [13].

Several authors researched the thermal analysis applied on human hair were executed thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) analysis to purpose of verify keratin structural changes occur in shaft hair after the use of cosmetics treatments.

This research the effect of oxidative hair dye emulsions, with or without conditioning agents on Caucasian hair. The hair was analyzed by DSC, TG, and Derivative Thermogravimetric (DTG) analysis.

Experimental

Material

The hair fibers were classified as untreated Caucasian light-brown hair tresses (Bella Hair[®]). Hairs measuring 20.0 cm in length and weighing approximately 2.0 g each were prepared for this study.

Equipment included a Thermogravimetric analyzer, Model TGA-50 and a DSC cell, model 50, both from Shimadzu[®].

The dye formulations were oil-in-water emulsions with light blond color containing: cetearyl alcohol, dicetyl phosphate, and ceteth-10 phosphate; cetearyl alcohol; caprylic/

capric triglyceride; BHT; propylene glycol; tetrasodium EDTA; sodium metabisulfite; aqua; p-aminophenol; 4-amino-2-hydroxyloluene; resorcinol; erythorbic acid; *t*-butyl hydroquinone; and ammonium hydroxide. As conditioners agents were used: silanetriol and panthenol; PEG-12 dimethicone; hydrolyzed silk, hydrolyzed milk protein, and lactose.

Methods

Preparation of tresses

Each hair strand was first washed for 30 s with 15.0% (w/v) sodium lauryl sulfate to remove impurities. All were wetted with warm (37.0 ± 5.0 °C) distilled water constant flow of $240.0 \text{ mL min}^{-1}$ for 1 min and then dried at room temperature (22.0 ± 1.0 °C) and relative humidity (RH $60 \pm 5\%$), for 12 h prior to the analysis.

Preparation of oxidative hair dyes light blond color

The emulsion base of oxidative hair dye light blond color was prepared for conventional method in which oil and aqueous phases is heated at 70.0–75.0 °C and the aqueous phase are added to the oil phase, gradually and continuously, with aid of constant slow agitation.

The conditioning agents were measured or weighed in the proportion of 3% w/v each and added into oxidative hair dye light blond color just before of the application, in order to prevent possible interactions in the stability of the conditioning substance considering the raised pH of the formulation, which might influence the effectiveness of the coloration process.

Application of hair dye

For the hair dye treatment, 1.5 g of each dye and more 1.5 g of emulsion commercial (LBS[®]) containing 20.0% (v/v) hydrogen peroxide was applied on the previously treated hair acted for 40 min. Then the samples were washed in the manner described previously. The samples were classified as: untreated (**A**); treated with: oxidative hair dye light blond color without conditioners (**B**); and oxidative hair dye light blond color with conditioning agents: silanetriol (and) panthenol (**C**); PEG-12 dimethicone (**D**); hydrolyzed silk, hydrolyzed milk protein, and lactose (**E**).

Thermogravimetry and derivative thermogravimetry

All TG/DTG experiments were performed on a thermo balance model TGA-50 (Shimadzu[®]), in the temperature range 25–800 °C using Pt crucible with approximately 15.0 mg of sample, heating rate of 10 °C/min and

under dynamic air atmosphere (50 mL/min). The TGA-50 equipment condition was verified with a standard reference of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The blank TG/DTG curves were obtained under the same experimental conditions for baseline correction.

Differential scanning calorimetry

All DSC experiments were carried out on a DSC-50 cell (Shimadzu[®]), in the temperature range 25–550 °C, using Al partially closed crucible with about 2.0 mg of sample, heating 10 °C/min and under dynamic N₂ atmosphere (100 mL/min). The DSC-50 cell was verified with indium (mp 156.6 °C; $\Delta H_{\text{fus}} = 28.54 \text{ J/g}$), and zinc (mp 419.6 °C). The blank DSC curves were obtained under the same experimental conditions for baseline correction.

Results and discussion

For better characterization of materials, it is important to combine data from TG/DTG and DSC measurements, as the DSC detects events associated with mass loss, while the TG/DTG indicates thermal events related to mass variation [14]. Thermal analysis can be applied to a wide range of materials such as polymers, synthetic, and natural substances, foods, pharmaceuticals, and cosmetics in general [15].

Monteiro et al. [16] showed how TG and DSC analyses could be used to quantify the degradation level of denaturation of human hair keratin after the chemical treatments (hair bleaching and chlorinating). The results obtained by the TG analyses show that hair fibers treated with chlorination and bleaching solutions have a low water content and a subsequent keratin degradation exhibiting fewer degradation stages than the control untreated hair sample. The results indicate that these treatments initially cause a transformation in the keratin structure. In other words, previous oxidative treatments lead to a greater degradation of the keratin in the hair fiber. DSC analyses confirm the effect of bleaching and chlorinating treatments on the damage, showing a lower keratin denaturation enthalpy, which is due to the increased disorganization of the keratin structure.

Barba et al. [17] determined the water content of hair after and before treatments (bleaching and relaxing) using TG analyses. 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. 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, decreasing in their external water content.

Wortmann et al. [18] realized that by applying DSC on human hair in water, the thermal stability of hair's major morphological components could be determined. DSC analysis of human hair in water yields results for the denaturation temperature T_D and the related enthalpy ΔH . The enthalpy depends on the structural integrity of the α -helical material in the intermediate filaments (IF), while T_D is kinetically controlled by the cross-link density of the matrix (IFAPs) in which the IFs are embedded.

Belletti et al. [19] studied the effects of a cosmetic hair product on hair hydration. This study used both DSC and gas chromatography (GC) techniques in order to precisely evaluate the water content in hair fiber. 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 DSC and GC techniques for a precise evaluation of the water content in hair fiber. DSC determine 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 evaluation of hair tresses was conducted to determine whether the values obtained with these techniques corresponded to the moisturizing sensation perceived by consumer.

Cao [20] developed the DSC methodology for studying the melting behavior of the α -form crystallites in wool keratin, which has also been applied to human hairs. It has been demonstrated that human hair shares the same thermal characteristics as those revealed for wool. Silicone oil was found to be an effective thermal medium for DSC determination of the melting enthalpy of the α -form crystallites in human hair. The melting peak of hair conditioned at 20 °C and 65% relative humidity was about 175 °C, and the melting enthalpy, 12.8 J/g, equivalent to 14.5 J/g for dry hairs.

Wortmann et al. [21] determined the glass transition of human hair and its dependence on water content using DSC. The relationship between the data is suitably described by the Fox equation, yielding for human hair a glass transition temperature of $T_g = 144$ °C, which is substantially lower than that for wool (174 °C). This effect is attributed to a higher fraction of hydrophobic proteins in the matrix of human hair, which acts as an internal plasticizer. The applicability of the Fox equation to hair as well as wool implies that water is homogeneously distributed in α -keratins, despite their complex semicrystalline morphological structure. To investigate this aspect, hair was rendered amorphous by thermal denaturation.

During the coloration process, the hair dyes provide exaggerated opening of the cuticle, aiming at optimizing the absorption of the colorants in the cortex. This

mechanism reduces the softness, brightness, and combing of hair which the necessary and indispensable, attributes of healthy hair [8]. The incorporation of conditioners agents with known protective action into formulations of permanent dyes products could decrease the damage caused on the tresses by the coloring process.

TG/DTG curves of hair samples for: untreated (A), treated with oxidative hair dye blond color without conditioners agents (B), B plus silanetriol (and) panthenol (C), B plus PEG-12 dimethicone (D) B plus hydrolyzed silk, hydrolyzed milk protein, and lactose (E) are shown in Fig. 1a–e and Table 1 present thermogravimetric data.

Figure 1a–e and Table 1 showed that the hair presents four mass loss events characteristic of the thermal behavior of this material. The first event, observed T_{peak} around 60 °C with mass loss between 11.68 and 14.79%, for A and D, respectively. This event was attributed, according to Barba et al. and Monteiro et al. [16, 17], to the water release in the range of 25–150 °C. Monteiro et al. [16] showed that the second and third mass loss stages are related to the denaturation of hair keratin, with organic degradation of hair microfibrils and matrix, at T_{peak} around 290.7 and 307.6 °C. According to Monteiro et al. [16] in the temperature range of 350–550 °C the complete degradation of the hair keratin carbonic chains takes place (Fig. 1a). The loss of water occurs up to 180 °C, according to Barba et al. [17]. The research shows that the degradation of the organized structures completes at about 400 °C and the subsequent complete degradation of keratin and the hair structure completes up to 700 °C.

Evaluation of mass loss of the different hair samples demonstrated that these chemical hair treatments impair the hair fibers by reducing their moisture content with respect to the untreated hair (Table 1). These treatments influenced the mass loss process because the hair presented more damage of the cuticle [9]. However, the incorporation of conditioning agents (silanetriol and panthenol; PEG-12 dimethicone; and hydrolyzed silk, hydrolyzed milk protein, and lactose) into oxidative hair dyes formulations did not decrease the damage caused on the tresses by the coloring process according to TG/DTG analysis.

TG/DTG curves of hair samples for: untreated (A), treated with oxidative hair dye blond color without conditioners agents (B), B plus silanetriol and panthenol (C), B plus PEG-12 dimethicone (D), B plus hydrolyzed silk, hydrolyzed milk protein, and lactose (E) are shown in Fig. 2a–e and Table 2 shows the temperatures and enthalpy values and T_{peak} .

The analyses of the DSC curves treated with oxidative hair dye light blond color, either with or without conditioning agents (Fig. 2a–e) confirmed the presence of three endothermic and two endothermic events characteristic of the thermal behavior of this material. The first event, observed

Fig. 1 TG/DTG curves of **a** untreated hair, **b** treated hair with oxidative hair dye blond color, **c** treated hair with oxidative hair dye blond color additive with silanetriol and panthenol, **d** treated hair with oxidative hair dye blond color additive with PEG-12 dimethicone, **e** treated hair with oxidative hair dye blond color additive with hydrolyzed silk, hydrolyzed milk protein, and lactose samples obtained in air dynamic atmosphere (50 mL/min) and heating rate of 10 °C/min (Full line TG curve, hatched line DTG curve)

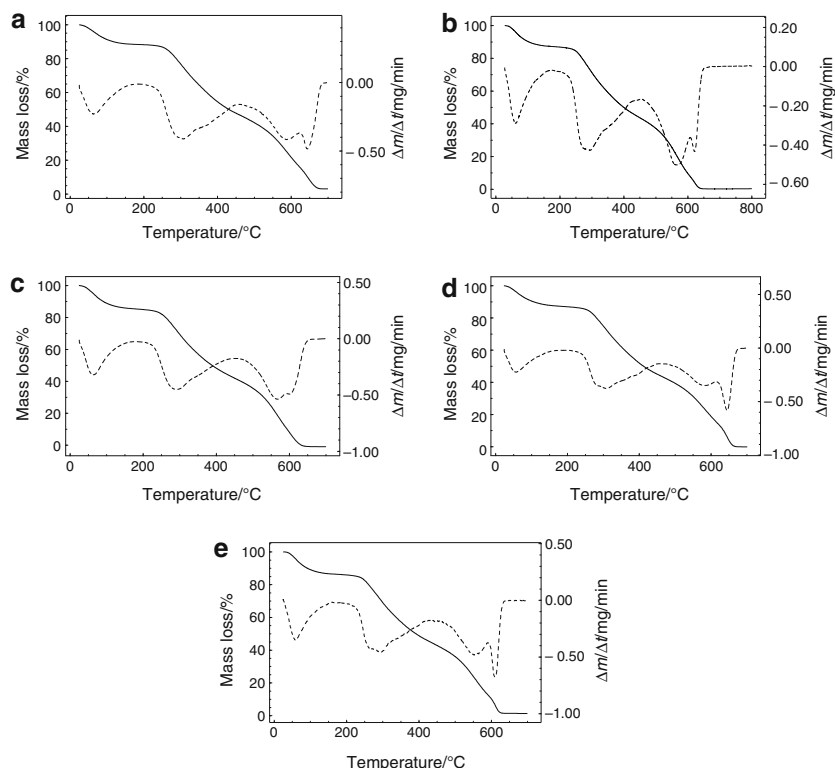


Table 1 Thermogravimetry (TG) analyses of hair samples obtained in air dynamic atmosphere (50 mL min⁻¹) and heating rate of 10 °C min⁻¹

Samples	Mass/mg	Mass loss event							
		1st		2nd		3rd		4th	
		$T_{\text{peak}}/^{\circ}\text{C}$	Mass loss/%	$T_{\text{peak}}/^{\circ}\text{C}$	Mass loss/%	$T_{\text{peak}}/^{\circ}\text{C}$	Mass loss/%	$T_{\text{peak}}/^{\circ}\text{C}$	Mass loss/%
A	15.221	62.7	-11.68	307.6	-41.48	587.2	-31.36	644.3	-12.32
B	14.726	61.4	-12.9	293.8	-43.54	564.5	-35.89	620.9	-7.7
C	15.569	63.8	-14.79	292.8	-43.62	567.6	-30.17	601.7	-12.51
D	13.54	56.5	-12.94	307	-43.49	586.8	-27.49	644.9	-16.05
E	15.745	59.4	-13.82	290.6	-42.12	552.1	-31.32	609.8	-11.52

A untreated hair, **B** treated hair with oxidative hair dye blond color, **C** treated hair with oxidative hair dye blond color additive with silanetriol and panthenol, **D** treated hair with oxidative hair dye blond color additive with PEG-12 dimethicone, **E** treated hair with oxidative hair dye blond color additive with hydrolyzed silk, hydrolyzed milk protein, and lactose

T_{peak} around 50.0 °C corresponded to the water evaporation [19]. The third and fourth events denote endothermic reactions of keratin polypeptide chain denaturation. This profile change is due to the damages caused to hair keratin structure, mainly to the cystine disulfide linkages which maintain the α -keratin conformation [16]. The second and fifth events denote exothermic reactions of keratin. The second event corresponded to glass transition, the phenomenon where the α -form crystallites in hair keratin transform into the amorphous β -form [20, 21]. The fifth event likely corresponds to the oxidative degradation of the organic material [16].

The conditioning agents (silanetriol and panthenol and PEG-12 dimethicone) incorporated in oxidative hair dye blond color had dislocated the beginning of the third event

in 20 °C and thus inhibited the presence of the fourth event and have characterized conditioning agents gave thermal protection to the hair. In addition, these active increased the enthalpy energy in the first event approximately in 120 J/°C. These profiles changes can be explained because the mechanism action of conditioners agents PEG-12 dimethicone and silanetriol involved their deposition on hair shaft of a film protection that improve wet combability, reduces flyaway, and confers softness to the hair [13]. Even so panthenol, a provitamin of pantothenic acid, can give an increase in volume to the hair [12], this does not interfere in DSC curves. Although, the active compounding of hydrolyzed silk, hydrolyzed milk protein, and lactose even though they are used to contribute to conditioning of

Fig. 2 DSC curves of **a** untreated hair, **b** treated hair with oxidative hair dye blond color, **c** treated hair with oxidative hair dye blond color additive with silanetriol and panthenol, **d** treated hair with oxidative hair dye blond color additive with PEG-12 dimethicone, **e** treated hair with oxidative hair dye blond color additive with hydrolyzed silk, hydrolyzed milk protein, and lactose samples obtained in N₂ dynamic atmosphere (100 mL/min) and heating rate of 10 °C/min

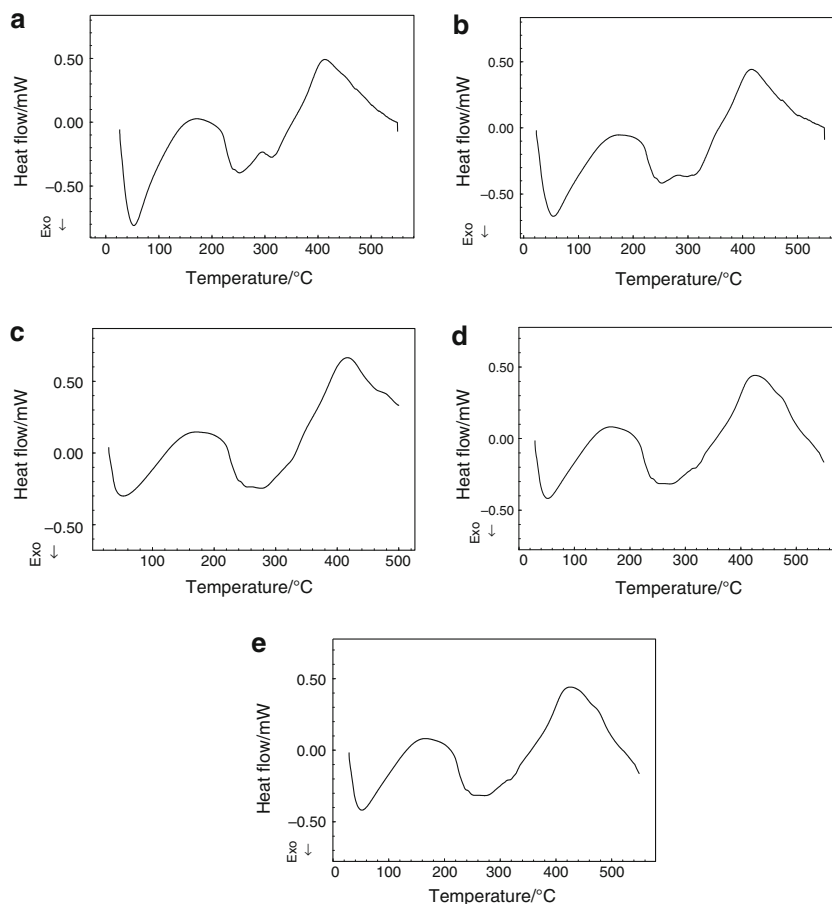


Table 2 Differential Scanning Calorimetry analyses of hair samples obtained in N₂ dynamic atmosphere (100 mL/min) and heating rate of 10 °C/min

Samples	Mass/mg	Variation enthalpy events									
		1st		2nd		3rd		4th		5th	
		T _{peak} /°C	ΔH/J/g	T _{peak} /°C	ΔH/J/g	T _{peak} /°C	ΔH/J/g	T _{peak} /°C	ΔH/J/g	T _{peak} /°C	ΔH/J/g
A	2.34	53	-287.4	172	34.3	252.1	-71.3	312.2	-18.2	412.9	339.1
B	1.87	53.9	-267.8	173.6	27.6	252.5	-39.4	297.9	-39.7	415.5	243.1
C	1.66	52.4	-146.4	171.2	40.2	277.1	-139.3	-	-	416.4	268.4
D	2.1	51.8	-155.4	165.8	32	272.1	-163.7	-	-	425.9	363.1
E	2.07	48.1	-220.6	172.9	40.3	256.9	-67	344.9	-9	412.7	352.7

A untreated hair, **B** treated hair with oxidative hair dye blond color, **C** treated hair with oxidative hair dye blond color additive with silanetriol and panthenol, **D** treated hair with oxidative hair dye blond color additive with PEG-12 dimethicone, **E** treated hair with oxidative hair dye blond color additive with hydrolyzed silk, hydrolyzed milk protein, and lactose

hair [11, 12]. These active compounding was not determine by DSC analysis.

Conclusions

Evaluation of mass loss of the different hair sample treated with oxidative hair dyes light blond color demonstrated that these chemical hair treatments impair the hair fibers,

reducing their moisture content with respect to the untreated hair. The incorporation of conditioning agents (silanetriol and panthenol; PEG-12 dimethicone; and hydrolyzed silk, hydrolyzed milk protein, and lactose) into oxidative hair dyes light blond formulations did not decrease the damage caused to hair by the coloring process when analyzed using TG/DTG. The addition of conditioning agents (silanetriol (and) panthenol and PEG-12 dimethicone) into formulations of oxidative hair dyes

decreased the damage caused to hair by the coloring process, because the DSC curves demonstrated that those conditioning agents (silanetriol (and) panthenol and PEG-12 dimethicone) dislocated the beginning of the third event in 20 °C and they inhibited to the presence of the fourth event, have characterized the thermal protection to the hair.

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