Journal of Thermal Analysis and Calorimetry (2018) 132:1429–1437
https://doi.org/10.1007/s10973-018-7095-0

DSC measurements applied to hair studies

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Received: 10 November 2017 / Accepted: 20 February 2018 / Published online: 28 February 2018

Abstract
The present review showed the importance of using the differential scanning calorimetry (DSC) in the evaluation of the hair damage. Many hair-straightening treatments necessarily involve a heating process, which even at low temperatures can cause damage to hair. Several researches demonstrated the influence of the exposure to heat in various types of hair, correlating it with the increase in the temperature. In this sense, the importance of this research is in raising awareness to the consumers and professionals (cosmetic formulators, researchers, hair stylists and dermatologists) about the issues of employing heat in the modification of the hair. To this, the present review refers to a broad and updated bibliographic collection comprising several studies related to the investigation of the thermal events that occur in the hair under heating until 300 °C, including the denaturation of the α-keratin, employing DSC. This protein forms a crystalline structure in the hair cortex and provides the hair mechanical properties such as strength and elasticity. But once denatured, the damage done to the hair may be irreversible. However, studies related to thermal decomposition of this protein are necessary due to the increased use of thermal hair styling tools, which can be associated, or not, with chemical treatments. Yet, in the literature, few reviews on this important tool of characterization and evaluation in hair samples are available. Thus, additionally, the objective of this work is to support researchers to direct the study with most feasible experimental conditions to achieve more potent results employing DSC.

Keywords Hair · Denaturation · α-Keratin · DSC · Thermal analysis

Introduction

Hair is mostly constituted of a protein, named α-keratin. In each hair fiber, thousands of α-keratin chains are intertwined in a spiral construction, in the form of overlapping plaques, resulting in a long and thin protein "cord." These proteins interact strongly with each other, in different ways, resulting in the characteristic shape of each type of hair: smooth, curled, wavy, etc. [1].

Human hair is primarily composed of three components: the cuticle, cortex and medulla. Keratin, which is a strong protein, is dispersed throughout the hair matrix, resulting in the hair strength. The cuticle is responsible for the protecting outer layer. The cortex has the largest mass of the three layers and contains spindle-shaped cells that run along the hair fiber. The center layer is the medulla, which contains amino acids responsible for the hair color. All the layers are held together by the cell membrane complex (CMC) [2]. Figure 1 (our authorship) presents the micrographs of the oriental hair sample, in detail the cuticle, cortex and CMC.

The keratin chains are cysteine rich and the sulfur from cysteine of adjacent chains form disulfide bonds providing a strong cross-link between the keratin chains. The disulfide bonds contribute to the shape, stability and texture of the hair and remain intact when the hair is wet allowing the hair to resume its original shape. Other weaker bonds link

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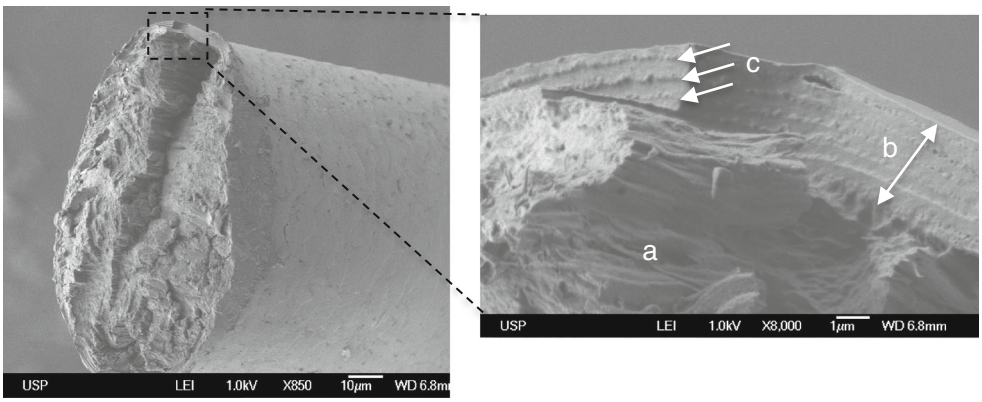

Fig. 1 Micrograph of the oriental hair sample with details to **a** cortex, **b** cuticle and **c** CMC [33]

the keratin polypeptide chains together such as van der Waals interactions, hydrogen bonds and Coulombic interactions known as salt links [3].

Human hair is similar to wool fiber in chemical compositions and molecular structures [4–7], and many physical properties of these materials are determined by the microfibril–matrix complex: helical, low-sulfur microfibrils embedded in a non-helical high-sulfur matrix [8].

Differential scanning calorimetry (DSC) and thermogravimetry (TG) are thermal analysis techniques that have been used to explore various biological materials such as hair, for example. This work aimed to collect several scientific publications that investigate and contribute to the expansion of knowledge regarding the denaturation process of α-keratin in hair. This review is about the application of DSC in the investigation of the hair, but in some of the reviewed researches, the TG was used as an associated technique and it was incorporated in this work. According to [9], four main parameters of DSC are important to analyze the hair samples: peak temperature of the dehydration event (1) and water removal enthalpy (2), peak temperature of the denaturation event (3) and denaturation enthalpy of the α-helix of keratin (4); this latter event indicates the changes that occur in the crystalline structure of the fiber. To facilitate discussion in DSC analysis, some abbreviations to quote variables common to all publications were used: peak temperature and water removal enthalpy are T_d and ΔH_d, respectively; peak temperature and enthalpy of denaturation of the α-helix of keratin are T_D and ΔH_D, respectively. In the case of human hair, there are two dominant components: (1) intermediate filaments (IFs) that are embedded in an amorphous matrix containing the (2) proteins associated with intermediate filaments (IFAPs). The IFs correspond to the crystalline filamentous phase embedded in matrix, which also comprises the remainder of the morphological components, such as the IFAPs (main component), but also including the cuticle and CMC. The IFs have a α-helix structure and the organization of these filaments; the bonds to other filaments and their support function depend on IFAPs [10]. These components, to a large extent, determine the mechanical properties of hair, which, according to their molecular structure, are important for the performance and effects of cosmetic treatments to be studied. ΔH_D depends on the amount and structural integrity of the IF helical material, while the decomposition temperature is kinetically controlled by the IFAPs in which the IFs are incorporated into the human hair cortex. The higher the cross-link density in IFAPs and the higher their viscosity, difficult the α-helix to β-sheet transition in the IFs and vice versa [10, 11]. This fact reflects in the mechanical properties of the hair, such as elasticity and strength.

Over time, the thermal behavior of hair keratin has been studied by two ways of measuring DSC: dry and wet medium (aqueous medium during the heating phase). So, the results obtained by different authors (and described in this review) are results of the different methods employed in the experiments. In the literature, there is a large amount of studies debating what can occur in the endothermic event of the denaturation of the α-keratin, more precisely about the physical meanings of the values of enthalpy and T_D of that process. The literature reported that in dry-DSC conditions, the results showed that hair α-keratin has a characteristic endothermic peak at ∼ 230 °C under heating, which did not occur with wet-DSC conditions, when this event is pronounced at ∼ 150 °C. In the DSC studies on human hair with various moisture contents, [12] similar results were found. According to [13] "dry-DSC" experiments at temperatures above 230 °C show the melting (thermal denaturation) of α-helices and pyrolysis of the matrix, simultaneously. The "wet-DSC" measurements seem to enable the separation of the effects related to ordered regions from those of material pyrolysis. And the data from "wet-DSC" experiments cannot be evaluated without the knowledge of the contribution of the interface between IFs and IFAPs [13].

Dry- and wet-DSC measurements

Dry-DSC measurements comprise investigations carried out allowing the hair keratin content to evaporate with the increase in temperature and humidity. Research in dry environments shows endothermic effects above 200 °C, sometimes with the presentation of double peaks in the curve [14, 15]. Wet-DSC measurements investigate the hair keratin in excess of water, in sealed and resistant pressure capsules that maintain the water during the heating. This method shows the endothermic effects around 150 °C. The analysis of the endothermic peaks shows that any of the methods is based on the model of physical and mechanical properties that describe the behavior of keratin fibers and the similarities with the heating behavior of globular proteins [9–11].

Hair studies employing DSC: the evolution of studies

The first studies involving thermal analysis of keratin sample of wool fibers revealed the similarity of these materials with the keratin present in human hair keratin [16–20].

A search in the literature has found that in 1960, [16] were early authors investigating the thermal properties of various keratin fibers by differential thermal analysis (DTA). The authors observed that when a hair fiber is heated, a series of changes and/or phases occurs that precede its degradation, which was around 230 °C. They reported that between 80 and 140 °C the removal/evaporation (endothermic event) of the water freely and strongly attached to the hair fiber occurs. The authors noted the presence of two events: at approximately 110 °C, representing the loss of adsorbed water and another at about 160 °C referring to the endothermic loss of strongly bound water at the hydrophilic sites in the hair fibers.

In 1963, [17] evaluated different samples of wool and goat hair by DTA and no significant differences were observed between the studied samples. The DTA curves presented three endothermic events: between 130–145, 220–230 and 230–250 °C, which the authors attributed to water vaporization, carbonization and the release of gaseous decomposition and liquefaction products, respectively.

In 1972, [21] studied virgin and chemically treated hair samples by TG/DTA. The authors reported an event of thermal decomposition by TG with loss of mass at 252 °C for virgin hair samples and observed that this temperature increases with different types of treatments (with 37% formaldehyde solution: 276 °C, and 30% H_2O_2 solution: 270 °C). They explain that this fact is due to the high reactivity of the formaldehyde with the functional groups of keratin. The DTA results evidenced the endothermic fusion and T_D at 235 and 243 °C, respectively, in virgin hair samples, and these increased in the treated hair samples (with formaldehyde solution 36%: 240 and 252 °C, H_2O_2 30% solution: 250 and 270 °C). Formaldehyde is a straightener active agent, but currently Brazilian Government Health Agency (ANVISA) prohibits it, since it was proved to be very harmful to health in certain concentrations. However, some cosmetic industries still manufacture (illegally) products containing formaldehyde to straighten the hair (called "progressive brushes" or "acidic brushes").

Later, [8] in 1987 and [22] in 1992 showed that the T_D could be detected adequately and also evaluated for fibers by dry-DSC (value obtained around 240 °C). In 1992, [15] used DSC to study the interactions between water and keratin of the treated and untreated Caucasian hair samples. According to the authors, removal of loosely bound water occurred at about 70 °C and melting/denaturation of the α-helix at about 233 °C. Dry-DSC measurements in virgin, bleached and permanently wavy hair samples were investigated by [20]. In the virgin hair samples, the authors observed DSC curves with double peaks. They attributed these results to the different cortical cell fractions in terms of cysteine content. They observed that bleaching hair shifted the T_D to higher temperatures and a decrease in the area of the denaturation peak and attributed this to loss of crystalline material (ΔH_D).

In 2005, [23] obtained similar results, which related an increase in the T_D after hair tresses were bleached and chlorinated. According to them, this increase is due to the fact that these two processes promote the increase in ionic interactions, increasing the stability of the keratin structure and changing the denaturation temperature to higher values. The reactive environment may have increased the concentration of cysteic acid, produced by the oxidation of cystine and as a consequence shifting the denaturation temperature to higher values. In contrast, ΔH_D values decreased with the increased immersion time in the oxidant solution. That is, more energy was required to disrupt the keratin crystalline structure of the untreated hair than to disrupt the chemically treated hair. According to [24], in 2010, this increase in T_D is indicative of some weakening of the fiber, possibly due to new molecular forces set up within it compensating or even overriding the effects of the lost disulfide bonds.

Corroborating the data obtained by [22, 23] and [24], Fig. 2 shows our results (dry-DSC measurements) employing virgin and bleached Caucasian hair samples. The experimental conditions of these results are described in a separate section further below. The DSC curves of the

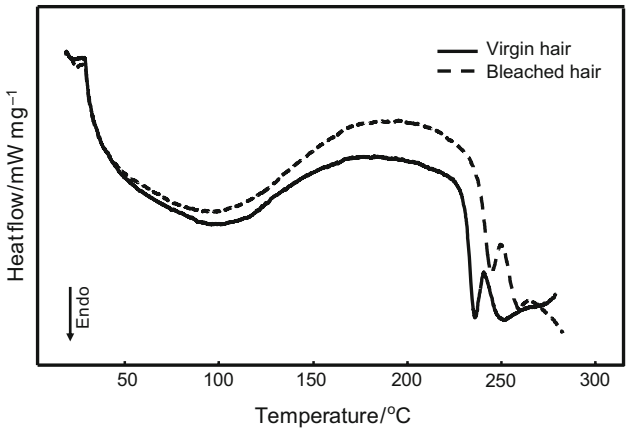

Fig. 2 DSC curves obtained at 10 °C min^{-1} under N_2 atmosphere (50 mL min^{-1}), partially closed Al capsule containing 2 mg of virgin and bleached Caucasian hair samples [33]

bleached hair sample exhibited an increase in the T_D, from 236 to 245 °C. The virgin and bleached hair samples showed denaturation enthalpy at 7.0 and 6.0 J g^{-1}, respectively. Wortmann et al. [10] and Marsh et al. [25] observed the opposite behavior in T_D in bleached hair tresses, but these results were obtained in wet-DSC medium. The authors reported that bleaching promotes increased cysteic acid concentration and thus increased ionic interactions. In the wet medium, the increase in the content of anionic groups induces an increase in water content. This fact leads to a continuous decrease in the viscosity of the matrix and thus T_D. Some authors attribute this change to a matrix plasticization or loss of matrix cross-linking density (formation of a three-dimensional cross-link). When the keratin matrix is plasticized by water, denaturation of α-helix microfilaments occurs at lower temperatures [26].

In 1993, [27] showed that the cross-link density of the matrix that surrounds the intermediate filaments kinetically controls the T_D of the hair samples. The new forces, which may be hydrogen or salt linkages, are susceptible to moisture, but still capable of rendering thermal stability to the fiber, at least under the ambient conditions. In fact, the authors have reported that in the wet-DSC the T_D decreases after bleaching of the hair. According to the authors, the pattern of changes in the T_D is due to the UV-induced cross-linking within the cortex region. The marked increase in T_D after bleaching is attributable to the more even distribution of these new bonds within bleached hair than that in the UV-exposed virgin hair. A study, in 1995, developed by [28] evaluated dyed and undyed hair by DSC. The authors showed that the dyed hair samples presented a greater tendency to absorb water/moisture than the undyed hair samples. They also reported that dyed hair showed a significantly higher tendency to bind to the water more strongly, based on the T_D and ΔH_D. In our study, there was an increase in ΔH_d values of bleached Caucasian hair samples, corroborating the results obtained by [28], as shown in Table 1.

Several studies of the literature describe this phenomenon as a consequence of the greater porosity of the bleached hair [23, 29–33].

In 1997, [14] developed a method by wet-DSC to analyze wool samples using silicone as a mean of analysis and there were similarities in the thermal characteristics of human hair and the wool keratin samples. In a later study, in 1999, [34] studied the thermal behavior of Caucasian hair samples by DSC employing the method previously developed, but using two different means: silicone and water. According to the results, silicone showed to be effective a mean to determine the thermal melting enthalpy of crystals of α-helix of human hair samples. The results indicated that human hair samples ($\Delta H_D = 14.5$ J g^{-1}) are more crystalline than wool samples ($\Delta H_D = 10.0$ J g^{-1}). In 1998, [11] confirmed that orthocortex cells have a lower melting temperature than para-cortex cells. The orthocortex has a lower concentration of disulfide bonds than the para-cortex. They considered that the occurrence of the keratin denaturation double endotherm of the wool sample is probably due to the content of the cysteine and disulfide bonds, being sufficiently greater to separate the peaks. The DSC curve showed the two peaks of denaturation of keratin at 230 and 240 °C, referring to ortho- and para-cortical cells, respectively. In 2002, [10] studied the effects of chemical treatments in hair by wet-DSC and noted that the denaturation enthalpy depends on the amount and structural integrity of the material α-helical intermediate filaments in the cortex of human hair. This dependency showed that morphological components were similarly affected by bleaching, cosmetic treatment that involves oxidative substances.

The bleaching increases the porosity of the hair, which also increases the water absorption, causing damages to the hair (like the decrease in the protein structure) when the same is heated by thermal hair styling tools. In this way, it is important to emphasize that thermal hair styling tools should not be used in wet hair and the use of the cosmetic thermal protector before these treatments is a

Table 1 Dry-DSC measurements of virgin and bleached Caucasian hair samples (22.0 ± 2.0 °C; 20.0 ± 2.0% R. H.) [33]

Sample	T_d/°C	ΔH_d/J g^{-1}	T_D/°C	ΔH_D/J g^{-1}
Virgin hair	96	203	236	7.0
Bleached hair	96	234	245	6.0

suitable because the heat can cause more damage to the bleached hair than virgin hair.

In 2003, a study by [30] combined the DSC and gas chromatography (GC) techniques to quantify the dehydration energy and content of the water of the dyed hair samples treated with *leave-on* and *rinse-off* products. The results indicated a difference in the values of ΔH_D and the percentage of water present in the control and treated hair samples, and this fact can be attributed the ingredients of cosmetic product. The authors suggested two hypotheses to explain the greater energy required to release water from the hair: The treatments increase the water content in the hair fibers samples, or/and the treatments prevent the release of water and therefore, require more energy. Such interference may be due to the formation of a barrier (film) and/or the presence of hydrophilic substances in the composition.

In 2004, a research developed by [35] studied the thermal behavior of hair samples by TG and DSC. The TG curves presented a mass loss between 5 and 8%, corresponding to the water content absorbed by the hair. DSC curves of the hair samples showed melting enthalpy of α-helix between 230 and 233 °C and thermal decomposition of the hair fiber after 250 °C.

In 2005, [12] studied the behavior of the T_D of human hair samples by DSC with different moisture contents. The authors adopted a technique using silicone as thermal mean. The denaturation temperature of the α-helix in human hair varied according to the moisture content (205–155 °C for dry and moisture content of 23% R.H. hair samples, respectively). However, the melting enthalpy of the dry hair samples was kept almost constant, leading to the conclusion that there are well-defined crystallites in human hair keratin.

Many consumers perform thermal and chemical straightening on wet hair (or in places with high relative humidity). However, these procedures may cause greater damage to the structure of the hair, and this way, studies with different methodologies are very important to explain the behavior of the hair subjected to these thermal treatments.

Still in 2005, [23] evaluated the changes in the denaturation of human hair keratin submitted to bleaching and chlorinating treatments. The authors observed an increase in T_D of hair by dry-DSC measurements and attributed this increase to the fact that these two processes promote the increase in ionic interactions, increasing the stability of the keratin structure and changing the T_D to higher values. The reactive environment may have increased the concentration of cysteic acid, produced by the oxidation of cystine and therefore shifting the denaturation temperature to higher values. In contrast, ΔH_D values decreased with increasing immersion time in the oxidant solution. That is, more energy was required to disrupt the keratin crystalline structure of the untreated hair than for the chemically treated hair. In 2007, [29] also reported an increase in ΔH_D of bleached Caucasian hair samples subjected to the cosmetic formulation by dry-DSC. Three endothermic peaks around 235, 244 and 250 °C were attributed to denaturation of keratin. Above the temperature of 350 °C, there was a complete oxidative degradation of the hair.

In 2008, the denaturation of the α-helix proteins and the effects of the reducing and oxidative cosmetic treatments in hair samples employing wet-DSC measurements were studied by [36]. The results showed that there were differences in thermal denaturation fraction of the α-helical human hair samples subjected to such treatments. The kinetic parameters (activation energy and pre-exponential factor) were determined from DSC curves by applying the Friedman method.

In 2009, [37] proposed a non-isothermal kinetic mechanism to describe the process of thermal denaturation of α-keratin in hair samples by wet-DSC. According to the authors, the kinetic mechanism is autocatalytic and the calculation of the activation energy allowed concluding that the thermal denaturation process corresponds to the breaking of S–S bonds between the main morphological components of the matrix.

Still in 2009, [38] used wet-DSC and combing techniques to test the efficiency in the thermal protection of the cosmetic compositions (*acrylates copolymer VP/DMAPA and polyquaternium 55*) in hair subjected to heat flat iron. This method was used for the quantification of the hair fiber fragmentation as a measure of the alleviation of weakening of the hair fiber caused by thermal protective composition. This method indicated that two polymers provided higher thermal protection not only to the surface but also to the cortex of the hair fibers. In 2010, [24] studied the changes in human hair submitted to chemical and photochemical oxidative processes. DSC was utilized along with other analytical techniques as a tool to understand the results. The authors verified that the decomposition temperature of the hair sample increases with UV irradiation time and that it increases more prominently after a bleaching step. The increase in T_D is indicative of some embrittlement of the hair fiber, possibly due to new molecular forces set up within it compensating or even overriding the effects of the lost disulfide bonds. Upon irradiation and/or bleaching, the hair fiber progressively becomes brittle as evidenced by the increased denaturation temperature, as discussed previously.

In 2010, [39] investigated the thermal damage caused by using heat styling and thermal protection of the cosmetic products (*polyquaternium-55 polymer, VP/DMAPA acrylates copolymer and VP/acrylates/lauryl methacrylate copolymer*) by wet-DSC. The results indicated the decrease

in the α-keratin content around 97% with pre-treatment with *VP/acrylates/lauryl methacrylate copolymer*. In 2011, [9] studied the thermal decomposition of the hair samples by DSC heated to different temperatures (230, 240 and 250 °C) and demonstrated by MEV images that the material of the cortex melts at about 240 °C and flows out of the surrounding cuticle area, thereby forming microtubes of enfolded cuticle material. According to the author, the cortex which contains about 21–22% of ordered (crystalline) material melts, while the cuticle which is composed of amorphous cross-linked material remains intact. They attributed this result to the different morphologies of both layers, which is most likely the reason for the formation of these microtubes.

Studies by [32] showed the influence of dye containing conditioning agents (*silanetriol and panthenol*, *PEG-12 dimethicone*, hydrolyzed silk protein, hydrolyzed milk and lactose) in hair by TG and DSC. The results showed that oxidative treatment damaged hair fibers, reducing the moisture content in relation to treated hair. The incorporation of conditioning agents in formulation decreased the damage caused to the hair from the hair dyeing.

Still in 2011, [40] identified the compounds degradation formed in the thermal degradation of samples from sheep's wool, human hair and chicken feathers by the techniques of TG/DSC (dry-DSC) coupled with the FTIR and GC-MSD (gas chromatography–mass selective detector). Only small differences were observed between the studied keratin samples. The degradation started with the formation of ammonia and CO_2 (from 167 to 197 °C, respectively); the thermal degradation started with the formation of ammonia and CO_2 (from 167 and 197 °C, respectively), then the formation of inorganic sulfur-containing compounds (SCS, SCO, H_2S and SO_2 at 240, 248, 255 and 253–260 °C, respectively) and water at 255 °C. According to the authors, thiols are formed in two stages (257 and 320 °C) and nitriles are formed in maximum at 340 °C until about 480 °C. Phenol and 4-methylphenol are the most important degradation compounds, formed at 370 and 400 °C, respectively. Nitrogen was present mainly as aliphatic nitriles/aromatic amides and pyridines, whereas sulfur was found principally as sulfides, thiols, thiophenes and triazoles.

These data are alarming because in the day-to-day life hair can be subjected to thermal treatments around 200 °C and some chemical treatments employing heat flat iron to temperatures substantially higher than 200 °C. Based on the results of [39], it was possible to determine which gases can be eliminated during these types of treatment. However, if these volatiles were formed during heating of hair, the thermal decomposition of hair components may be derived of: (a) fatty material, for example the 18-methyl eicosanoic acid, or 18MEA, a fatty acid attached itself to the cysteine of the protein layer and provided hydrophobicity to hair, (b) and/or protein material (amino acids containing sulfur and nitrogen, for example) increasing the damage. Many spectrophotometric methods to quantify hair protein loss were used over the years and have been suggested for the purpose of measuring total protein from the hair in the association with the DSC results [41].

In 2012, [42] studied thermal denaturation of α-keratin in human hair samples by modulated DSC. The authors reported that this event started at 210–220 °C and is related to pyrolysis of cortex proteins. [43] investigated the possibility to measure protein denaturation of the hair samples with fast differential scanning calorimetry and observed the phenomena of water evaporation and pyrolysis. The authors stated, however, that the protein denaturation peaks were obscured by the water evaporation and pyrolysis phenomena, as the current set up only allows dry-DSC measurements.

In 2013, [44] reported an influence of the pH values on the treatment of keratin in hair by wet-DSC measurements. The hair damaged by oxidative treatment with low-pH solution shows a significant increase in enthalpy and a shift in the T_D toward higher temperature for the denaturation of the keratin. The DSC results were associated with the amino acid analysis, tensile measurements, X-ray analysis and Raman spectroscopy. However, the results did not indicate significant changes in chemical structure or crystallinity of the keratin to account for the shifts of T_D and ΔH_D. The authors proposed a three-phase model for keratin fibers, in which the non-helical terminal domains of keratin promote filament interactions and control the thermal properties of keratin intermediate filaments. The interface phase, whose strength was increased at low values of pH, scaffolds the intermediate filaments and, in this way, controls the thermal stability. The thermal denaturation of the intermediate filaments could occur only after the scaffold was irreversibly damaged.

The effect of three botanical actives (*Cystoseira compressa extract, Lepidium meyenii extract and Carob tree extract*) in hair samples was studied by [31]. Scanning electron microscopy (SEM) and brightness measures were selected to evaluate the efficacy of these raw materials in the dyed hair samples. The authors verified that the application of botanical extracts reduced the permeability of the fiber and increased their crystalline integrity. With an efficacy study of hair products, the *Cystoseira compressa seaweed* and *Carob tree extracts* indicated a higher capacity on cystine reformation of the damaged cortex cells and a higher coating capacity, respectively. *Lepidium meyenii* and *Carob tree extracts* indicated an increase in the tensile strength of the hair samples providing an improvement in the integrity of the hair fibers. The authors suggested that this increase could be explained by two

hypotheses: the first is that there was an increase in the water content in the hair fibers due to the botanical actives. The other possibility was that some functional groups present in the extracts bonded with cystine within the hair fiber restored from some broken disulfide bonds in the oxidation treatment.

In 2013, [45] studied the efficiency of a cationic silicone (*quaternium 22*) incorporated in a microemulsion conditioner and applied in hair by DSC measurements. The results showed a reduction in the temperature of denaturation caused by thermal damage. The improvement was 70–80% for thermal protection, which can be attributed to improvement in the deposition of silicone quaternium-22 from the microemulsion. The hair denaturation temperature is a significant parameter in assessing the degree of damage to the keratin structures.

In 2015, [46] evaluated hair samples treated with hair-straightening formulations containing 2.0, 5.0 and 10.0% of formaldehyde by DSC and the study showed that increase in formaldehyde concentration in the formulation decreased the crystalline integrity of the fibers causing a decrease in the ΔH_D values. This is a challenge to the researchers of the cosmetic industry, especially those that produce the "progressive brushes." These products use formaldehyde as a straightener active and employ thermal hair styling tools to promote better efficiency in the straightening of the hair fibers. Formaldehyde is one of the best known and belongs to this class of straighteners, but it is prohibited by regulatory agencies of cosmetic products in Brazil, since it is harmful to health in certain concentrations, as discussed previously.

Still in 2015, [47] characterized samples of hair of the main ethnic groups (afro-ethnic, oriental and Caucasian) by DSC and TG. DSC results showed two main events up to 250 °C for all hair samples analyzed: dehydration (endothermic event), which was observed in the TG curves and the melting/denaturation peak temperature of the crystalline phase of the hair keratin (endothermic event). A third peak, endothermic event, appears soon after the T_D, forming a bimodal shape. This behavior can be related to the ortho- and para-cortical cells, respectively, according to a previous study by [11]. In 2016, [13] reported difficulty in the interpretation of dry-DSC and wet-DSC measurements data from hair samples and the effect of cosmetic treatments. According to the authors, the two ways of investigating the hair fibers by DSC showed some obstacles that have to be considered, especially when such data are used for product claims substantiation. Additionally, regarding the DSC, other techniques like X-ray diffraction, tensile stress–strain should be employed in this type of research to support the results and thus provide more robust data.

Thus, there is a need for research involving a greater variety of techniques in order to clarify and broaden the knowledge about the thermal denaturation of hair. Techniques such as SAXS (small angle X-ray scattering), Fourier transform infrared spectroscopy and mass spectrometry are interesting alternatives and, when associated with DSC, may enlarge the scientific findings.

The following describes the experimental part that corroborates the scientific findings cited in this article.

Materials and methods

Material

The virgin and bleached hair tresses were commercialized by De Meo Brothers® (NY, USA).

Methods

DSC analysis

The hair tresses were washed with a 10% w/v dispersion of sodium lauryl sulfate with digital massage for 2 min. They were then rinsed with distilled water to completely eliminate the detergent [32]. The hair samples were cut into snippets and stored under room conditions (25 °C, 65% H.R.) to ensure constant water content. Dry-DSC measurements were taken on hair snippets samples using a cell DSC model 50 (Shimadzu® Corporation, Kyoto, Japan), heating rate of 10 °C min^{-1} (25–550 °C), under dynamic N_2 atmosphere (100 mL min^{-1}) and Al capsule partially closed containing 2 mg of sample [33]. The DSC curves of the experiments are shown in Fig. 2.

Conclusions

This review collected researches about DSC methods in the hair characterization studies. In the literature, there are two of DSC methods employed in several studies proposed in hair samples, dry-DSC and wet-DSC measurements, and they have differences between them. Both methods were used for hair analysis and have been widely used to evaluate many hair product claims. The literature reports that to evaluate the efficacy of cosmetic products in hair, the most indicated method is wet-DSC. However, to evaluate the modifications in the hair with the routine use of thermal hair styling tools, the dry-DSC measurement can be an indicated method, as it reflects the reality of the procedure the consumers use, which employs heat in direct contact with the hair fibers. However, for more robust and reliable results to support the results of DSC, this one should be associated with other techniques such as stress–strain measures, FTIR, and X-ray diffraction.

It was also observed that several factors can contribute to the embrittlement of the hair fiber, such as the use of thermal hair styling tools in virgin, discolored and/or dyed hair. The heat treatments can also cause loss of fatty and/or protein materials in the hair. And this damage can be increased if the hair is wet during the heating of these equipments. However, some cosmetic ingredients like the silicones, polymers and other film forms can affect keratin binding and its molecular structure, improving the performance of the products of thermal protection.

Therefore, the DSC is a useful tool in the evaluation of hair fibers submitted to different types of treatments and can help the researchers in the cosmetic area.

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