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Thermoanalytical characterization study of hair from different ethnicities

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Abstract A characterization study of the samples of hair and animal keratin was performed to enhance the understanding of the thermal properties of the hair of the main ethnic groups. The mechanical, physicochemical and thermal properties of Caucasian, Oriental and African-ethnic hair have been widely described; however, this research adds knowledge about the thermal and analytical properties of these types of hair. To achieve such objective, thermogravimetry (TG), differential scanning calorimetry (DSC) and elemental analysis techniques were employed. To estimate the thermal stability of the hair samples, TG carried out a non-isothermal TG method kinetic study. The results obtained of TG/DTG showed similarity between the samples of hair and animal keratin, for all the events of thermal decomposition involved with mass loss. African-ethnic hair sample presented the lower thermal stability. This fact can be related to the data literature that showed that this type of ethnicity has the less tensile strength and breaks more easily than others types of the hair. Oriental hair sample showed to be, from the non-isothermal TG method kinetic study, more thermally stable than the other samples. DSC results showed that the hair samples presented melting/denaturation of the crystalline phase; however, animal keratin sample did not present such.

Keywords Hair · Ethnicities · Characterization · Thermal analysis

Introduction

Human hair is a complex biological fiber with a nanocomposite structure. The properties of the hair vary significantly with ethnic origin, environment, chemical and physical treatments. Chemically, the main component of human hair is the keratin, a group of proteins, which account for 65–95 % of hair mass. Keratin fibers are described as being formed of crystalline rod-like components made of α-helix (the intermediate filaments, IFs) embedded in an amorphous matrix that has a relatively high amount of cysteine. The human hair is also composed of lipids, water, melanin and trace elements [1–3].

Some X-ray diffraction studies investigated the crystalline structure of hair fibers, and the authors found two distinct X-ray patterns (α-helix and β-sheet) in the normal and stretched states of the fiber [4, 5].

The classification of the hair in racial groups included: Caucasian, Oriental and African-ethnic. On the chemical aspect, in terms of protein and amino acids, the three types of the hair are similar. The African-ethnic hair has a higher degree of irregularity in the diameter when compared to other ethnic types. It is also known that the cross section of the fiber is more oval than the others ethnicities, which are more cylindrical. It also presents less resistance to stretch, breaks more easily and requires a greater force to be combed, with lower water content compared to Caucasian hair [1, 3, 6, 7].

African-ethnic, Caucasian and Oriental hair were evaluated by X-ray analysis, cross-sectional measurements,

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tensile testing and water swelling analysis. The results on the morphology, geometry and mechanical properties of the samples confirmed the heterogeneity of diameter (presence of constrictions of the cross section along the fibers), ellipticity and weakness of the African-ethnic hair. The high prevalence of fractures in African-ethnic hair and the high variability of its cross section along the fiber may account for the brittleness of this type of hair, which is experienced every day by people of African origin during combing and grooming [8].

Thermal analysis covers techniques widely used to characterize hair samples besides a wide variety of materials and products in health, pharmaceutical and cosmetic areas [9–12]. Extensive studies have been carried out to investigate the thermal behavior, dehydration/hydration effects, melting behavior of the α-crystallites and kinetic study in hair [13–23].

Furthermore, thermal analysis can be used in studies of reactions in the solid state in order to determine kinetic parameters such as activation energy (E_a), the frequency factor (A) and reaction order [24–27]. From these aspects, it is possible to measure the variation of a property of the sample when it is heated (dynamic kinetic study) or maintained at a constant temperature (isothermal kinetic study). The kinetic study based on TG is an effective method in the elucidation of the probable mechanisms of solid-state reactions such as thermal decomposition and dehydration [28].

For this study, the thermal profile of virgin hair samples was carried out within the temperature range of the second event of thermal decomposition (related to hair keratin denaturation) and involved the determination of the reaction mechanism and kinetic parameters using thermogravimetric non-isothermal curves.

The denaturation temperature measures the thermal stability of proteins and is influenced by the heating rate and protein concentration as well as by the biochemical environment, e.g., pH [29]. In alkaline medium favors is favorable to cystine breakage and to the hydrolysis of the amide bonds and formation of lanthionine and lysinoalanine. Breaking of the cystine disulfide bond, located preponderantly in the matrix, leads to the decrease in viscosity and the decrease in denaturation temperature as a consequence; the decrease in enthalpy indicates that part of the helical segments of the IFs were damaged as a result of high pH value and there is less crystalline material to denature thermally [1, 30, 31].

Thus, this research aimed at the physicochemical and thermoanalytical characterization of the hair samples of different ethnic groups by the non-isothermal kinetic study of the different types of hair.

Materials and methods

Material

Virgin black hair samples of Caucasian, Oriental and African-ethnic are commercialized by De Meo Brothers® (NY, USA) in form of the continuous locks (2 g and length of about 10 cm). Animal keratin sample was obtained by Eversil Pharmaceuticals Indústria e Comércio Ltda.

Equipment

Thermogravimetric analyzer, Model TGA-51 and DSC cell, model 50, both Shimadzu® Corporation, Kyoto, Japan. Analyzer model CHIN 2400, Perkin Elmer, Waltham, MA, USA.

Methods

The hair samples were characterized by analytical techniques: TG/DTG, DSC and EA. The kinetic study by non-isothermal method (Ozawa method—TG technique) of hair keratin degradation was used to compare the different ethnic groups.

Preparation of the hair samples

The hair locks were washed with a 10 % *w/v* dispersion of sodium lauryl sulfate with digital massage for 2 min. Then, they were rinsed with distilled water to completely eliminate the detergent [32]. Then, the hair locks were cut into snippets and stored under room conditions (25 °C, 65 % R.H.) to ensure constant water content.

Thermogravimetric (TG) analysis

TG measurements were conducted on hair snippets and animal keratin samples using thermobalance model TGA-51 (Shimadzu) under dynamic air atmosphere (flow rate of 50 mL min^{-1}); temperature range from 25 to 900 °C; heating rate 10 °C min^{-1}; and Pt crucible containing about 15 mg of sample.

DSC analysis

DSC measurements were conducted on hair snippets and animal keratin samples using a cell DSC model 50 (Shimadzu) of the following experimental conditions being adopted: heating rate of 10 °C min^{-1}, range of temperature of 25–550 °C under dynamic N_2 atmosphere (100 mL min^{-1}) and Al capsule partially closed containing 2 mg of sample.

Elemental analysis (EA)

The content of the elements C, N, H and S of the samples of hair and animal keratin were obtained using the equipment CHIN 2400 Elemental Analyzer® (Perkin Elmer).

The non-isothermal TG method kinetic study of the hair samples

The kinetic study of virgin hair samples included the determination of the kinetic parameters (activation energy, frequency factor and reaction order) related to the hair keratin decomposition, using non-isothermal TG curves by the method of Ozawa [33]. These experiments were performed using thermobalance, heating until 300 °C, heat flow of 5; 7.5; 10; 15 and 20 °C min^{-1} under an atmosphere of air (50 mL min^{-1}) using a Pt crucible and 15-mg hair sample. However, some adjustments in the method were necessary in order to avoid the influence of water in the hair samples on the results of the TG curves, which leads to poor reproducibility. The hair samples snippets were heated to 120 °C and maintained at this temperature until the water was removed. The heating was then stopped so that the new parameters were added to the thermogravimetry equipment (heating until 300 °C). The mass loss for data processing was at 10 %, according to the kinetic analysis program developed by Shimadzu. The angular coefficient (slope) of the graph that correlates log β versus $1/T$ (K^{-1}) (where β is heat flow, T is temperature in K) provides the E_a (activation energy) of the process. The values of the frequency factor (A) and reaction order were also obtained in this kinetic study. The reaction order was obtained from the graph that correlated the residual mass of the sample by the reduced time in minutes [34].

Results and discussion

Table 1 shows the data of mass loss (Δm) in %, the range temperature and peak temperature (in °C) of each event of the samples. The TG/DTG results (Fig. 1) demonstrated that the thermal behavior of the samples of Caucasian, Oriental and African-ethnic virgin hair and animal keratin presented three main and similar mass losses: The first event refers to the evaporation of water, the second and third ones refer to keratin polypeptide chain denaturation [35] and thermal decomposition. Liu et al. [36] studied powder of duck fiber sample by TG and DSC and obtained the temperature range of 20–150 °C to dehydration event [36]. In this research, it is observed in Table 1 that the temperature range obtained of keratin animal sample was 25–167 °C [36].

From the TG/DTG curves, comparing to the three ethnicities, it was observed that the African-ethnic hair sample presented the lowest water concentration. This fact can be confirmed in the results of EA (Table 2) since the African-ethnic hair sample presented the lowest hydrogen content. African-ethnic hair demonstrated a particular behavior when placed in contact with water. Its radial swelling percentage is lower than that observed in Oriental and Caucasian hair [8]. Thus, because of its wavy shape, this type of hair presents itself as drier because the sebaceous glands are less active in this group, and beyond that fact, oiliness distribution over fiber is irregular [37].

African-ethnic hair sample showed temperature thermal decomposition lower ($T_{peak\ DTG}$ values: Caucasian hair: 308 °C; Oriental hair: 296 °C and African-ethnic hair: 290 °C) than to the others hair samples. This fact can be confirmed by DSC results presented in Table 3. Marti et al. [38] obtained onset denaturation temperature of 238.7 °C in Merino wool sample by TG.

After the 700 °C (TG/DTG curves), a residue of about 1–2.5 % of the samples of hair and animal keratin remained related to inorganic material. This is because if there is considerable exposure to chemical elements, drugs or through ingestion, and after a certain period, the substance can be present in the hair [39, 40]. Elements present in the hair, such as Ca, Mg, Na, K and Cl, are considered macrominerals, while, for example, Fe, Zn, Cu, Mn, I, Cr, Se and Mo are considered trace elements [41].

Literature data indicate that the major component in the hair is keratin, other species in smaller quantities, materials

Table 1 TG/DTG results: the mass (%), the range temperature and peak temperature (°C) of each event of Caucasian, Oriental and African-ethnic hair samples and animal keratin

Events	Sample											
	Keratin			Caucasian			Oriental			African-ethnic		
	ΔT/°C	$T_{peak\ DTG}$/°C	Δm/%	ΔT/°C	$T_{peak\ DTG}$/°C	Δm/%	ΔT/°C	$T_{peak\ DTG}$/°C	Δm/%	ΔT/°C	$T_{peak\ DTG}$/°C	Δm/%
1°	25–167	76	7.4	25–200	63	12.3	25–195	61	13.3	25–170	59	10.4
2°	167–450	310	45.2	200–460	308	42.6	195–450	296	40.4	170–432	290	44.3
3°	450–780	584	46.0	460–690	578	42.6	450–685	569	45.1	432–650	575	43.9

ΔT temperature range of the decomposition, $T_{peak\ DTG}$ temperature of the peak, Δm mass loss

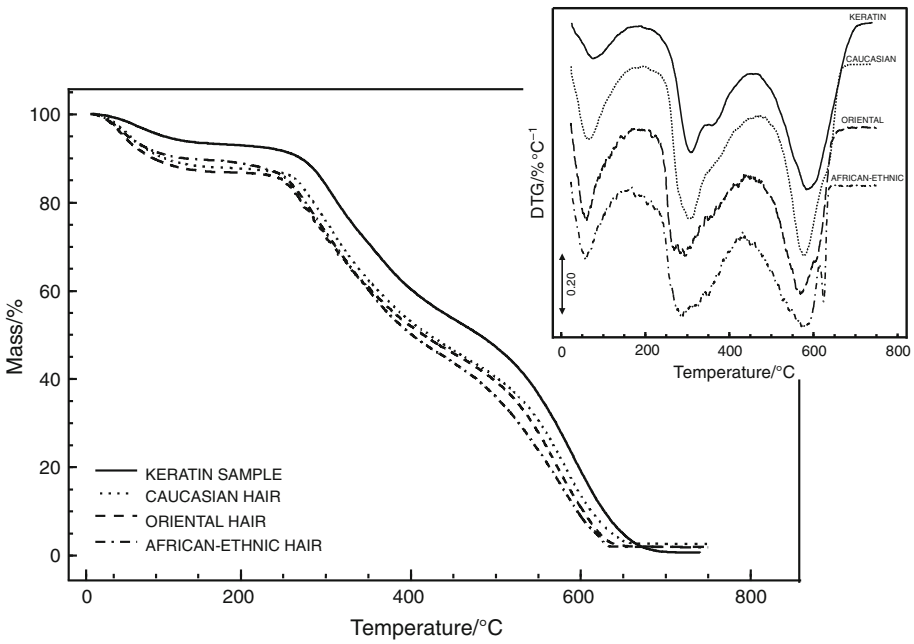

Fig. 1 TG/DTG curves obtained at 10 °C min^{-1} under dynamic air atmosphere of the samples of Caucasian, Oriental and African-ethnic virgin hair and animal keratin

Table 2 AE results (contents of C, H, N and S) in % of Caucasian, Oriental and African-ethnic hair samples and animal keratin

Sample	C/%	H/%	N/%	S/%
Keratin	47.00	4.76	13.41	3.86
Caucasian	42.96	7.31	13.81	3.64
Oriental	42.89	7.08	13.84	3.47
African-ethnic	41.34	6.38	12.28	3.43

C carbon, *H* hydrogen, *N* nitrogen, *S* sulfur

such as greases and inorganic elements [8, 42]. This fact explained the presence of the main components of the proteins (C, N, H e S) detected in the hair samples by EA (Table 2).

The animal keratin sample showed lower hydrogen content than that found in the hair samples, which corroborates with TG/DTG results, and it is explained by the smaller amount of water in its matrix (Table 1). This fact clarified the higher values of %C compared to others samples. According to the results, it was observed that Caucasian and Oriental hair samples showed similarity in the concentration of these elements, unlike the African-ethnic hair sample, which presented the lowest concentrations. By TG results, African-ethnic hair sample showed the lowest water content in its matrix, which proves the decrease in the H content and, consequently, increases the content of C and N.

According to Popescu and Höcker (2007), the elemental analysis of hair presented around 50 % C, 7 % H, 16 % N and 5 % S. The percentages differ slightly with the source of the hair, but keep a remarkable constancy around the mentioned values. The highest % S resulted from the highest cysteine content [43]. Choi et al. [44] detected 3.3–4.3 % S in the human hair using pyrolysis–gas chromatography.

The % S presented in all samples was lower when compared to % C and % N, and this fact corroborates with literature data indicated that the concentration of amino acids containing sulfur (such as cysteine) in the hair are smaller than the other amino acids having only atoms of C and N.

Table 3 DSC results: ΔH (J g^{-1}), the onset and peak temperatures (°C) of Caucasian, Oriental and African-ethnic virgin hair samples and animal keratin

Events	Sample										
	Keratin		Caucasian hair			Oriental hair			African-ethnic		
	T_{peak}/°C	ΔH/J g^{-1}	T_{peak}/°C	T_{onset}/°C	ΔH/J g^{-1}	T_{peak}/°C	T_{onset}/°C	ΔH/J g^{-1}	T_{peak}/°C	T_{onset}/°C	ΔH/J g^{-1}
1°	–	–	235.8	230.0	−7.25	235.2	229.4	−7.51	223.3	213.2	−6.98
2°	268.8	−768.3	249.4	243.0	−4.2	249.9	244.0	−3.8	238.7	232.2	−6.60

1°—melting/denaturation event; 2°—denaturation event

Table 3 shows the data of enthalpy (ΔH) in J g^{-1}, the onset and peak temperatures (in °C) of each event of the samples. ΔH is the energy uptake for the unfolding of the α-helical material during denaturation in hair [29].

The DSC curves (Fig. 2) showed two main events up to 250 °C for all hair samples analyzed: dehydration (endothermic event), which was observed in the TG/DTG curves, and melting/denaturation peak temperature (T_m) of the crystalline phase of the hair keratin (endothermic event). A third peak (T_D), endothermic event, appears soon after the T_m, forming a bimodal shape.

The melting endotherm of α-form crystalline in wool keratin often appears to be bimodal. Cao et al. [45] investigated the origin of this bimodal endotherm and related the bimodal peak that arises from the overlapping of the melting endotherm of α-form crystallites with the thermal degradation of other histological components. A study by Wortmann and Deutz [46] confirmed that ortho-cortical cells have a lower melting point than para-cortical cells, which could elucidate for the bimodal peak. The ortho-cortex contains a smaller concentration of disulfide linkages than the para-cortex. They considered that the occurrence of double denaturation endotherms of keratin of the wool is probable due to the cystine content and disulfide linkages, which are large enough and make possible to separate the peaks [46].

Caucasian and Oriental hair samples presented T_m (peak) values, 235.8 and 235.2 °C, respectively, showing the similarity in thermal stability between them. Literature studies showed the denaturation temperatures (230–240 °C) of keratin hair [47–49]. Chandrashekara and Ranganathaiah [50] studied oriental virgin hair by DSC and presented a denaturation temperature of 243.7 °C.

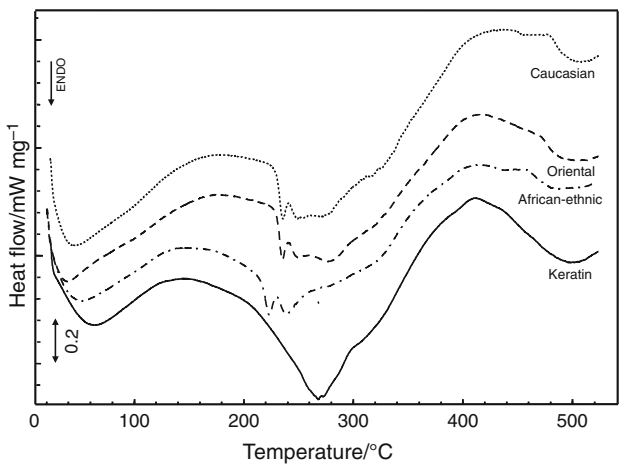

Fig. 2 DSC curves obtained at 10 °C min^{-1} under N_2 atmosphere (50 mL min^{-1}), closed partially Al capsule containing 2 mg of samples of Caucasian, Oriental and African-ethnic virgin hair and animal keratin

The African-ethnic hair sample presented a lower T_m (223.3 °C) compared to the T_m values of Caucasian and Oriental hair samples (about 12 °C). This fact is important in the development of products for African-ethnic hair, because these are the most susceptible to chemical transformation processes like hair straightening involving heat treatments, which are being widely used in this treatment. Often, such hair treatments used "flat iron" that achieves temperatures above 250 °C. ΔH values related to the melting/denaturation event obtained were 7.25, 7.51, 6.98 J g^{-1} for Caucasian, Oriental and African-ethnic hair, respectively. Fernandes et al. [51] evaluate African-ethnic hair by DSC and obtained the denaturation temperature and denaturation enthalpy values of 229.7 °C and 6.8 J g^{-1}, respectively.

The behavior of the α-keratin at high temperatures depends on the viscous matrix, which kinetically impedes the unfolding of the helix and thus significantly enhances its tolerance temperature. Water acts as an effective plasticizer in the matrix and this way the denaturation temperature decreases with the increase in water content [29, 49, 52]. Tonetti et al. [53] studied a qualitative method to identify different textile animal hair fibers (cashmere, wool, yak and goat fibers) by DSC. The study detected differences in transition enthalpy and temperature of the crystalline material that constitutes the ortho- and para-cortex of the samples. Wool fibers show a DSC curve bimodal endothermic peak in the temperature range of 230–255 °C; cashmere shows a single endothermic peak at 241 °C and a shoulder at 236 °C; and the DSC curves of yak and goat fibers showed a broad endothermic event at 237 °C [53].

The apparent fragility of African hair was consistent with the significantly increased structural damage (breaks, partial breaks, knots and longitudinal splits) observed by SEM, compared to the others ethnic groups [54]. African-ethnic hair has a larger diameter, lower water content, flattened elliptical cross section compared to Caucasian and Oriental ethnics. It is tightly curled and less shine when compared to Oriental hair and higher amount of sebum. It has high grooming friction, which combined with low tensile strength makes it more difficult to manage [3, 55].

The animal keratin sample presented three events mentioned above, except melting/denaturation temperature, indicating an amorphous matrix and absence of crystalline material.

Kinetic study non-isothermal TG

This mechanism has enabled the obtaining of kinetic triplet E_a, A (pre-exponential factor) and reaction order, which is considered to characterize kinetically the process [28].

It has been found in the literature papers using kinetic study Ozawa method non-isothermal TG in hair samples. Figure 3 presents the TG curves obtained by kinetic study and their kinetic parameters of the Caucasian hair sample. The kinetic parameters of the Oriental hair sample were also obtained under the same conditions, but the illustration was not shown.

The kinetic parameters values of the Caucasian and Oriental hair samples are exhibited in Table 4. It was not possible to calculate the kinetic parameters values of African-ethnic hair samples, probably due to the complex nature of this type of ethnicity compared to the others hair samples. From the results of EA (Table 2), the African-ethnic sample hair showed a lower content of the main constituent elements (C, N, H and S) of the capillary matrix. A smaller amount of organic material can result in a different thermal behavior. Comparing the DSC curves of all hair samples, it was observed the African-ethnic hair showed that immediately after the dehydration event the baseline started a shift toward endothermic, which does not occur in other types of hair. In the last ones, there was a partial plateau after dehydration, indicating greater thermal stability.

The value of reaction order was three for both ethnic hair samples (Caucasian and Oriental), showing these to be a complex process involving a series of parallel reactions.

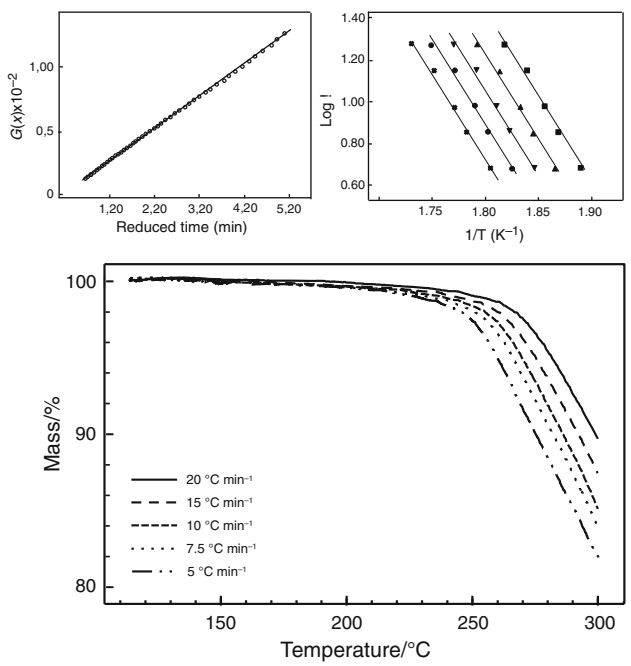

Fig. 3 TG curves overlap obtained at 5, 7.5, 10, 15 e 20 °C min^{-1} under dynamic air atmosphere (100 mL min^{-1}) of samples of Caucasian and plots of $G(x)$ versus reduced time and log β versus $1/T$ (K^{-1}) for determination parameters

Table 4 Kinetic parameters obtained from the kinetic study by the non-isothermal method (Ozawa [33]) of Caucasian and Oriental hair samples

Hair	E_a/kJ mol^{-1}	A	Reaction order	α
Caucasian	147	2.49×10^{13}	3	0.97–0.87
Oriental	162	7.29×10^{14}	3	

According to the E_a results, Oriental hair sample exhibited more thermal stability than Caucasian hair sample.

Istrate et al. [26] proposed a three-phase hard α-keratin model utilizing a non-isothermal kinetic model of thermal decomposition of Caucasian fibers by DSC. According to authors, the kinetic function results indicated that the mechanism of α-keratin thermal denaturation is more complex than the first-order kinetics and cannot be reduced to a single step. Additionally, those results indicated that the scission of S–S bonds were the limiting step of the thermal denaturation process [26].

Some modifiers are able to change the kinetics of the protein denaturation during heating, e.g., pH can change both the activation enthalpy and frequency factor. Studies showed that the modification affecting activation entropy appears to be linked to the hydration of the protein [29].

Conclusions

The association of the techniques (TG/DTG, DSC and EA) used allowed characterizing the samples of hair and animal keratin. The last one showed that is similar thermally.

DSC investigations suggest that is possible to differentiate thermally the hair samples of different ethnicities. The present study suggests that an African-ethnic hair sample is the most thermally fragile if compared to other types. These results reinforce existing literature data.

The presented methodology is able to complement the mechanical and morphological studies in African-ethnic hair from the literature. Therefore, thermal analysis can be used as a tool for assessing the thermal stability of hair samples. The combination of various techniques proved to be effective in characterizing different hair types.

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