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THERMAL ANALYSIS OF HUMAN HAIR IN NON-ISOTHERMAL AND ISOTHERMAL CONDITIONS

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Abstract: *This paper presents the thermogravimetric analysis of four (European) human hair samples under non-isothermal and isothermal conditions, in air. The thermal stability of these samples was evaluated using the following criteria: T_{onset} - the initial temperature at which the thermal degradation starts and apparent activation energy for this stage. The European hair type was determined to have more thermal stability. Therefore, if T_{onset} the temperature at which their thermal decomposition starts was compared with that obtained by other researchers in similar conditions for three types of human hair (Caucasian, Oriental and African), values 30 up to 70 ℃ higher would be established. Thermal resistance tests run in isothermal conditions (230 ℃, for 1 minute) established that only the P1 sample (dyed coarse hair) showed percent mass loss bellow 1%. For this sample, the thermogravimetric data, as well as the kinetic data confirmed a better thermal stability.*

Keywords: thermal stability, human hair, dynamic and isothermal conditions.

1. Introduction

Heat is frequently used to dry, straighten or curl hair in beauty salons, but also at home. The majority of existent studies from the literature on thermal analysis of human hair are conducted under dynamic conditions with various heating rates and in air or inert gas [1-5].

In a recent study, C. R. R. C. Lima et al. [4] used the following techniques: thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) to analyze thermal stability of animal keratin and three types of human hair (Caucasian, Oriental and African). The conducted study established that the African hair had the lowest thermal stability. This pattern is due to this type of hair having a lower content of main constituent elements (C, N, H and S) of the capillary matrix. The Caucasian hair type thermal stability was also analyzed in dynamic conditions by R. M. da Gama et al. [4] with a view to

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show the influence of treating it with oxidative hair dye. A percent mass loss evaluation showed that treating hair with light blonde color dye leads to hair damage and reduces its moisture content in relation to untreated hair.
Zhou et al. [6] confirmed that European and Caucasian hair types damage under the action of flat irons, using a wide range of instrumental techniques (FTIR imaging spectroscopy, DSC, dynamic vapor sorption, AFM, SEM, and thermal image analysis). They also established that degradation can be significantly reduced if using polymeric pre-treatments. Out of thermal analysis methods, they used DSC to confirm the damage of thermally treated hair. M. Brebu and I. Spiridon [7] conducted a comparative analysis of the decomposition mechanism for human hair (European), sheep wool and chicken feathers under dynamic conditions, with a rate of 10°C/min within the 25-600°C range in He gas, applying TG/MS/FTIR and GC/MS combined techniques. Within the 170-300°C range, they determined the prevalent decomposition gases: NH_3, CO_2, SCS, SCO, H_2S and SO_2, while nitriles and aromatics, of which phenol and 4-methylphenol are the most important degradation compounds [7], are present for temperatures higher than 300°C.

In our study, the European hair samples were analyzed in dynamic conditions with a rate of 10°C/min within the 25-700°C range and in isothermal conditions at 230°C in air, with a view to establish the degree to which using flat irons can contribute to hair damage by applying the TG technique. Another objective of the study is to evaluate the thermal stability of the analyzed hair samples by applying the following criteria: T_{onset} - the initial temperature at which the thermal degradation starts and apparent activation energy for this stage, considered important in the literature [8-10].

2. Materials and methods

To determine the thermal resistance of (European) hair, we took into account the following hair samples, which can be characterized as follows: **P1** – dyed coarse hair, **P2** – coarse hair, not dyed, **P3** – soft hair, not dyed and **P4** – curly hair, not dyed.

Thermal analysis is defined by the property changes that can appear in some samples when they are studied at different temperatures and at an imposed variation of the temperature. Properties that can be changeable at temperature variations are the physical and chemical characteristics like viscosity, density, concentration, electrical resistance, thermal conductivity.
The characteristics of thermal analysis are correlated to the samples properties. Samples can be analyzed in a large spectrum of temperature under dynamic or isotherm conditions, sample weight is between 0,1µg- 10 mg, the sample can be

solid, liquid or gel. Analysis time is also an important parameter that can vary from minutes to hours.

The following methods can be used in thermal analysis:

- thermogravimetric analysis (TG)
- derivative thermogravimetric analysis (DTG)

Thermogravimetric analysis (TGA) is also named thermogravimetry (TG) and is one of the most popular thermal methods. It consists in recording the sample weight function of temperature or time when sample temperature increases linearly over time (m = f(T); m = f'(t)). This method measures the sample weight variation depending on the temperature while the sample is subjected to a controlled temperature variation. The results of the variation of sample weight among the variation of temperature can be represented graphically like a thermogravimetric curve. Generally, the temperature grows over time but it is also possible to determine the variation of sample weight in isotherm conditions. Sample weight decrease is due to degradation and dehydration processes. It is known that thermogravimetry technique is used to determine the solvent content and it is also used for analysing the degradation and reaction processes. If the weight of a sample does not change among the variation of temperature, it means that the sample is stable or that the sample presents thermal stability in that thermal range. There is also the possibility that the sample weight increases. This aspect is explained through the existence of an absorption process of some components in the sample.

The thermal analysis was executed using a Mettler Toledo TGA-SDTA851^e derivatograph in air with the flow of 20ml/min, heating rate of 10ºC/min within the 25-700ºC range and 2÷4 mg sample weight. The operational parameters were maintained constant for all samples in order to obtain comparable data [11]. The four hair samples were also subject to the following experimental protocols: they were heated with the constant rate of 10ºC/min up to 230°C, they were maintained at this temperature for one minute and the isothermal stage percent mass loss was analyzed.

3. Results and discussion

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves shown in figures 1 and 2 allowed us to determine the main thermogravimetric characteristics: T_{onset} – temperature at which the degradation starts; T_{peak} – temperature at which the degradation rate is maximum; T_{endset} – temperature at which the degradation process ends; W - the mass percentage loss; DTA characteristics and the residue quantity are illustrated in table 1.

The analysis of the findings reveals that humidity removal, which ranges from 6 to 8%, occurs during the first stage in all the samples. This stage is followed by three or four degradation stages depending on the type of analyzed hair. The

residue quantity ranges from 4 to 8% at 700°C. These values are a bit higher than those obtained by C. R. R. C. Lima et al [4] for the three types of human hair (Caucasian, Oriental and African), analyzed under similar conditions. It was also established that the lowest the water release stage percent mass loss was registered for the dyed hair sample, as it was also reported by R. M. da Gama et al. [4], who compared light blonde treated hair and untreated hair in their study.

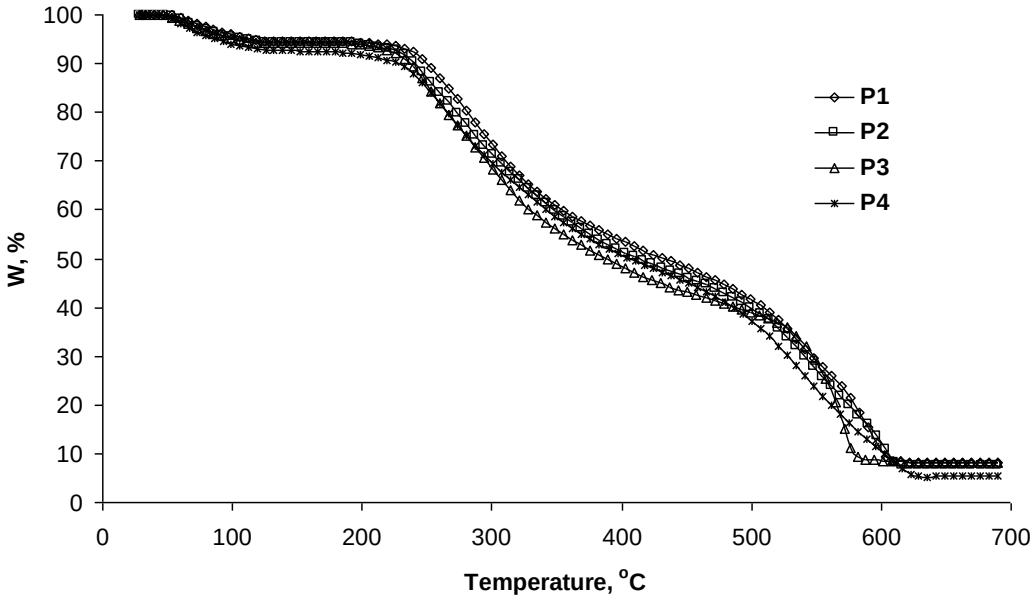

Fig. 1. TG curves

If we consider the T_{onset} degradation temperature in the first degradation stage as the thermal stability criterion and overlook humidity removal, the following series for the thermal stability may be suggested for the four types of hair analyzed:

$$\mathbf{P4 \cong P2 < P3 < P1}$$

An even bigger residue quantity, over 7%, may be noticed in samples **P1** and **P3**.
If the degradation temperature in the first degradation stage - T_{onset} measured by for the European hair type is compared with that obtained by C. R. R. C. Lima et al [4] for three types of human hair (Caucasian, Oriental and African), values 30 up to 70°C higher are observed. Therefore, we can confirm that the European hair type has a higher thermal stability.

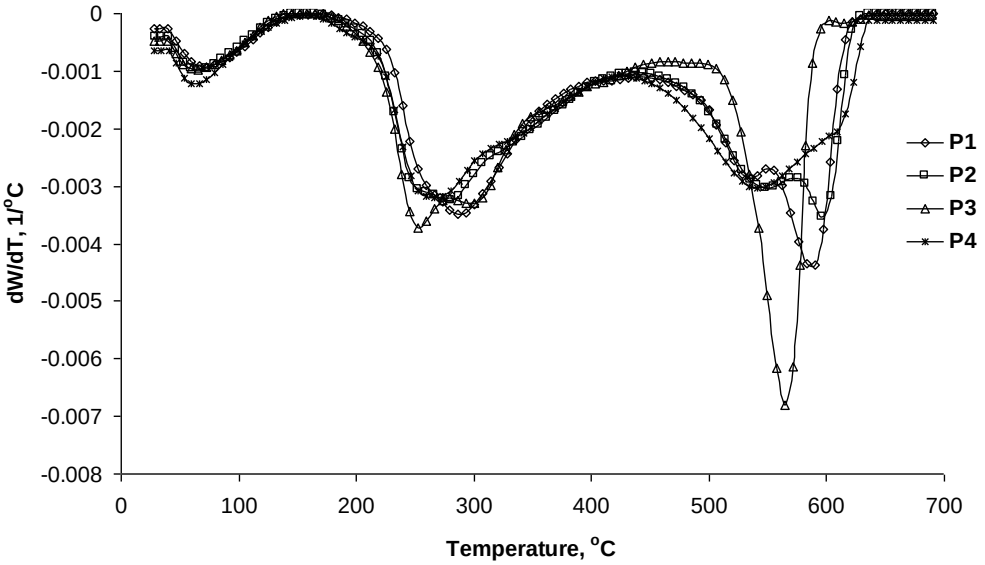

Fig. 2. DTG curves

Table 1. Thermogravimetric characteristics

Sample	*Stage of thermal degradation*	T_{onset} *(°C)*	T_{peak} *(°C)*	T_{endset} *(°C)*	*W (%)*	*DTA characteristics*
P1	I	45	67	120	6,26	Endo
	II	**240**	291	356	44,15	Exo
	III	510	534	568	25.79	Exo
	IV	568	589	604	16,41	Exo
	Residue				*7,39*	
P2	I	45	65	117	6,39	Endo
	II	**232**	251	305	26,55	Exo
	III	305	281	374	20,40	Exo
	IV	505	546	568	22,66	Exo
	V	568	601	611	17,07	Exo
	Residue				*6,93*	
P3	I	45	61	113	6,36	Endo
	II	**235**	253	281	19,27	Exo
	III	281	303	423	34,60	Exo
	IV	532	565	580	32,15	Exo
	Residue				*7,62*	
P4	I	46	61	119	7,94	Endo
	II	**231**	264	302	23,09	Exo
	III	302	331	374	23,17	Exo
	IV	488	540	570	28,38	Exo
	V	570	608	625	12,91	Exo
	Residue				*4,51*	

In order to validate the thermal stability series above according to the thermogravimetric data for the various types of hair analyzed, we proceeded to determining the kinetic parameters: apparent activation energy (Ea), reaction order (n) and pre-exponential factor (lnA). Kinetic processing was done using the STAR software, which applies the Freemann-Caroll method [12].

Assuming that the thermal degradation of materials may be considered a solid-gas system reaction, which may be graphically represented as follows:

$$A(s) \rightarrow B(s)+C(g)$$

where A is the solid material under analysis, B is the solid intermediary product formed during the degradation and C is the volatile product resulting during the process.
Admitting that the reaction is of the n order, the degradation reaction rate observes the following kinetic law:

$$-\frac{dC_A}{dt} = k \cdot C_A^n \quad (1)$$

If we note W_∞ the total mass loss, and W_t- the mass loss at a particular moment, then:

$$W_r = W_\infty - W_t \quad (2)$$

W_r is being the concentration at a particular moment of the reactant.
where:

$$\frac{dW_t}{dt} = k \cdot W_r^n \quad (3)$$

Admitting that temperature increases linearly in time, then:

$$\frac{dT}{dt} = a \text{ şi } dt = \frac{dT}{a} \quad (4)$$

If we replace dT depending on this equality, the velocity equation becomes:

$$\frac{dW_t}{dT} = \frac{k}{a} \cdot W_r^n \quad (5)$$

In equation (5), dW_t/dT is the speed of reaction expressed in mg/°C.
The speed constant depends on temperature according to a Arrhenius law:

$$k = A \cdot e^{-\frac{Ea}{RT}} \quad (6)$$

The velocity equation becomes:

$$\frac{dW_t}{dT} = \frac{A}{a} \cdot e^{-\frac{Ea}{RT}} \cdot W_r^n \tag{7}$$

for which the calculation methods of the kinetic parameters in the thermogravimetric data rely on.
The application of the ratio under differential or integral form leads to two groups of kinetic parameter assessment methods: differential methods and integral methods.
The differential method was deducted by Freeman-Carroll [12] and uses the logarithmic form of the equation (7).

$$\ln \frac{dW_t}{dT} = n \ln W_r + \ln \frac{A}{a} - \frac{Ea}{R} \cdot \frac{1}{T} \tag{8}$$

The experimental determinations reveal W_t=W(T) values and the difference is:

$$\Delta \ln \frac{dW_t}{dT} = n \, \Delta \ln W_r - \frac{Ea}{R} \Delta\left(\frac{1}{T}\right) \tag{9}$$

or

$$\frac{\Delta \ln \frac{dW_t}{dT}}{\Delta \ln W_r} = n - \frac{Ea}{R} \frac{\Delta\left(\frac{1}{T}\right)}{\Delta \ln W_r} \tag{10}$$

If we draw the $\left(\Delta \ln \frac{W_t}{dT}\right) / \Delta \ln W_r = f\left(\Delta(1/T)/\Delta \ln W_r\right)$ graph according to equation (10), using the slope of the straight line we may calculate the Ea apparent activation energy and the origin intercept reveals the reaction order n.
Ralation (10) is used to assess the kinetic parameters. The findings gathered for the four types of hair analyzed are shown in table 2.

Table 2. Kinetic characteristics

Samples	*Stage of thermal degradation*	*n*	*Ea (KJ/mol)*	*lnA*
P1	II	0.98±0.001	**47.88**±0.78	4.49±0.18
	III	0,79±0,001	151,61±4,83	17,23±0,73
	IV	0,23±0,001	127,56±2,07	12,66±0,29
P2	II	0,76±0,001	**30,86**±1,14	0,81±0,26
	III	0,47±0,001	127,41±1,46	13,35±0,22
	IV	0,51±0,001	167,51±3,78	18,17±0,53
P3	II	0,74±0,001	**69,80**±3,64	10,84±0,85
	III	0,37±0,001	42,83±1,36	3,78±0,29
	IV	0,48±0,001	279,50±1,55	35,21±0,23
P4	II	0,42±0,01	**32,99**±0,94	1,67±0,22
	IV	0,42±0,001	91,20±1,33	7,85±0,21

(A –pre-exponential factor; Ea – apparent activation energy; n – reaction order)

The apparent activation energy values for the first degradation stage written in bold in table 2 confirm the fact that samples **P3** and **P1** have better thermostability than samples **P2** and **P4**, respectively.

Considering that the use of hair straighteners an flat irons consists of heating the hair at 230°C at the most for one minute, the four types of hair analyzed were also subjected to resistance tests at constant temperature. Thus, after they have been heated at a constant rate of 10ºC/min up to 230°C, they were kept at this temperature for a minute and the mass percentage loss in the isothermal stage was analyzed. The results are shown in Figure 3.

The results revealed mass percentage losses below 1% only in the first type of hair, for which both the thermogravimetric and the kinetic data confirmed better thermostability. For the other types of hair, the mass percentage losses during the isothermal stage were below 2%. In these cases, it would be advisable to use the flat iron at temperatures lower than 230°C.

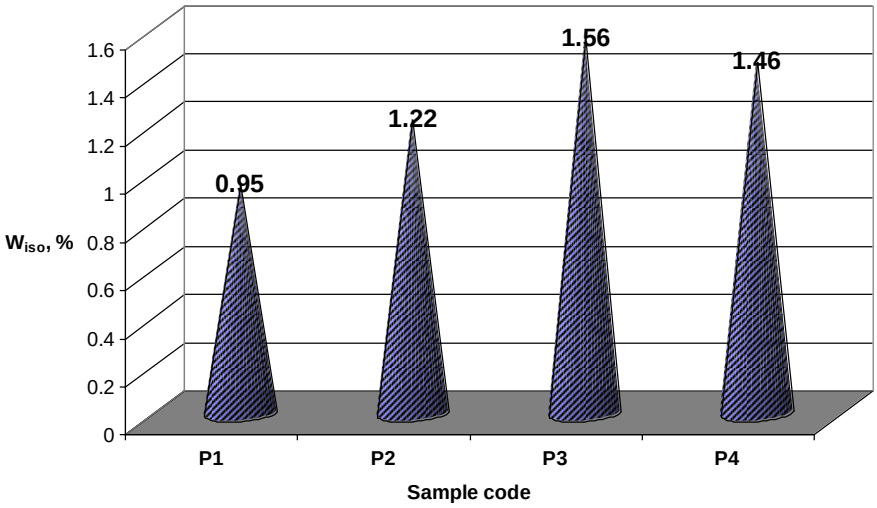

Fig. 3. Mass percentage loss at constant temperature (230°C)

Conclusions

- We analyzed the thermal resistance and stability of four types of hair.
- The degradation mechanism is complex, and includes four or five decomposition stages with different mass percentage losses.
- Based on the thermal and kinetic characteristics, the following thermal stability series was suggested: **P4** ≅ **P2** < **P3** < **P1.**
- The thermal resistance tests in isothermal conditions proved that only the first type of hair had mass percentage losses below 1%. In this type of hair, both the thermogravimetric and the kinetic data confirmed better stability.

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