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EVALUATION OF THERMAL TREATMENTS EFFECT ON HUMAN HAIR BY THERMAL ANALYSIS

BY

ANDREEA CĂLUIAN[1,2], TOMINA BRAN[1,3] and ELENA-LUIZA EPURE[1,*]

[1]“Gheorghe Asachi” Technical University of Iași, Romania,
“Cristofor Simionescu” Faculty of Chemical Engineering and Environmental Protection
[2]SC Delphi Technologies SRL, Romania
[3]Autoliv Romania

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Abstract. Hair provides a series of information about the health and lifestyle of people. The article’s topic is focused on the thermal analysis of different human hair samples. Three sample series were examined, so two series were prolong exposed at high and low temperatures, and the third series of samples was maintained at room temperatures. The thermal stability of these samples was evaluated using the T_{onset} as reference criteria. Even if small differences in the thermogravimetric behavior were observed at the analyzed samples, an interesting fact was observed in the first stage of degradation, the samples kept in warm experimental conditions had a higher thermal resistance than the similar samples from the other two series.

Keywords: human hair; TG/DTG; meteo-sensitivity; thermostability; thermal treatments.

1. Introduction

Long or short, curly or straight, blonde, brown, dark, red or gray, hair plays an important role in people’s physical appearance and social life but it can also provide information concerning the health and lifestyle of people.

*Corresponding author; *e-mail*: lepure@tuiasi.ro

According to recent studies it has been found that people with baldness have a 70% higher risk of getting heart disease compared to people who have rich hair. Medication, drugs and other substances that have ever been in a person's blood will be considered as "stored information" in the hair (Gaillard and Pépin, 1997). Therefore, hairs are precious evidence in forensic investigations (Seta *et al*., 1988).

Human hair is an epithelial formation, cylindrical and flexible with three tubular layers: cuticle (the outer protective layer waterproof, thin and transparent), cortex (the second layer determines the color, thickness, resistance, elasticity, and ripple degree) and medulla (the inner layer that contains a group of specialized cells with a high concentration of lipids). The cortex is organized in macrofibrils and microfibrils (Spei and Holzen, 1987), the latest are axially oriented as crystalline filaments and are embedded within an amorphous matrix (Swift, 1997).

Hair is considered to have the highest rate of growth in the body, the average life being of about five years, after which it dies and falls. The rate of hair growth and its density on the scalp decreases one the aging. Hair color and texture are genetically determined and can vary significantly from one person to another. The color is determined by the melanin secreted in the follicle, while the texture depends on the composition of the keratin. Depending on ethnicity the shape of cross-section hair is different, so Asians have round hair, the Africans flat shape and Europeans oval one (Franbourg *et al*., 2003).

Hair resistance is determined by the cross-linked structure of keratin (Asquith, 1977), a sulfurous scleroprotein found in its component. Keratin comprises two amino acid containing large amounts of sulfur, methionine, and cystine, but only the latest dictates the resistance of hair (Swift, 1997; Robbins, 1994). Cystine disulfide bridges stabilize the three-dimensional structure of proteins through intramolecular and intermolecular cross-links. This is the main reason why these proteins can maintain their biological activity and resistance to harsh environmental conditions such as thermal, mechanical or chemical stresses (Robbins, 1994).

Human health and productivity are affected by the climate change. To what stage the weather conditions can have a negative influence on the human body? Human meteo-sensitivity varies depending on the human genetic background, in consequence, it will react differently to the climatic factors.

The hair provides a heat-insulating barrier of the head to the action of the environmental factors. It can keep us from the harmful effects of the strong solar ray, but also prevents the loss of body temperature of the head area. The focus of this study is on the degradation level of human hair after they have been exposed to extreme temperature conditions. To obtain this information we used thermal analysis.

Recent thermal studies (Lima *et al*., 2016; Da Gama *et al*., 2011; Mihăilă *et al*., 2017) have shown that hair stability depends on the ethnicities or the cosmetic procedures, such as bleaching, dyeing, and straightening.

2. Experimental

2.1. Materials

The hair samples were collected from European male and female volunteers of various ages (Table 1) and used without any other treatment (washing, degreasing, etc.). Each sample was divided into three groups. Prior to thermal measurements, the samples were maintained either in an air-conditioned room at a constant temperature of 25°C (series called "A"), either at 40°C ("C" series) or at -10°C ("R" series"), for 7 days.

Table 1
Physical Characteristics of Collected Samples

Sample code	Age of the person	Gender	Characteristics of the sample
P1C	22	male	dark color, natural
P1B	22	male	dark color, curly, natural
P2	22	female	brown color, curly, natural
P3	21	female	blonde color, bleached
P4	21	female	dark color, natural
P5	21	female	dark brown color, natural
P6	33	female	dark color, natural
P7	52	female	light brown color, curly, natural

2.2. Analysis Methods

The analysis methods considered in this paper were thermogravimetry (TG) and differential thermogravimetry (DTG) analysis. Thermogravimetry is based on weight modification testing during a controlled heating process. Differential thermogravimetry measures the rate of material mass changes. The thermal analysis was performed using a Mettler Toledo TGA-SDTA851e derivatograph in air atmosphere, with a flow rate of 20 mL/min and a heating rate of 10°C/min with a temperature range of 25-700°C and the weight of the samples between 2 and 4 mg.

2.3. Results and Discussion

The main thermogravimetric characteristics are T_{onset} – the temperature at which the degradation begins, T_{peak} – the temperature at which the degradation rate is maximum, T_{endset} – the temperature at which the degradation process is completed (Table 2).

Table 2
Thermogravimetric Characteristics of Samples

Code	Degradation stage			Onset (°C)			Enset (°C)			Peak (°C)			Mass loss (%)		
	A	R	C	A	R	C	A	R	C	A	R	C	A	R	C
P1C	I	I	I	48	46	47	119	102	98	67	64	59	6.53	9.57	6.93
	II	II	II	229	233	232	260	359	356	251	274	278	10.82	41.65	43.07
	III	III	III	262	491	493	376	571	565	278	538	541	35.08	33.37	27.11
	IV	IV	IV	512	608	582	562	629	613	544	605	579	21.29	8.43	14.57
	V	-	-	588	-	-	608	-	-	595	-	-	15.42	-	-
	residue amount												**10.86**	**6.98**	**8.32**
P1B	I	I	I	49	48	63	115	112	130	69	63	100	6.67	7.23	2.84
	II	II	II	229	226	228	372	283	365	275	271	365	45.71	33.11	48.58
	III	III	III	513	283	507	592	391	624	555	336	624	35.40	15.37	41.45
	IV	IV	-	620	510	-	627	597	-	616	545	-	4.82	36.58	-
	-	V	-	-	597	-	-	629	-	-	626	-	-	2.72	-
	residue amount												**7.4**	**4.99**	**7.13**
P2	I	I	I	41	50	48	113	124	112	64	66	88	7.42	9.02	2.86
	II	II	II	231	232	232	387	379	372	217	278	272	47.73	47.53	46.08
	III	III	III	514	518	510	576	565	607	541	546	583	29.13	25.78	41.48
	IV	IV	-	597	600	-	614	614	-	589	602	-	8.05	12.17	-
	residue amount												**7.67**	**5.5**	**9.58**
P3	I	I	I	49	48	47	117	123	126	71	64	68	12.27	7.58	7.62
	II	II	II	245	243	243	357	352	343	291	283	288	42.27	43.67	41.57
	III	III	III	480	528	512	558	607	610	542	592	597	31.24	39.43	42.61
	IV	-	-	590	-	-	611	-	-	600	-	-	13.06	-	-
	residue amount												**1.16**	**9.32**	**8.2**
P4	I	I	I	48	42	46	109	128	140	73	56	70	8.30	6.94	3.84
	II	II	II	233	234	232	387	369	374	277	277	271	47.11	45.38	46.32
	III	III	III	502	517	496	576	618	625	554	540	537	25.16	37.91	41.58
	IV	-	-	587	-	-	617	-	-	600	-	-	14.54	-	-
	residue amount												**4.89**	**9.77**	**8.26**
P5	I	I	I	47	47	51	104	111	132	70	66	81	7.04	10.51	5.59
	II	II	II	229	236	235	378	373	374	284	277	270	47.97	48.87	50.34
	III	III	III	518	518	522	594	610	608	594	595	591	39.02	37.11	39.65
	residue amount												**5.97**	**3.51**	**4.42**
P6	I	I	I	50	46	45	116	108	142	68	60	65	7.97	6.10	6.40
	II	II	II	232	231	232	366	365	367	272	263	267	44.13	43.50	45.73
	III	III	III	501	509	485	637	572	632	550	551	537	42.60	28.79	41.96
	-	IV	-	-	572	-	-	625	-	-	608	-	-	11.84	-
	residue amount												**5.3**	**9.77**	**5.91**
P7	I	I	I	46	46	38	120	111	117	69	58	77	6.03	6.56	3.59
	II	II	II	235	230	233	375	363	367	275	275	277	48.47	43.82	47.70
	III	III	III	514	509	516	627	623	624	543	547	549	38.33	40.34	40.46
	residue amount												**7.17**	**9.28**	**8.25**

The analysis of the results reveals that in all of the cases the evaporation of the water present in hair occurs in the first stage. This stage is followed by 2, 3 or 4 other stages of degradation depending on the analyzed sample. At a temperature of 700°C, there is a residue amount ranging from 1 to 11%. The largest quantities of residue resulted from P1C_A, P4_R, and P6_R degradation.

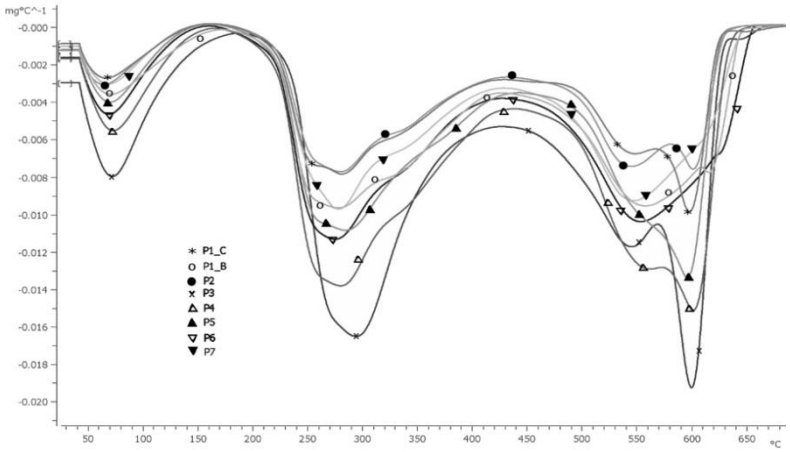
Samples P1C_R, P2_R and P5_R show the highest mass losses in the first stage, if the series of cold-conditioned samples is taken as a reference point.

After the thermogravimetric test, an interesting fact was observed from the collected data, namely, in the first stage of degradation, the samples from the C series have a higher thermal resistance than the similar samples from the other two series, A and R. For P1B_C, P2_C, P5_C both T_{onset} and T_{peak} (in the first degradation stage) have higher values than the samples maintained at room temperature. Simultaneously these samples have small mass losses. Although the degradation of P7_C samples starts faster than P7_A (at 38°C compared to 46°C), T_{peak} for P7_C is higher than P7_A. As with previous samples, the percentage of mass lost by P7_C is lower than P7_A.

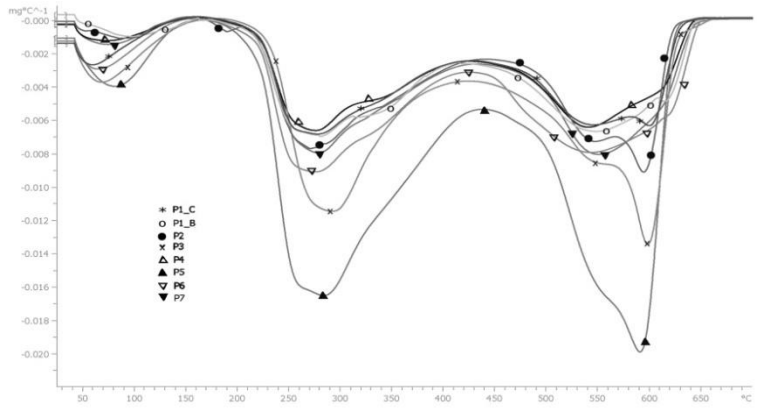
These facts lead to the idea of a false "stabilization" of the type C samples. In fact, we suspect that the C samples lost a certain amount of water while they were stabilized at a higher temperature (warm conditions), the loss being accompanied by a molecular rearrangement. Most likely the formation of new sulfur bridges between protein residues, especially cysteine, in a first phase causes the raise of the degradation temperature. Maybe not by chance the samples belonged to people with curly hair. Starting the second stage of degradation, the thermal behavior becomes similar to that of the samples A and R series.

If we consider the T_{onset} temperature as a criterion of thermal stability, the following ordering for type A samples can be established: P2<P7<P5<P1C= P4<P1B = P3<P6. It can be stated that getting older will not result in lower hair stability. The P7 sample belonging to the person aged 52 years does not show the slightest stability. Moreover, the P6 sample belonging to the person aged 33 years has the highest thermal stability. Clearly, the hair expresses people's individuality.

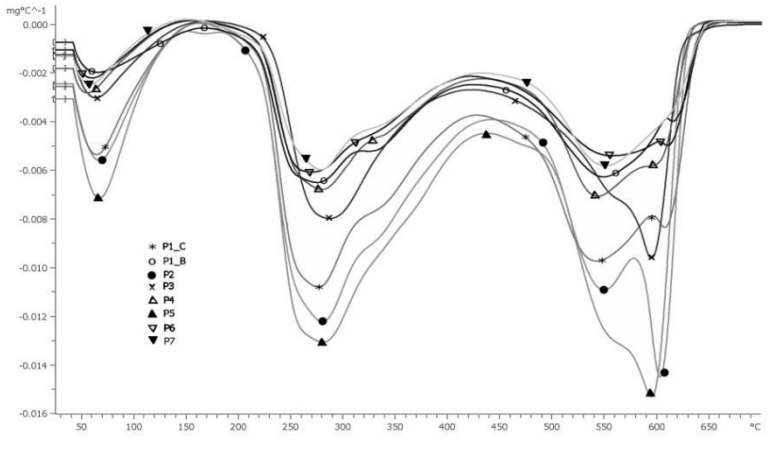
DTG curves (Fig. 1) show degradation peaks between 30 and 700ºC. Significant differences are recorded in the peak temperatures and in the shape (sharp peaks or peaks with shoulders) between samples. For the same sample, in all the three series, small shifts between peak temperatures and the profile of curves are observed. But, different intensities of the decomposition process are shown. The first process, between 50 and 100°C, was attributed to water elimination from the sample.



a



b



c

Fig. 1 − DTG curves for series A(*a*), C(*b*) and R(*c*).

The peaks observed between 220°C and 350°C were assigned to the thermal denaturing of α-helices within ordered keratin fibers (Cao, 1999) or to the cystine content of the amorphous matrix (Popescu and Gummer, 2016) of the capillary tissue. Above 400°C is hair's organic matter oxidation.

3. Conclusions

Small differences in the thermogravimetric behavior were observed at the analyzed samples. These differences consist of shifting the temperatures characteristic to the degradation process, of the number of degradation stages and in the percentage losses of mass. The heat treatments bring changes in the molecular organization without significantly influencing the polymeric matrix. The structural hair proteins with high stability and low solubility seem to offer sufficiently good protection against high temperatures, due to the sulfur bridges between cysteine residues. The cuticle, the same layer that protects the hair from harmful cosmetic actions, manages to counteract the thermal effect.

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EVALUAREA EFECTELOR TRATAMENTELOR TERMICE ASUPRA PĂRULUI UMAN, PRIN ANALIZĂ TERMICĂ

(Rezumat)

Părul oferă o serie de informații despre sănătatea și stilul de viață al oamenilor. Subiectul articolului este axat pe analiza termică a diferite probe de păr uman. Au fost examinate trei serii de probe, astfel, două serii au fost expuse prelungit la temperaturi ridicate și scăzute, iar a treia serie de probe a fost menținută la temperatura camerei. Stabilitatea termică a acestor probe a fost evaluată utilizând T_{onset} ca și criteriu de referință. Chiar dacă la probele analizate s-au observat diferențe mici în comportamentul termogravimetric, un fapt interesant a fost observat în prima etapă de degradare, probele păstrate în condiții experimentale la temperaturi ridicate au avut o rezistență termică mai mare decât probele similare din celelalte două serii.