Journal of Thermal Analysis, Vol. 36 (1990) 2269-2275

THERMAL INVESTIGATIONS ON YELLOW WOOLS

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Thermal investigations (TG, DTG) were carried out on the wool of Polish Mountain, Polish Lowland, Polish Merino and Polish Long-fleeced sheep in order to find dependences between the yellowing of the wool fibres and their structure. The thermal investigations were made on a single lock, taking into account the upper (yellow) and the lower (white) parts of the staple.

A relationship has been sought between the yellowing of wool fibres and their supermolecular structure in an attempt to characterize the fibres with regard to differences in discoloration between the upper (yellow) part and the lower (white) part of the same lock. The changes in structure were assessed by using thermal analysis.

The investigations were carried out on a sample of a lock of hairs emerging from the same hole in the sheep skin, separately for the fibres form the upper part (always yellow) and the lower part (white) of the same staple.

Experimental

The material under investigation was taken from the fleece of Polish Mountain, Polish Lowland, Polish Merino and Polish Long-fleeced sheep in experimental breeding stations.

The samples were taken within one lock from the back of the sheep during the same clip.

The samples were cleaned and divided into the upper (yellow) and the lower (white) part of the staples and then extracted with methylene chloride.

The thermal investigations were carried out with a Q-1500 D derivatograph in an atmosphere of static air at a linear heating rate of 10 deg/min.

Mass loss was recorded as a function of temperature.

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Results and discussion

The thermogravimetric curves (Fig. 1) show four DTG peaks, corresponding with the temperature T_1, T_2, T_3 and T_4. The DTG peak occurring at 68-77° (T_1) corresponds with the desorption of water physically bound to the fibre. The intensivity of this effect depends mainly on the sorption ability and humidity of the wool fibres.

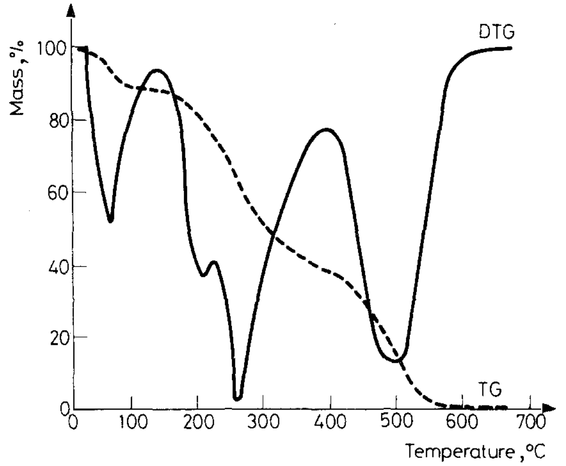

Fig. 1 TG and DTG curves of wool fibres

The DTG peak T_2 corresponds with transitions resulting from heating of the wool fibres between 160° and 220°. In this temperature range the following processes may occur [1-4]. In the amorphous and crystallographic regions of the wool fibres, supercontraction, disordering of the α-helical region of keratin, chemical and reactions between the -NH_2 and -COOH groups take place, which cause crosslinking of the keratin amorphous region through imide bonds with the release of volatiles (H_2O, NH_3).
At about 240°, changes take place which lead to the decomposition of disulphide bonds, principally in the matrix rich in these bonds [5]. Increase of the temperature above 250° lead to degradation of the fibrillar region [6]. Tables 1-4 list results of the thermal investigation which correspond with these temperatures (T_3 and T_4), and with the temperature of loss of half the mass of the fibre (T_5), i.e. the temperature at which half the dry fibre mass is destroyed.

Table 1 Thermal transitions in wool fibres from fleece of Polish Mountain sheep

Lot	Water desorption, %		T_3, °C		E, kJ/mol Stage I		T_4 °C		E, kJ/mol Stage II		T_5, °C	
	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow
A	9.2	10.0	260	256	65.8	58.1	492	468	98.9	94.2	348	322
B	10.9	13.4	260	256	66.4	56.2	496	508	101.3	102.8	340	320
C	11.6	13.8	264	252	62.3	61.0	524	536	111.4	201.2	360	296
D	11.0	12.6	256	252	65.0	58.3	520	492	109.2	99.0	376	320
E	11.3	12.5	260	252	67.7	59.4	500	500	96.6	98.1	352	328
F	10.8	11.7	256	260	69.1	62.3	528	472	113.5	95.5	352	348
G	13.7	13.5	256	252	63.5	60.2	460	464	90.8	96.5	316	316
H	12.4	11.9	260	256	68.6	60.4	472	460	94.7	89.6	332	340
J	11.7	14.0	252	256	64.6	62.5	489	510	97.0	105.1	340	300
K	11.8	12.0	252	252	60.3	55.8	464	512	96.6	109.8	320	308
L	14.7	12.7	258	260	62.5	59.1	452	456	88.1	93.5	324	320

E - activation energy; T_3, T_4 - DTG peak temperatures, °C; T_5 - temperature of loss of half mass of the fibre, °C

Table 2 Thermal transitions in wool fibres from fleece of Polish Lowland sheep

Lot	Water desorption, %		T_3, °C		E, kJ/mol Stage I		T_4, °C		E, kJ/mol Stage II		T_5, °C	
	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow
C'	10.9	12.1	260	256	65.4	60.3	492	500	99.7	101.4	322.	308
F'	10.3	11.5	262	258	65.3	62.1	506	480	103.1	98.3	350	338
G'	9.9	10.2	245	243	59.7	57.2	582	573	102.7	96.9	358	352
H'	12.2	13.4	260	260	65.1	63.0	494	498	100.8	102.5	342	308
J'	11.2	12.1	256	252	68.3	65.2	460	474	94.7	95.5	344	340
K'	11.3	10.9	240	238	58.6	55.2	594	582	105.8	100.2	345	340
L'	11.1	11.5	248	241	59.8	56.2	570	563	98.9	96.1	348	336
M'	10.7	12.6	260	252	66.5	62.5	490	503	102.4	105.2	353	342
T'	10.9	11.4	260	256	62.0	57.5	588	586	107.0	105.7	353	342
U'	9.6	10.7	244	241	58.9	55.6	582	584	102.3	108.9	356	348

E - activation energy; T_3, T_4 - DTG peak temperatures, °C; T_5 - temperature of loss of half mass of the fibre, °C

Table 3 Thermal transitions in wool fibres from fleece of Polish Merino sheep

Lot	Water desorptio %		T_3, °C		E, kJ/mol Stage I		T_4, °C		E, kJ/mol Stage II		T_5, °C	
	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow
C"	11.6	12.9	234	231	56.4	54.1	560	581	96.7	98.9	356	350
H"	9.1	10.8	256	248	63.2	59.0	520	532	97.4	99.8	364	348
J"	9.4	10.4	244	240	58.9	55.0	577	591	100.6	105.7	352	344
M"	10.3	10.8	248	241	61.0	57.3	586	586	102.5	101.9	353	344
N"	11.2	11.1	248	241	60.2	55.3	572	570	99.1	97.4	352	348
P"	10.5	10.7	247	241	58.7	56.0	594	592	105.4	101.3	368	352
S"	8.8	10.2	248	240	60.2	56.4	596	592	106.0	102.8	360	348
T"	10.3	10.4	242	240	57.9	53.3	604	592	110.1	108.8	356	348

E - activation energy; T_3, T_4 -DTG peak temperatures, °C; T_5 - temperature of loss of half mass of the fibre, °C

Table 4 Thermal transitions in wool fibres from fleece of Polish Long-fleeced sheep

Lot	Water desorption, %		T_3, °C		E, kJ/mol Stage I		T_4, °C		E, kJ/mol Stage II		T_5, °C	
	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow	Lower part, white	Upper part, yellow
a	12.7	12.8	254	252	65.2	62.6	562	564	94.7	96.3	341	332
c	13.8	13.7	244	242	61.1	58.7	572	556	100.1	93.7	332	316
d	10.9	12.7	242	240	59.2	57.0	576	568	100.3	97.4	344	336
e	10.6	12.7	252	250	64.8	60.4	588	562	108.0	96.7	365	336
g	13.3	14.2	242	240	58.7	56.1	572	568	101.8	98.6	328	332
k	13.4	14.0	248	236	66.3	60.2	576	561	103.1	94.4	336	332
l	11.2	11.0	248	240	64.0	61.3	576	572	104.2	98.3	352	348
o	13.5	14.2	252	248	67.0	62.6	584	580	107.9	102.6	332	326
r	14.8	15.0	252	248	64.4	61.1	572	580	100.7	106.1	328	320
s	13.1	14.1	248	246	63.5	59.1	560	556	94.3	92.0	324	321

E - activation energy; T_3, T_4 - DTG peak temperateres, °C; T_5 - temperature of loss of half mass of the fibre, °C

Computer programs according to the Freeman-Carrol methods [7] were used to calculate the overall kinetic parameters, i.e. the activation energy and order of reaction.

The thermal decomposition of wool fibres is a two-stage process. The first stage involves the transitions occurring in the temperature range 160-400° (peak temperatures T_2 and T_3 correspond to these transitions).

The second stage involves the rapid reactions of destruction in the temperature range 400-600° (temperature T_4 corresponds to these transitions).

In comparison with the lower part of the staple, wool fibres from the upper part of the staple are characterized by lower temperatures of destruction (T_2, T_4), which indicates the activation of S-S bonds.

The activation energies for fibres from the upper part of the staple testify to the lower energy necessary for cleavage of the chemical bonds.

The lowering of the temperature of half-destruction (T_5) is caused by the reduction in thermal resistance as a result of the looseness and damage to the structure of the fibres from the upper (yellow) part of the staple. Moreover, the results of thermogravimetric measurements showed a facilitated water desorption from the upper part of the staple as compared with the lower part of the same staple.

The upper (yellow) part of the staple is not too well preserved by lipids and is subjected to a more intensive penetration of alkali, sweat and an oxidizing environment.

Oxidation of the fibre interior is possible and leads to looseness of the structure of α-keratin as a result of cleavage of ester, thioester and disulphide bonds. Thermal investigation allows diagnostic possibilities as concerns the essential processes occurring in the yellow fibres.

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Zusammenfassung — Mittels Thermoanalyse (TG, DTG) wurden Untersuchungen an Fellen von Polnischen Berg-, Flachland-, Merino- und Langfellschafen durchgeführt, um einen Zusammenhang zwischen der Gelbfärbung der Wollfasern und ihrer Struktur festzustellen. Die thermischen Untersuchungen wurden unter Berücksichtigung der oberen (gelben) und unteren (weißen) Rohwollteile an einzelnen Faserbüscheln durchgeführt.