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# THERMAL STUDY OF DYED CHROME-TREATED KERATIN FIBRES

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DTA, TG and TMA were used to study wool samples of 64 quality, dyed and chromed in a dyeing bath at a low temperature (353 K), as well as by the conventional method involving boiling (369 K). The TMA data allowed establishment of the basic temperatures connected with the $\alpha - \beta$ transition of the wool keratin, the melting of the crystal regions and protein denaturation. It was shown that wool fibres chromed with 30 w.% $K_2Cr_2O_7$ at 353 K exhibit a decreased exothermic process in the range 700–750 K, which provides a possibility for evaluation of the effect of processing on the structural changes of the fibre keratin.

High-temperature dyeing of loose wool in acidic medium leads to many changes in the chemical structure and mainly in the supramolecular structure [1]. Changes in the physicomechanical properties of the fibres are an indication of structural changes caused in the material by the treatment process [2–4]. Several chemical and physicochemical methods are used to study these phenomena [5]. Thermodynamic methods are not widely applied for this purpose. The effects of dyeing and postchroming on the temperatures of transitions and thermodestruction of wool fibres are studied in the present work.

## Experimental procedure

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out with an OD 102 derivatograph under the following conditions: temperature range: 293–873 K, heating rate: 6 degree/min, initial weight of test sample: 230 mg, thermobalance accuracy: ±2 mg, standard: $Al_2O_3$, atmosphere: air (static), holder: a cone-shaped platinum crucible with an average diameter of 15 mm, and a Pt–PtRh thermocouple located a short distance away and in the centre of the sample.

Thermomechanical experiments were carried out with an apparatus consisting of a microscope and a heating furnace. An elementary woollen fibre was placed inside the furnace. One of its ends was fixed and the other was loaded with a predetermined weight. The furnace was heated at a constant rate and the movement of a mark on the fibre was observed. The mark displacement was measured and this allowed evaluation of the fibre deformation at any point. The error was within 0.1%. The thermomechanical relationship is given by the deformation *vs.* temperature plot. The following experimental conditions were used: loading: 0.2 cN, heating rate: 1 degree/min, and temperature accuracy: 0.5 K.

Fibres from Bulgarian merino loose wool, possessing the following characteristics, were studied: average thickness: 22.57 mkm (64 quality), average staple length: 62.07 mm, and residual grease content: 0.04%.

Wool fibres were dyed and postchromed in a laboratory Turbomat TM 6 (Ahiba) apparatus, with Morant Black 11 (CU) dye. Dyeing was carried out under the following conditions: temperature: 353 and 369 K, bath ratio: 1/1000, sample amount: 5 g, dye content in the bath: 5%, $Na_2SO_4$ content in the bath: 10%, and pH range: 3–3.5 adjusted by adding 60% $CH_3COOH$.

Postchroming was carried out in the same bath, using 30 and 50 w.% $K_2Cr_2O_7$ based on the dye content, and at the given temperatures of dyeing at pH 3, adjusted with concentrated $CH_3COOH$.

## Results and discussion

Figure 1 shows the deformation *vs.* temperature relationship (thermomechanical, TM curve) for the original test sample from Bulgarian merino wool of 64 quality. It is well known [1, 5] that a transition from the $\alpha$ to the $\beta$-form of the keratin crystal structure occurs on extension of the wool fibre up to 20%. Subsequent extension up to 70% results in complete transition to the $\beta$ crystal form. On the other hand, scission of cross-links occurs under the simultaneous action of heat and extension stress. Crystal destruction takes place too, i.e. the keratin crystal structure assumes its random $\beta$-form. Figure 1 illustrates the above theoretical concepts [5] concerning the struc-

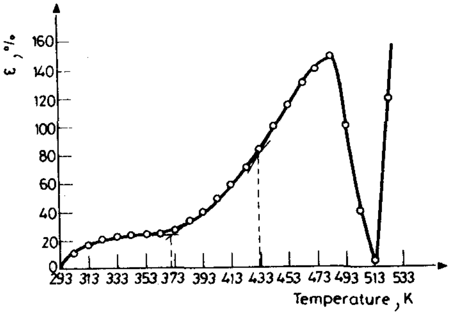

**Fig. 1** TMA curve of untreated wool fibres

tural changes of wool fibres under mechanical and heat action. In our earlier work [6] we divided the TMA curve into the following parts: 393–370 K: straightening of the fibre curliness; 370–431 K: $\alpha - \beta$ structure transition of the wool keratin; 431–483 K: the keratin structure turns to its random $\beta$-form; 483–513 K: denaturation of protein macromolecules; and above 513 K: yield breaking of the sample.

Figure 2 shows TMA curves for wool fibres pretreated with acetic acid. The form of the TMA curves is similar to those obtained for untreated test samples subjected to the action of a doubled load [6]. In the present work the load was constant at 0.2 N. It was much higher for the treated fibre as compared with the untreated test samples. The lowered strength was a result of the acidic hydrolysis of the keratin, which was very high at the given pH values. The estimated yield breaking at lower temperatures was evidence that destruction had taken place.

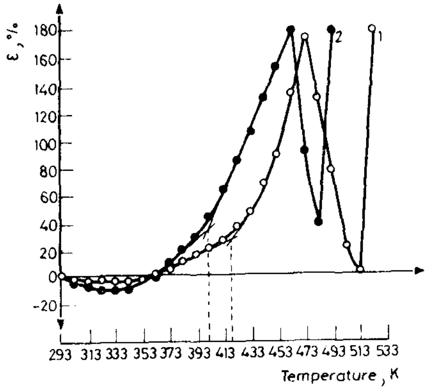

**Fig. 2** TMA curves of wool fibres treated by $CH_3COOH$ at pH = 2; 1 – 353 K, 2 – 369 K

Thermomechanical curves of the dyed unchromed wool fibres are shown in Fig. 3. It is interesting that the form of these curves is similar to those in Fig. 1. They differ in their initial parts. The TMA curves in Fig. 3 have a special initial part, which is due to an initial contraction. This contraction maintained in the temperature range 303–353 K.

The following theory has been assumed to explain the observed initial contraction: a scission of some intramolecular cross-links occurs during dyeing of the wool fibres (an interaction between the dye and the wool fibre takes place) and the keratin $\alpha$-coils tend to reach their most stable level, forming new links. The latter provoke the observed initial contraction. On the other hand, equilibration also occurs between the folding stress and the applied extension loading.

Figure 3 shows that the $\alpha - \beta$ transition of the keratin starts in the region where the deformation ceases its negative change and it begins to increase at a constant rate. The $\alpha - \beta$ transition of the keratin structure can be explained by a disturbance

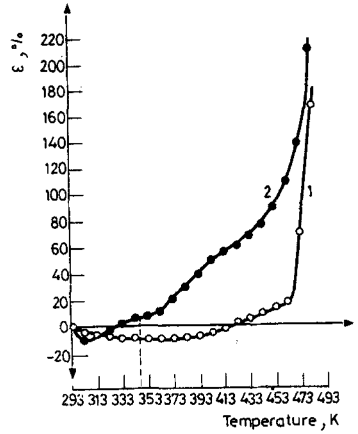

Fig. 3 TMA curve of wool fibres dyed in a bath with pH = 3.5; 1 – 353 K, 2 – 369 K

of the above-mentioned equilibrium, caused by the heat absorption. The latter and the simultaneous action of the applied load are sufficient to break the links stabilizing the $\alpha$-coils. From Figs 1, 2 and 3 it follows that the $\alpha - \beta$ transition occurs at lower temperatures under more severe processing conditions (Table 1). This is also the case for other observed temperature transitions. At the same time the absolute deformation value changes in the different parts of the TMA curves. Therefore, the fibres can be arranged in sequence in relation to the resulting destruction on dyeing, as follows: original test sample, wool dyed at 353 K and wool dyed at the temperature of boiling (369 K).

Figure 4 shows DTA and TG curves for the original test sample of Bulgarian merino wool of 64 quality. The DTA curves reveal three distinct peaks in the given temperature range. Two peaks, at 383 K and 516 K, correspond to endothermic processes,

**Table 1** Temperature transitions investigated by TMA study of wool fibres

| No | Temperature transitions | Wool treated at 333 K | | Wool dyed at 353 K | | Wool dyed at 369 K | |
|---|---|---|---|---|---|---|---|
| | | $T$, K | $\epsilon$, % | $T$, K | $\epsilon$, % | $T$, K | $\epsilon$, % |
| 1 | At the beginning of $\alpha - \beta$ transition | 370 | 24 | 357 | – 4 | 343 | – 10 |
| 2 | At the beginning of cross-links scission | 431 | 84 | 418 | 30 | 401 | 40 |
| 3 | At the beginning of protein denaturation | 485 | 140 | 473 | 175 | 463 | 180 |
| 4 | At the beginning of yield breaking | 513 | 10 | 513 | 0 | 483 | 38 |

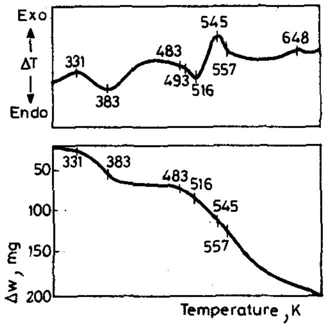

**Fig. 4** Thermal curves of untreated wool fibre

and the third peak, at 548 K, corresponds to an exothermic process. The first endo process is due to the evaporation of the absorbed moisture from the sample. The TG curve shows that at approximately 413 K the intensive weight losses stop; they amount to 9%, which is completely reasonable for the given type of fibres. The second endothermic process (beginning at 493 K) could be explained by the scission of intermolecular links and by the melting of crystal units in the wool fibre structure [7–9]. It is assumed that an exothermic process takes place simultaneously, due to the formation of intermolecular links in the course of keratin globulization and its thermal destruction. In the renge 563–733 K the DTA curve does not show that any process of change in the sample enthalpy occurs. However, in the same temperature range, the TG curve reveals considerable weight losses. From the latter results it is evident that processes with opposite thermal effects take place. This phenomena could be explained by oxidizing processes and link scission in the keratin macromolecules, leading to intensive thermal destruction of the material [10, 11]. The exothermic maximum at 648 K can be explained by the final thermal destruction of the solid residue.

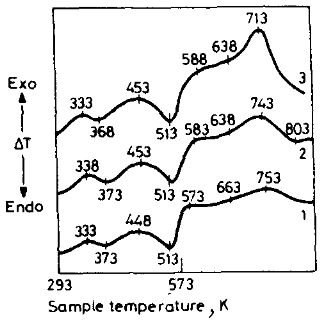

**Fig. 5** DTA curves of wool fibres dyed at 353 K: 1 – dyed, unchromed, 2 – dyed, chromed by 30 w.% $K_2Cr_2O_7$, 3 – dyed, chromed by 50 w.% $K_2Cr_2O_7$

The experiment revealed that changes occurring under different wool processing conditions do not influence the weight losses of the material considerably. Therefore, further discussions will be limited to the consideration of the DTA curves of the test samples. Figure 5 illustrates DTA curves of wool fibres dyed at 353 K and chromed with 30 w.% $K_2Cr_2O_3$, based on the dye content, for 60 min. DTA curves of samples dyed under the same conditions and chromed with 50 w.% $K_2Cr_2O_7$, based on the dye content, are given for comparison. It is seen that the DTA curve of the dyed but unchromed wool is most similar to those given in Fig. 4, i.e. the wool is less changed in the dyeing process. Evidence of this is the retention of a plateau in the curve above 573 K. This tendency is much stronger in the test sample dyed and chromed with 50% $K_2Cr_2O_7$ and the exo process shifts to lower temperature, 713 K. This sample therefore changes more significantly during dyeing and chroming.

The thermal curves of test samples dyed at 369 K which were expected to exhibit larger changes, were recorded to confirm the above conclusions (Fig. 6). Above 573 K, these DTA curves have a more abrupt course. Additionally, at 713 K the exothermic effect increases, which is evidence of a high quantity of solid residue in the material tested. Therefore, at temperatures over 700 K the intensity of the exothermic process is an indication of the changes in the wool fibres after dyeing and chroming. This provides an opportunity to optimize the technological conditions in fibre processing and finishing.

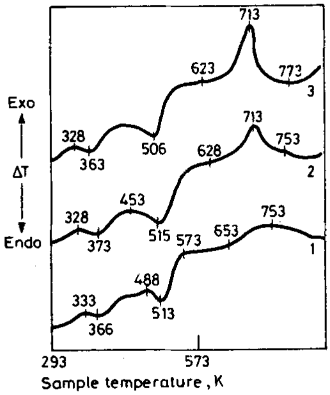

**Fig. 6** DTA curves of wool fibres dyed at boiling (369 K): 1 – dyed, unchromed, 2 – dyed, chromed by 30 w.% $K_2Cr_2O_7$, 3 – dyed, chromed by 50 w.% $K_2Cr_2O_7$

## Conclusions

Study of the thermal behaviour of wool fibres allows the establishment of typical temperature ranges connected with the structural transformations and chemical changes in the wool keratin. The results of thermal analysis yield the optimum limits of the technological parameters which cover mechanical and thermal effects simultaneously.

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**Zusammenfassung** — DTA, TG und TMA wurden zur Untersuchung von 64 in einem Farbbad bei niedriger Temperatur (353 K) als auch nach der herkömmlichen, einen Kochvorgang in sich einschliessenden Methode (369 K) gefärbten und chromgebeizten Wollproben unterschiedlicher Qualität herangezogen. Die TMA-Daten ermöglichten die Festlegung der sich auf die $\alpha-\beta$-Umwandlung des Wollkeratins, auf das Schmelzen der kristallinen Bereiche und auf die Denaturierung des Eiweisses beziehenden Temperaturen. Es wurde festgestellt, dass bei 353 K mit 30 Gew.-% $K_2Cr_2O_7$ chromgebeizte Wollfasern im Temperaturbereich von 700—750 K eine schwach exotherme Reaktion eingehen, die eine Möglichkeit zur Kontrolle der strukturellen Veränderungen des Faserkeratins bietet.

Резюме — ДТА, ТГ и ТМА были использованы для изучения 64 образцов шерсти различного качества, окрашенных и хромированных как при низкой температуре (353 K), так и обычным методом кипячения при температуре 369 K. Данные ТМА позволили установить главные температуры $\alpha \rightarrow \beta$ перехода для шерсти кератина, плавления кристаллических областей и денатурации протеина. Установлено, что шерстяные волокна, хромированные 30% раствором бихромата калия при 353 K, показывают уменьшенный экзотермический эффект в области температур 700—750 K. Это дает возможность оценки эффекта структурных изменений волокон кератина.