Thermoanalytical investigations of extended and annealed keratins*)

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Abstract: DSC investigations have been used to characterize the microfibril-matrix complex of keratin consisting of helical low-sulfur microfibrils in a nonhelical high-sulfur matrix. The corresponding DSC curves display one or two endothermic peaks in the temperature range 230 °–255 °C. The first peak is a microfibrillar peak and the second one a matrix peak (cystine decomposition peak). DSC investigations of extended keratins have shown that the microfibrillar peak is a helix peak. DSC investigations of annealed keratins confirm our earlier assumption that the helix peak is no helix melting peak but an irreversible helix unfolding, superimposed by various decomposition reactions. The matrix peak of the above described keratin samples is less reproducible than the corresponding helix peak and cannot be used for further characterization studies of keratins.

Key words: α-keratins, DSC-investigations, microfibril-matrix complex, helix peak, matrix peak.

1. Introduction

The keratins wool and hair are multicomponent fibres and consist of three main morphological components: cuticle, cortex, and cell membrane complex, which consist of further subcomponents; (see Fig. 1). This model gives a good overview of the single components and clearly shows that wool fulfils – like many other biological structures – the criteria of a composite structure. Wool and hair even display a *manifold* composite structure [2].

*) Dedicated to Professor E. G. Klesper on the occasion of his 60th birthday.

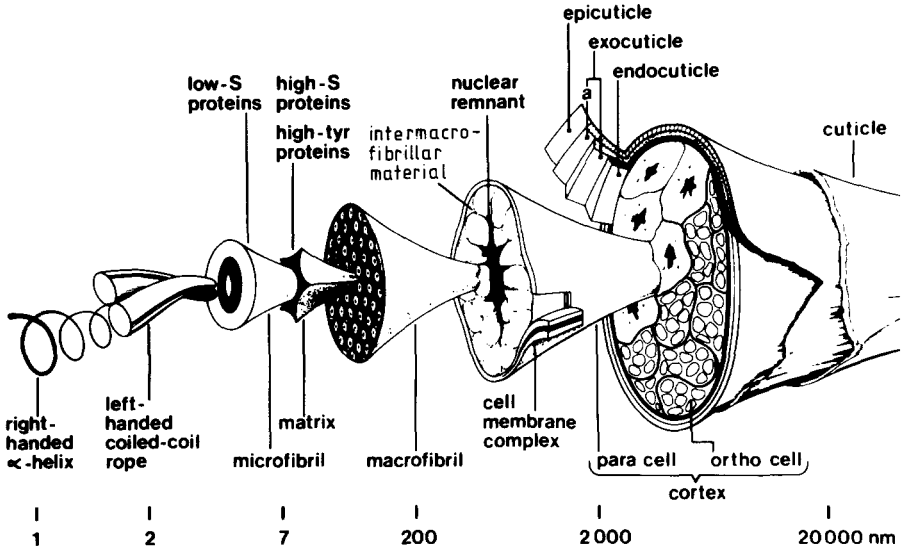

Fig. 1. Schematic diagram of a wool fibre [1]

Many physical properties of wool and hair are determined by the microfibril-matrix complex: helical, low sulfur microfibrils embedded in a nonhelical high sulfur matrix. The low-angle X-ray technique and the differential scanning calorimetry (DSC) technique are very powerful tools for determining the structure and the structural changes of the microfibril-matrix complex. In the DSC curves of α-keratins, one or two endothermic peaks are observed in the temperature range 230 °–255 °C (see Fig. 2) which have been interpreted contradictorily in terms of helix melting points [3–5] (i. e. microfibrillar origin) and cystine decomposition points [6–9] (i. e. matrix origin). DSC investigations of isolated microfibrillar and matrix proteins in the disulphide form have shown that the two endothermic peaks have a different origin: the first peak (lower temperature) is a microfibrillar peak and the second peak, a matrix peak [10]. This assignment has been confirmed by preliminary DSC investigations of stretched human hair samples. After the extension of human hair by between 10 % and 60 %, the microfibrillar peak was weakened with increasing extension while the intensity of the matrix peak is almost unchanged [11]. Since, by the extension of α-keratins, α-helices are transformed into β-keratin pleated sheet structures (α-β-transformation), it is evident that the microfibrillar peak is a helix peak. Furthermore, thermally pretreated ("annealed") hair samples also display a decrease in the two endothermic peaks caused by a successive destruction of the microfibril-matrix complex [11]. Therefore, additional DSC investigations of extended and annealed hair and wool samples should be performed.

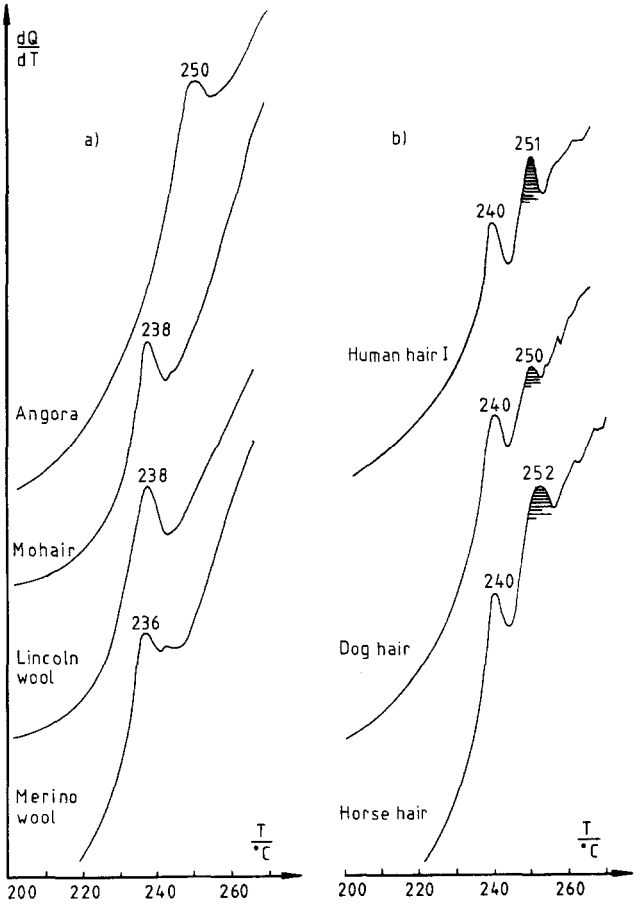

Fig. 2. DSC curves with one and two endothermic peaks

2. Experimental

The wool and hair samples were provided by the German Wool Research Institute; one of us (R. H.) provided the sample "human hair I".

The hair and wool samples were extended in a stretching frame in warm water up to the required extension and dried in the stretching frame for 24 h at 20 °C, and 1 h at 105 °C.

For all DSC investigations, we used a Perkin-Elmer DSC-2 equipment (nitrogen atmosphere; heating rate: 20 °C/min). The annealing of the keratin samples was performed in the same DSC equipment: the sample was first heated to the required temperature, annealed, cooled down to 50 °C and finally heated to 270 °C.

3. Results

DSC investigations of various human hair samples

Our first (preliminary) DSC investigations of stretched human hair samples were performed with a hair displaying strong microfibrillar and matrix peaks. We then found that not all hair samples yielded a good matrix peak. For this reason we investigated six different hair samples; only one sample (European human hair I) yielded a strong matrix peak (see Fig. 3a). Even the hair of one person (R. H.) yielded very different DSC curves regarding the matrix peak; see Figure 3b. All our following hair DSC investigations were therefore performed with carefully selected hair samples (R. H.) displaying a strong matrix peak.

DSC investigations of extended human hair samples

After the stretching of selected European hair samples by between 10 % and 80 %, the intensity of the microfibrillar peak decreased considerably and continuously with the stretching ratio, while the matrix peak exhibited a somewhat different behaviour (see Fig. 4). There was also a decrease of the matrix peak but it did not decrease continuously. After 30 % exten-

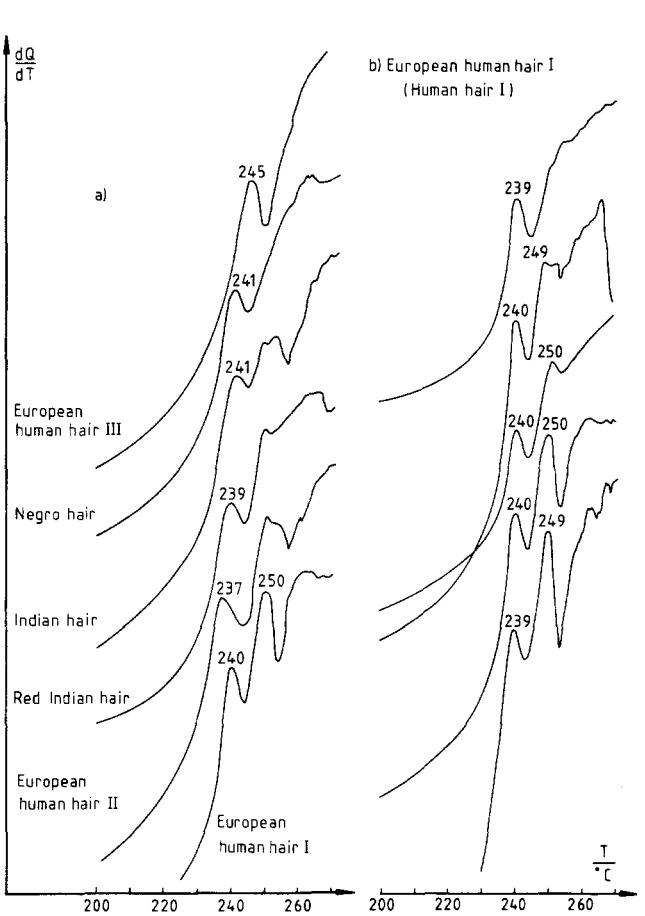

Fig. 3. a) DSC curves of various human hairs. b) DSC curves of human hair samples from *one* person

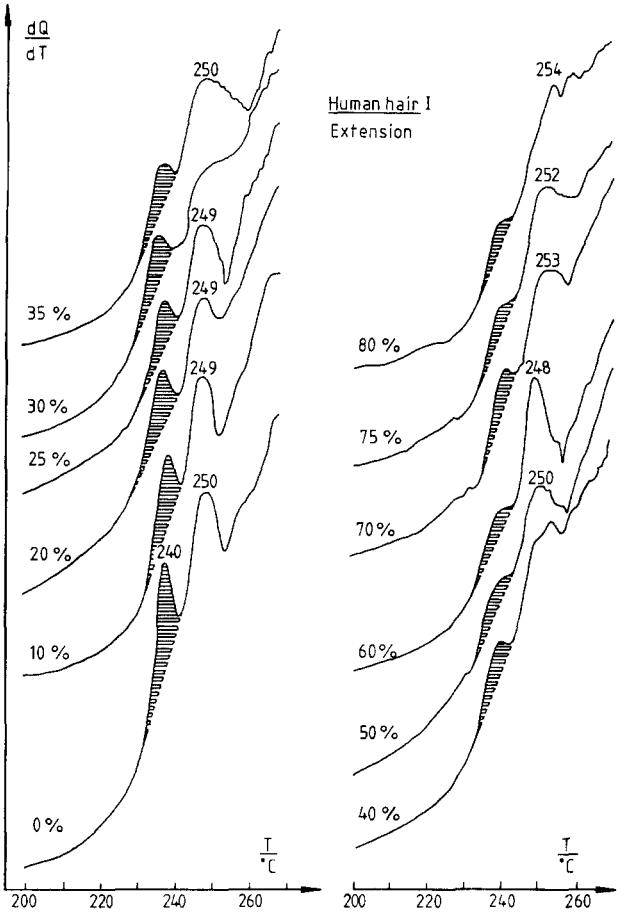

Fig. 4. DSC curves of stretched human hair

sion, it was nearly absent, while after 60 % extension a very strong matrix peak was observed. The determination of the relative helix content (the peak area of the unstretched sample is equal to 100 % relative helix content; all peak areas are corrected for 5.00 mg sample weight) shows that even at high extension values, a considerable amount of α-keratin is still present (see Fig. 5). This is in good agreement with the X-ray results.

DSC investigations of annealed keratin samples

Preliminary DSC investigations of a few annealed human hair samples have already shown that this method is very suitable for investigating the successive thermal destruction of the microfibril-matrix complex. Therefore these investigations have been now extended to annealed keratin samples with very different

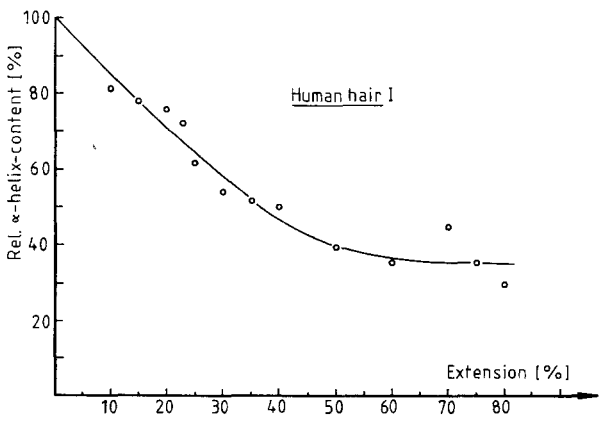

Fig. 5. Decrease of the relative α-helix content with the degree of extension

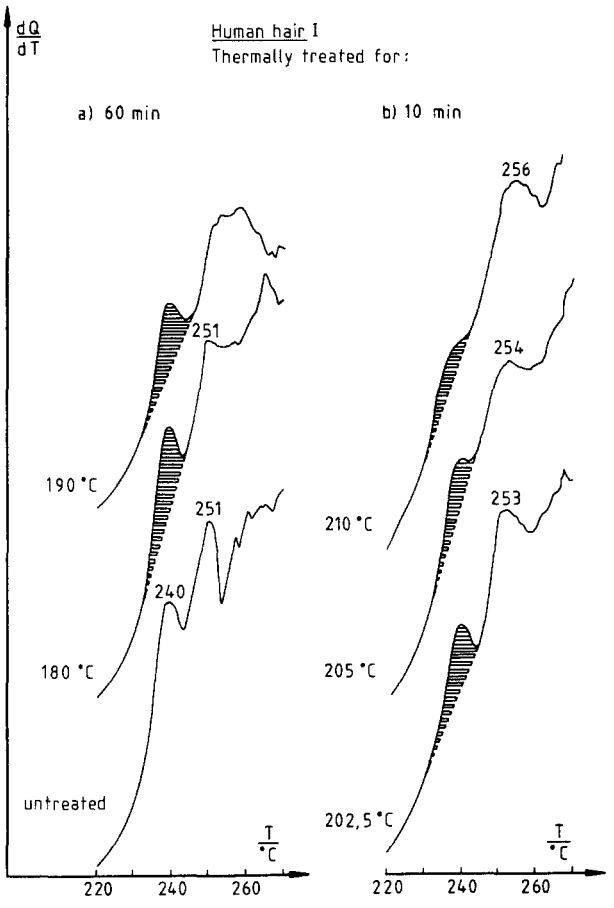

Fig. 6. DSC curves of annealed human hair samples

annealing times and annealing temperatures. At rather low annealing temperatures an almost selective damage of the matrix peak is observed (see Fig. 6a), while at higher annealing temperatures both peaks are damaged (see Fig. 6b). Then hair samples were annealed at a constant temperature. With increasing annealing times, both peaks were considerably damaged: see Figure 7. Almost the same annealing effects were also observed with Lincoln wool samples (Figs. 8 and 9) and mohair samples (both displaying only a microfibrillar peak, as already shown in Fig. 2a).

Discussion

The DSC investigations of various keratins have shown that only some sulfur-rich (matrix-rich) keratins yield two endothermic peaks – one microfibrillar peak and one matrix peak. Six different human hair samples were investigated but only one yielded a strong matrix peak. Since this hair sample fortuitously belonged one of us (R. H.) further hair samples from the same person could be investigated. Even in this case, not all DSC curves displayed a strong matrix peak. There were also curves with weak matrix peaks; sometimes the matrix peak was completely absent. It seems that great differences in the matrix peak intensities are caused by photochemical degradation effects (all hair samples were neither permanent waved nor bleached). Surface hair seems to be more damaged than covered hair. Therefore it is not possible to compare the hair of various persons (or races) if the site of the hair samples is not known.

DSC investigations of hair samples with strong matrix peaks have shown that only the changes of the microfibrillar peak are reproducible. The determination of the relative helix content yields nearly the same results as earlier investigations [11]. The intensity losses of the matrix peak, however, are *not* reproducible. In no case could a third endothermic peak be iden-

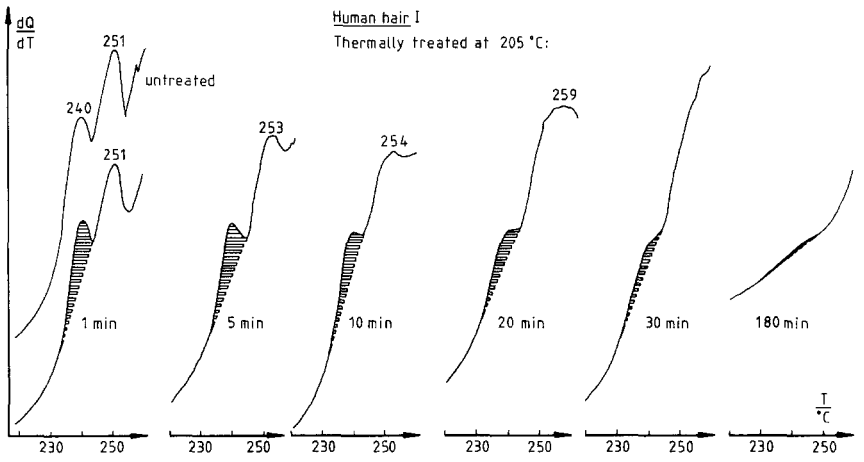

Fig. 7. DSC curves of human hair samples annealed at 205 °C

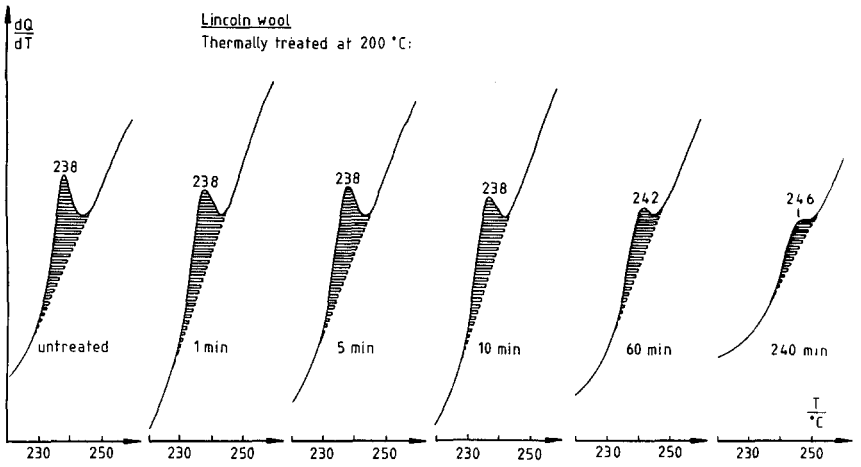

Fig. 8. DSC curves of Lincoln wool samples annealed at 200 °C

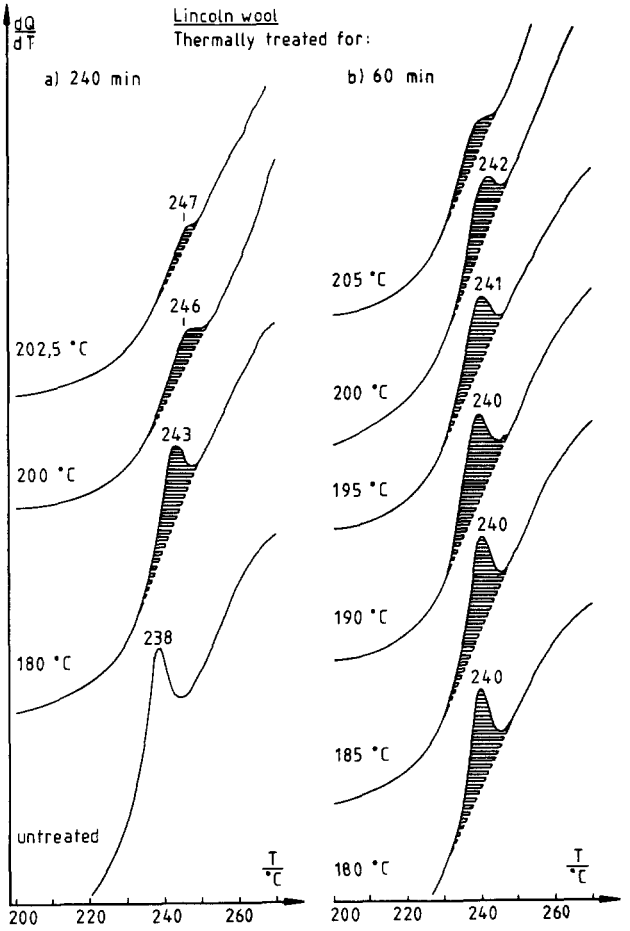

Fig. 9. DSC curves of annealed Lincoln wool samples with different annealing times and temperatures

tified between 255° and 260 °C, as described earlier [11], yet all stretching investigations have clearly confirmed that the two endothermic peaks have a different origin: microfibrillar peak and matrix peak.

DSC investigations of thermally treated (annealed) keratin samples are suitable for following the successive degradation of the microfibril-matrix complex. Very low annealing temperatures cause an almost selective damage to the matrix peak (see Fig. 6a). The corresponding DSC curves resemble those curves of photochemically damaged surface hair. *It seems that only completely intact human hair samples yield a strong matrix peak.* When synthetic polymers are annealed at a constant temperature, the degree of crystallinity normally increases with the annealing time. With keratins, inverse results are obtained: here the intensity of the microfibrillar peak decreases with increasing annealing time. When Lincoln wool samples are annealed at 200 °C, a considerable microfibrillar rest peak is still present even after 240 min annealing time. Apart from this, the annealing time was kept constant. In this case, small changes in the annealing temperature cause great changes in the intensities of the microfibrillar peaks: Figure 9. These results again clearly show that the microfibrillar helix peak is no helix melting point; normally polymers do not melt 35 °C below their (DSC) melting point. The helix peak is much more due to an irreversible helix unfolding, superimposed by various decomposition reactions. Amino acid analyses have shown that the thermally induced cystine degradation starts at about 190 °C [8]. This is exactly

the temperature at which a noticeable decrease in the peak intensity is observed (Fig. 9).

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