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Thermoanalytical determination of the relative helix content of keratins

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Since the pioneer research by Astbury et al. [1–3] it is well-known that the x-ray diagram of stretched keratin is quite different from that of unstretched keratin, which they interpreted in terms of a configurational change in the keratin molecule from a folded α- to an extended β-form. Today we know that this change involves the transformation of the α-helices into β-pleated sheet structures. Based on photographic evidence it was assumed that the onset of the α-β transformation always occurs at 20 %-30 % extension and that most of the extension takes place in the range of 30 %-50 %. Later, Bendit [4] investigated the α-β transformation with a Geiger counter x-ray diffractometer and found that the α-β transformation starts at extensions of 5 % or less and that even at 60 % extension there still exists a considerable amount of (rest-)helix content. Recently it was shown that similar results could be obtained with thermoanalytical (DSC-)investigations [5]: An endothermic peak in the temperature range of 230 °–240 °C has been indexed as the helix peak and the area under the peak represents a measure of the relative helix content of the sample. The peak area of an unstretched sample is equal to 100 % and decreases continuously with increasing extension of the fiber. DSC-investigations of various stretched keratin samples – Lincoln wool [5], human hair [5, 6], and mohair [7] – have shown that even with this rather simple technique the early onset of the α-β transformation and the considerable rest helix content of 60 % stretched samples could be detected. The DSC-technique is therefore more sensitive than the x-ray film technique. The three investigated keratin samples displayed a very sharp helix peak. Therefore, we have now extended our investigations on keratin samples with less sharp helix peaks where the evaluation of the peak areas is much more complicated.

Figure 1 shows that even in this case the same results were obtained in first approximation. Because of rather long and complicated correction procedures – not necessary for DSC-investigations – Bendit [4] and also, Skertchly and Woods [8] used only Lincoln wool with a very sharp x-ray diagram for their quantitative x-ray diffraction studies of the α-β transformation.

While the relative helix content of α-keratins can easily be determined, the determination of the absolute helix content is very complicated.

Turner and Woods [9] obtained only estimates of the proportion of α-helix in several materials from measurements of the x-ray diffraction patterns. Therefore, we have now extended our DSC-method for the determination of the relative helix content – normally used for differently stretched samples of one material – on various nonstretched keratin samples. In this special case mohair with the highest helix content (35 %) now has a relative helix content of 100 %. Surprisingly, the values obtained (see Fig. 2) are in rather good agreement with the values of Turner and Woods (see Table 1).

It therefore seems that the absolute and relative helix contents yield at least the right correlations between the various keratin samples.

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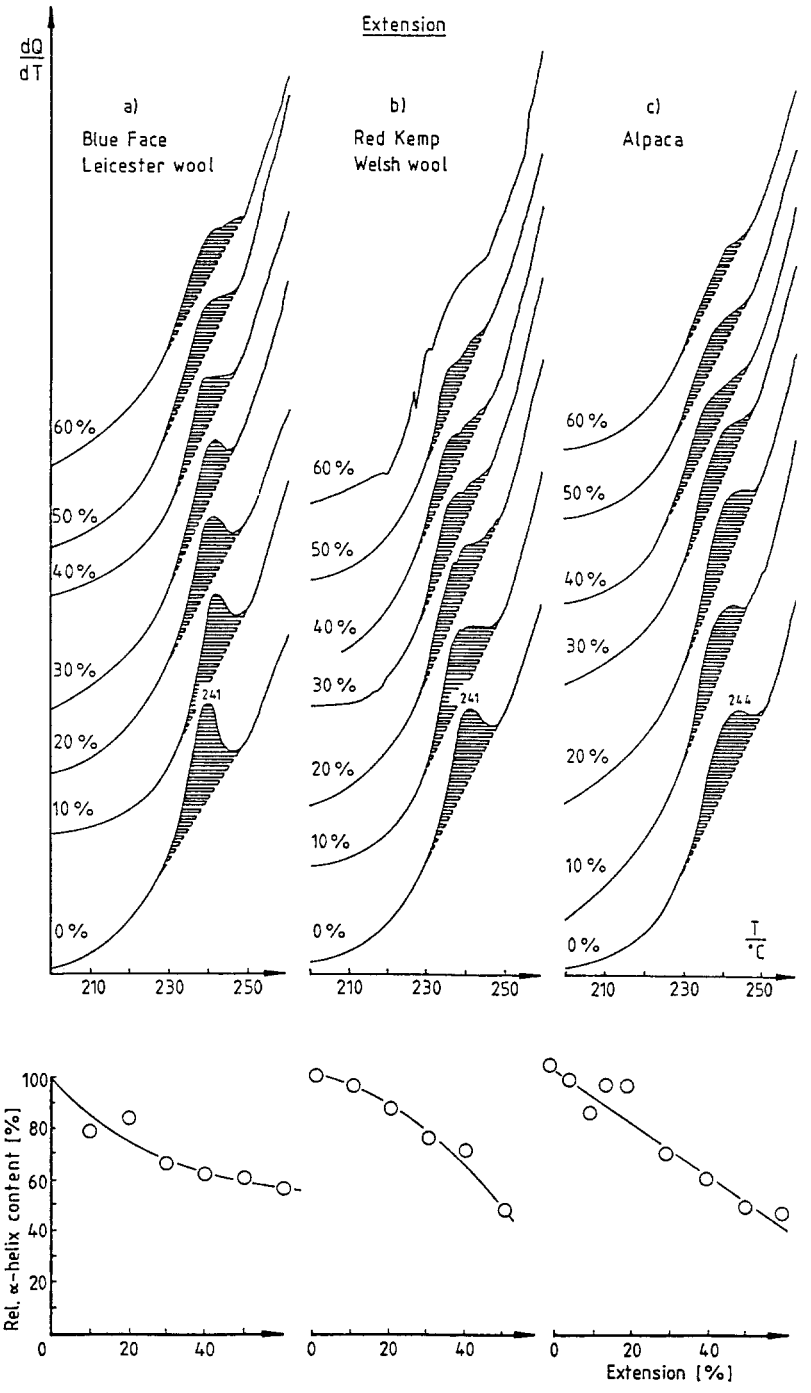

Fig. 1. DSC-curves and relative helix content of three differently extended α-keratins

Table 1. Absolute and relative helix content of various α-keratin samples

Sample	Absolute helix content [%]	Calculated relative helix content [%]	Measured relative DSC-helix content [%]
Mohair	35	35/35 ≙ 100	100
Lincoln wool	30	30/35 ≙ 86	85 (83–87)
Human hair	21	21/35 ≙ 60	60 (55–65)
Horse hair	25	25/35 ≙ 71	60 (55–65)

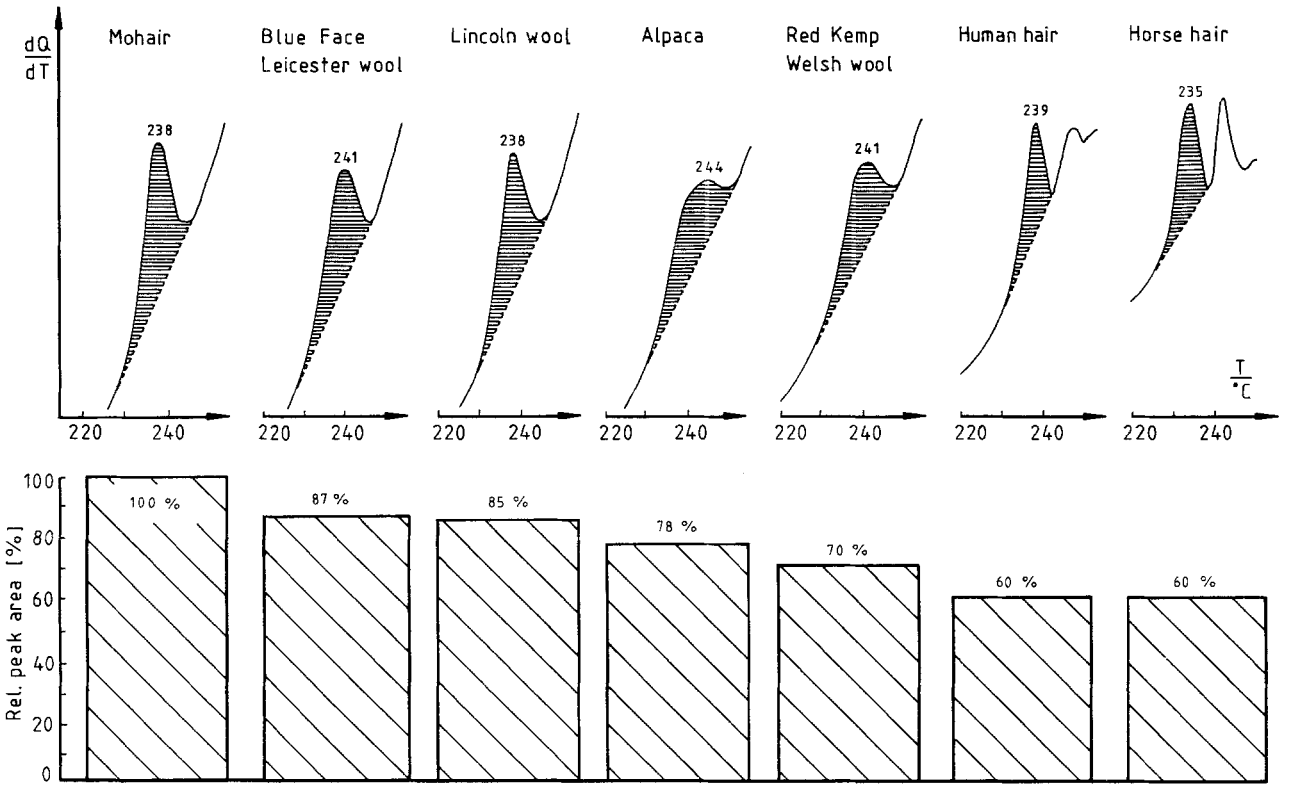

Fig. 2. Relative helix content of various α-keratins

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