ELSEVIER

Thermochimica Acta 335 (1999) 5–9

thermochimica acta

www.elsevier.com/locate/tca

# Melting study of the α-form crystallites in human hair keratin by DSC[1]

Jinan Cao

*CSIRO Wool Technology, P.O. Box 21, Belmont, Vic. 3216, Australia*

Received 4 January 1999; received in revised form 3 March 1999; accepted 6 March 1999

**Abstract**

The DSC methodology developed for studying the melting behaviour of the α-form crystallites in wool keratin has been applied to human hairs. It is found that human hair shares the same specific thermal characteristics with wool. Silicone oil provided a constant thermal environment, with the melting and degradation endotherms readily separated for a consistent quantitative analysis. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Human hair; Wool; α-helix; α-crystallites; Melting; DSC

## 1. Introduction

Keratin is a tough protein, including human hair, wool, nail, feather, animal claws etc. X-ray diffraction and microscopical studies have shown that human hair and wool share much the same crystalline structure as well as histological structure. Low-sulfur polypeptide macromolecular chains, that adopt a right handed α-helical coiled-coil structure, are assembled to construct protofibrils which are packed to form the intermediate filaments (e.g. [1]). The so-called α-form crystallites reflect the molecular ordering of the packing of the α-helical molecules within the intermediate filaments.

When human hair and wool fibres are stretched, X-ray diffraction shows that the α-form crystallites transform into β-form crystallites. This process is called α–β transition, and its mechanism has drawn the attention of scientists in various fields over the past six decades [2–4].

Extensive DSC studies have been carried out to investigate the melting behaviour of the crystallites in keratinous fibres [5–11]. In addition to other analytical methods, a quantitative determination of the melting enthalpy of the α-crystallites is considered a convenient yet accurate determination of α-crystallinity. However, unlike synthetic polymers, these natural biological materials are often difficult to characterise thermally, in particular when a quantitative determination is required, due to the co-existence of various biological heterogeneous components.

It is essential to understand the specific thermal characteristics in order to have a reliable quantitative analysis. Previous studies have shown that there are some specific thermal characteristics which complicate the interpretation of a DSC measurement of wool keratin. These characteristics are: (i) a relatively low melting enthalpy; (ii) a relatively low thermal degradation temperature of other histological components; and (iii) the moisture content dependence of the

[1]Presented at the 9th Chinese Conference on Chemical Thermodynamics and Thermal Analysis (CTTA), Beijing, China, August 1998.

0040-6031/99/$ – see front matter 
PII: S0040-6031(99)00055-6

melting temperature. Based on these understandings, the author has developed a method adopting silicone oil as the thermal medium for wool DSC analysis [10]. The aim of this study is to examine whether this silicone oil method is applicable to human hair. Compared to wool, far less quantitative thermal analysis has been carried out for human hair.

## 2. Experimental

Caucasian red hair and Asian black hair were washed using a normal commercial shampoo and rinsed using distilled water. Hair fibres were cut with scissors to powders that were then placed in a room at 20°C and 65% relative humidity for longer than 12 h. The moisture content for so conditioned hair samples was 11.6%, determined by drying the samples in a vacuum oven for 120 min at 60°C. Around 10 mg (accurately measured) of the hair powder sample was packed into a 75 μl stainless steel DSC cell. The cell was sealed with an O-ring (25 bar), or sealed after injection of around 30–40 μl distilled water or silicone oil. All the measurements were carried out using a Perkin-Elmer DSC 7. The heating rate used in this study was 5 K/min, and the flow rate of nitrogen gas was about 30 ml/min.

## 3. Results and discussion

Fig. 1 shows the DSC curve for the Caucasian red hair, measured using an open pan. An initial broad endotherm is observed from 40°C to 120°C. This is considered to be due to moisture evaporation. There is an endotherm with a peak temperature of 230°C, presumably corresponding to the melting of the α-form crystallites in hair. However, the whole curve is seen to shift upwards, which could result from thermal degradation/pyrolysis of the sample. In fact, a semi-coke like sample was observed after the run finishing at 260°C, suggesting that the sample had experienced severe thermal degradation/pyrolysis. The peak area, as illustrated in Fig. 1, shows 8.9 J/g for the melting enthalpy, or 10.1 J/g on a dry weight basis.

Fig. 2 shows two DSC curves for the Caucasian red hair, measured using a sealed pan without injecting any thermal medium. Initial evaporation of water

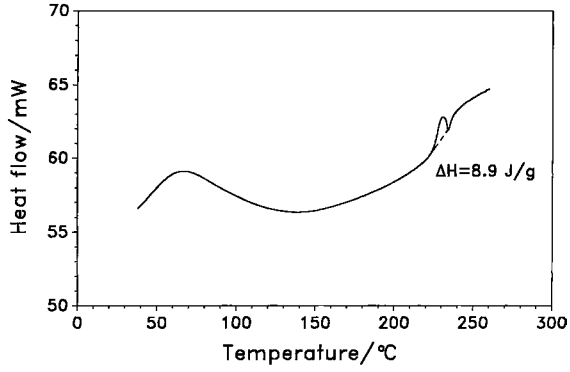


Fig. 1. DSC curve for a Caucasian red hair sample, measured using an open pan.

quickly builds up high pressure inside the pan, suppressing further evaporation. A much flatter baseline is observed. There is an endotherm with a peak temperature of 174°C on the curve, corresponding to the melting of the α-form crystallites. The depression of the melting point of the α-crystallites with increasing water content of the sample has been explained by Flory's theory [12], which suggests that water molecules in hair interact with the polypeptide when the crystallites melt. A higher melting entropy, and therefore, a lower melting point ($T_m = \Delta H/\Delta S$) would be expected as the moisture content is increased. The curve does not return to the baseline after the endotherm, and instead a considerable curve shift can be identified. Assuming that the bottom of the valley at around 179°C is the baseline, as illustrated in

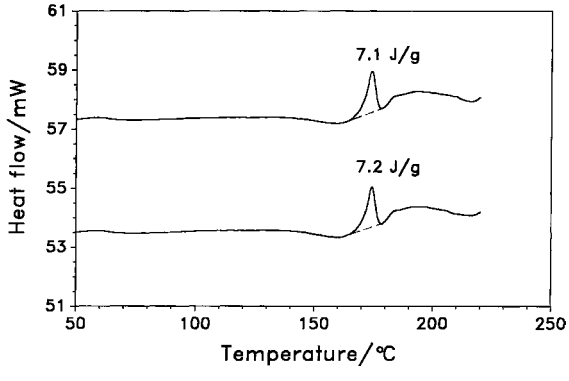


Fig. 2. DSC curves for a Caucasian red hair sample, measured using a sealed pan without thermal medium.

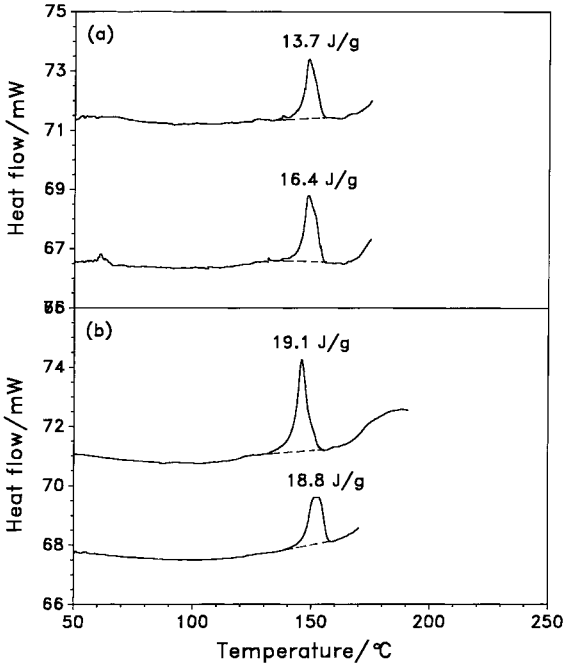


Fig. 3. DSC curves for a Caucasian red hair sample (a) and an Asian black hair sample (b), measured using a sealed pan with water as the thermal medium.

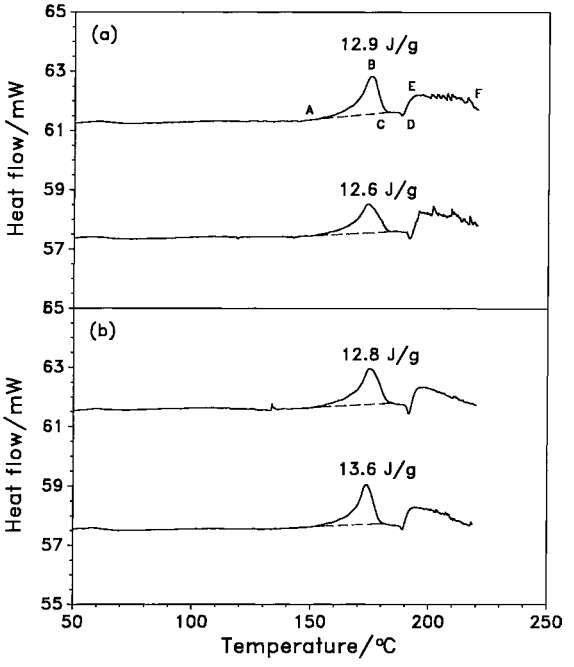


Fig. 4. DSC curves for a Caucasian red hair sample (a) and an Asian black hair sample (b), measured using a sealed pan with silicone oil as the thermal medium.

Fig. 2, one obtains an average melting enthalpy of 7.2 J/g, or 8.1 J/g on a dry hair basis.

DSC measurements using distilled water as the thermal medium were also carried out. The curves for the Caucasian red hair are displayed in Fig. 3(a), and those for the Asian black hair in Fig. 3(b). The endotherm with a peak temperature of near 150°C is considered the melting endotherm of the α-form crystallites in hair. It appears that the curve does return to the baseline after the endotherm, allowing an easy determination of the peak area. However, Fig. 3 shows that the endotherm varies in terms of shape and size from measurement to measurement. To avoid the risk of pan bursting, the measurements were usually run only up to 180°C.

Further DSC measurements were carried out using silicone oil as the thermal medium, and Fig. 4 shows the results. A melting endotherm (marked ABC) with the peak temperature around 175°C is observed. A minor exotherm at around 192°C is also obvious, after which a broad endotherm appears. This broad endotherm (marked DEF) is considered to be due to thermal degradation of other histological components in hair. The origin of a tiny exotherm cannot be identified easily at this stage. These DSC runs were carried out below 220–230°C to avoid possible pan bursting at higher temperature.

The reproducibility of the curve, in terms of curve shape, peak temperature and total peak area, is reasonably satisfactory. No significant difference between the Caucasian red hair and Asian black hair is detected. The average melting enthalpy for the eight runs performed is determined to be $12.8 \pm 0.53$ or 14.5 J/g (=12.8/0.883) on a dry weight basis. Note that the other four runs, $\Delta H = 11.8$ and 13.3 J/g for the Caucasian hair, and $\Delta H = 12.7$ and 12.9 J/g for the Asian hair, are not shown in the figures.

The above-observed phenomena are similar to those observed for wool keratin [10,11], and can be consistently interpreted as given below.

There are actually two thermal (major) events occurring in the temperature range. One is the melting of the α-form crystallites, denoted by Curve ABC in Fig. 4; and the other, the thermal degradation of other

histological components, marked by Curve DEF. The temperature at which these two events occur varies according to the environment of the sample.

When a DSC experiment is carried out using an open pan, the melting endotherm shifts towards the high temperature side, and so does the thermal degradation, causing a partial overlapping of the BC segment with the DE segment. The DSC curve over the temperature range above 235°C in Fig. 1 is similar to Curve DEF in Fig. 4. This similarity becomes more convincing if one carefully compares Fig. 2 to Fig. 4. On account of the overlapping of the BC and DE segments, the bottom of the valley after the melting endotherm is higher than the baseline. A lower enthalpy is obtained in Figs. 1 and 2. Thus, these DSC methods do not present a quantitatively accurate determination of melting enthalpy, which in turn results in a misleading assessment of the crystallinity of human hair samples.

The function of silicone oil seems to be to push the degradation endotherm to a higher temperature, permitting an easy separation of the two thermal events. The plateau part (Curve CD) on the curves in Fig. 4, therefore, represents the baseline of the DSC runs. This explains why consistent and reproducible results have been obtained when silicone oil is employed as the thermal medium.

On the other hand, when the DSC runs are performed using water as the thermal medium, the physiochemical functions of water appear to have driven the degradation endotherm DEF to a low temperature, resulting in a complete overlapping. A plateau appears after the endotherm, and no further endotherm can be observed until 180°C (see Fig. 3). Thus, the obtained enthalpy is always greater than that obtained using silicone oil. As the thermal degradation endotherm varies in size and shape due to some subtle factors, a different overlapping occurs. This explains why the variation in shape and size in the case of water is greater than that in the case of silicone oil.

To further investigate the role of water, hair samples with higher moisture content were measured using silicone oil as the thermal medium. Hair powders were placed in a humidity chamber set at 25°C and 95% relative humidity for 12 h. The moisture content for these conditioned hair samples was found to be 19.2%. The DSC curves for the sample, measured in the presence of silicone oil, are displayed in Fig. 5 in which the melting endotherm has shifted to around 161°C due to more moisture in the samples, and the thermal degradation endotherm, still clearly distinguishable, shows quite a different shape from that given in Fig. 4. In particular, the DE segment has stretched to extend into the BC segment of the melting endotherm, causing a slight overlapping. For this reason, no clear plateau after the melting endotherm can be observed. The average melting enthalpy for the runs is found to be 10.7 J/g, with obvious variation. When translated into dry basis, a figure of 13.4 J/g for the melting enthalpy is obtained. This figure is slightly lower than that obtained for the case given in Fig. 4, which is considered to be caused by the slight overlapping. The tiny exotherm observed in Fig. 4 is not observable in Fig. 5.

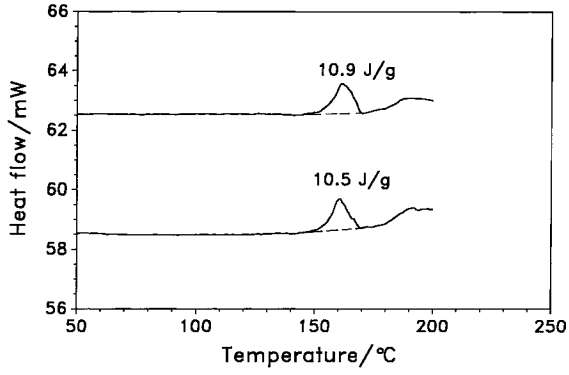


Fig. 5. DSC curve for the Caucasian red hair and Asian black hair samples containing higher moisture content, measured using a sealed pan with silicone oil as the thermal medium.

## 4. Conclusions

It has been demonstrated that human hair shares the same thermal characteristics as those revealed for wool. Silicone oil was found to be an effective thermal medium for DSC determination of the melting enthalpy of the α-form crystallites in human hair. The melting peak of hair conditioned at 20°C and 65% relative humidity was about 175°C, and the melting enthalpy, 12.8 J/g, equivalent to 14.5 J/g for dry hairs. This indicates that human hair exhibits higher crystallinity than merino wool (c.f. 10.0 J/g for dry wool).

## Acknowledgements

This research was supported by the Australian government, and Australian woolgrowers through a grant from the Woolmark Company.

## References

[1] H. Zahn, in: G.E. Rogers et al. (Eds.), Proc. Symp. on the Biology of Wool and Hair, Chapman & Hall, London, UK, 1989, p. 495.
[2] W.T. Astbury, A. Street, Phil. Trans. R. Soc. London A230 (1931) 75.
[3] L. Pauling, R. Corey, Nature 166 (1951) 550.
[4] L. Pauling, R. Corey, Nature 171 (1953) 59.
[5] W.D. Felix, M.A. McDowall, H. Eyring, Text. Res. J. 33 (1963) 465.
[6] A.R. Haly, J.W. Snaith, Text. Res. J. 37 (1967) 898.
[7] H. Sakabe, T. Miyamoto, H. Inagaki, Sen-i Gakkaishi 38 (1982) T517.
[8] M. Spei, R. Holzen, Colloid Polym. Sci. 267 (1989) 549.
[9] F.J. Wortmann, H. Deutz, J. Appl. Polym. Sci. 48 (1993) 137.
[10] J. Cao, K. Joko, J.R. Cook, Text. Res. J. 67(2) (1997) 117–123.
[11] J. Cao, J. Appl. Polym. Sci. 63 (1997) 411–415.
[12] U. Eisele, Introduction to Polymer Physics, Springer, Berlin, Germany, 1990.