

Origin of the Bimodal "Melting" Endotherm of α -Form Crystallites in Wool Keratin

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ABSTRACT: The melting endotherm of α -form crystallites in wool keratin appears often to be bimodal. The origin of the bimodal endotherm has been considered to correspond to the differential melting of the α -form crystallites in the domains of ortho- and para-cortical cells. An alternative interpretation is presented, in which the bimodal peak arises from the overlapping of the melting endotherm of α -form crystallites and the thermal degradation of other wool histological components. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 411–415, 1997

Key words: DSC; melting; bimodal; α -crystallites; wool keratin

INTRODUCTION

The cortical cells of wool contain a two-phase composite structure consisting of low-sulfur intermediate filaments within a high-sulfur amorphous matrix. The spindle-shaped cortical cells are packed together within the wool fiber. Two types of cortical cells, ortho and para, have been identified mainly according to their dyeability. The ortho-cortex, which is more readily stained in basic dyes, contains a lower concentration of disulfide linkages than the para-cortex. The ortho- and para-cortical cells form a distinctive bicomponent structure, which are arranged in fiber cross sections bilaterally for Merino wool but cylindrically for Lincoln wool.¹

When Haly and Snaith² investigated the melting behavior of α -form crystallites in wool using differential thermal analysis (DTA) nearly 3 decades ago, they found that the endotherm corresponding to the melting of α -form crystallites was often but not always bimodal.² Haly and Snaith proposed that the two peaks of the bimodal endotherm might correspond to the melting points of

α -form crystallites and β -form crystallites (alternative crystalline form of keratin), but were more likely to result from the differential melting of α -form crystallites in the domains of the ortho-cortex and the para-cortex, respectively. Hereinafter, the latter hypothesis is referred to as the ortho- and para-interpretation.

The origin of the bimodal endotherm has attracted a lot of attention from researchers in wool science. Crighton^{3,4} investigated the effects of chemical modifications of merino wool on the melting endotherm using a high-pressure DTA in 1990, and found that the bimodal endotherm shifted differently, depending on the type of modifications. Crighton concluded that the bimodal endotherm was linked to the differential stabilities of the ortho- and para-cortical cells.

More recently, Wortmann and Deutz⁵ investigated the correlation between the cystine content and melting point of a series of keratin materials, i.e., nail, mohair, and wool, etc. For seven keratins used in this study, the authors found a significant positive correlation between the cystine level and the melting temperature. From this, Wortmann and Deutz concluded that the ortho- and para-explanation of the bimodal endotherm was satisfactory, because the cystine content in the para-

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cortex of merino wool was, statistically, slightly higher than that in the ortho-cortex.

However, in a recent study on the melting behavior of α -form crystallites in wool keratin, it was found that the appearance of the bimodal endotherm depended on the environment and the heating rate of a DSC measurement.⁶ This finding has led the present author to believe that the differential melting of α -form crystallites in the domains of ortho- and para-cortical cells might not be the interpretation of the observed bimodal endotherm. It will be shown in the following that the bimodal endotherm can be interpreted in terms of overlap between the melting endotherm of α -form crystallites and the thermal degradation endotherm of other histological components of merino wool.

EXPERIMENTAL

Samples

Cleaned merino wool in the forms of top and fabric were used in this study. A lincoln wool top was also used for comparison. Wool top was cut to a powder (wool snippets) using scissors. For fabric, three small discs were punched from the merino wool fabric to fit the DSC sample holder.

DSC Experiments

Wool samples were placed in a room with constant relative humidity 65% and temperature 20°C for more than 2 days to adjust the regain of the samples. Around 10 mg of accurately weighed wool powder samples were packed into a 75 μ L stainless steel DSC cell and pressed into a cake intimately contacting with the DSC cell; or three pieces of wool fabric discs (around 12 mg) were placed into the cell. The cells were then sealed with an O-ring (25 bar) in one of three ways: (1) in air, (2) under dry nitrogen and (3) in air after the injection of 30–40 mg silicone oil into the cells.

For the DSC experiments in excess water, the identical conditions as those employed by Wortmann and Deutz⁵ were used to facilitate comparison, i.e., 5–6 mg wool snippets were packed into a 75 μ L stainless steel cell; 50 μ L of distilled water was then injected into the cells before they were subsequently sealed with an O-ring (25 bar). All the experiments were carried out in a Perkin-Elmer DSC 7. The instrumental calibration was

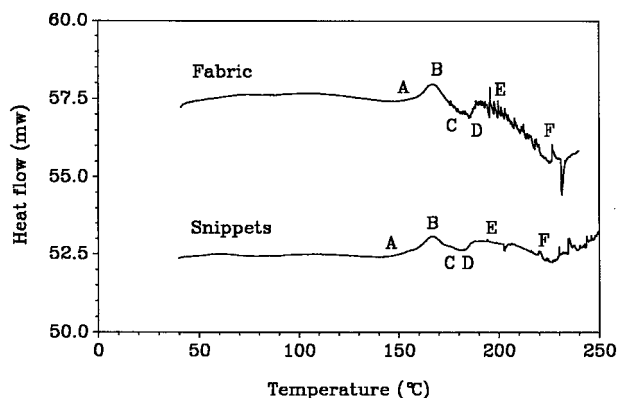


Figure 1 DSC curves for a merino wool fabric and merino wool snippets conditioned at 65% r.h. and 20°C, measured using silicon oil as a thermal medium.

carried out using indium as a standard at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

As demonstrated in a separate article of the author,⁶ the thermal analysis of wool is much more complicated than other polymeric materials. This is caused by a low melting enthalpy and a relatively low thermal degradation temperature for the other histological components as well as the moisture dependence of the melting behavior^{7,8} of the α -crystallites and the thermal degradation. This complexity is further compounded by the supercontraction of wool fibers, which can change the contact between the sample and sample holder during heating. It has been shown that efforts to shift the thermal degradation to a higher temperature and to keep consistent thermal conduction during heating are essential to have an interpretable DSC measurement for wool.⁶

Results in Silicone Oil

Figure 1 shows the DSC curves for the wool fabric and wool snippets from room temperature to 250°C, measured in the presence of silicone oil at a heating rate of 5°C/min. An endotherm, ABC, corresponding to the melting of α -form crystallites in the intermediate filaments of wool keratin, with a peak temperature at about 167°C was observed. A broad endotherm, DEF, was found on the DSC curves from about 185°C. This endotherm has been considered to be the endotherm corresponding to the thermal degradation of me-

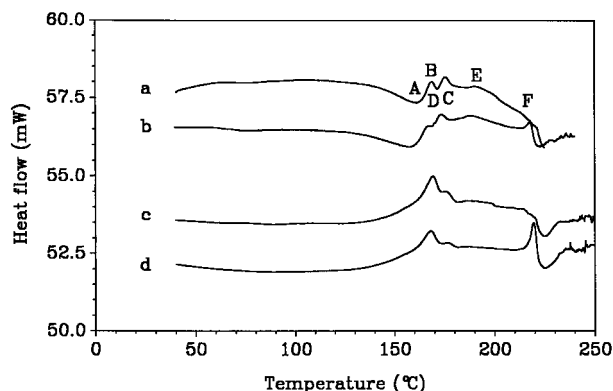


Figure 2 DSC curves for (a) merino wool fabric in air; (b) merino wool fabric in N_2 ; (c) merino wool snippets in air; and (d) merino wool snippets in N_2 . All the samples were conditioned at 65% r.h. and 20°C.

merino wool because gas generation and significant color change from white to yellow for the wool fiber were associated with this endotherm.⁶ As the thermal degradation proceeded, the gas pressure inside the sample pan rose. The pressure leak caused Curve DEF part to be often (not always depending on how good the O-ring seal was) a noisy one. These curves (in particular, the ABC melting segment) are highly reproducible.

The fact that no obvious bimodal melting endotherm could be detected if a DSC measurement was carried out in the presence of silicone oil as a thermal medium has led to an alternative explanation to the ortho- and para-interpretation. If this interpretation reflects the intrinsic difference in the ortho- and para-cortex, one expects to observe the bimodal endotherm, because the merino wool samples contain both the cortical cell types. In the present author's opinion, it is the thermal degradation endotherm, which could occur at lower or higher temperature according to experimental conditions, that causes the appearance of bimodal "melting" endotherm when it overlaps with the melting endotherm of α -crystallites of wool under certain experimental conditions.

Results in Air or Nitrogen Gas

The DSC curves for the wool fabric (curve a) and wool snippets (curve b) obtained without using silicone oil as a thermal medium are shown in Figure 2. The curve shape and peak size changed slightly for the different sample forms. An obvious bimodal endotherm with peak temperatures around 165 and 172°C was observed.

The observation of the bimodal endotherm for

the DSC curves can be interpreted in terms of overlap between the melting of α -crystallites and thermal degradation endotherm. In the absence of the insulation effect of silicone oil from air, the thermal degradation temperature shifts to lower temperatures, causing the overlapping. This can be seen by comparing the curves with those shown in Figure 1. As the thermal degradation shifts to lower temperature, curve segments BC and DE overlap with each other, resulting in a bimodal like "melting" endotherm. This also explains why the baseline after the "melting" shifts upwards significantly.

It follows then that if a DSC experiment carried out under an inert atmosphere would show different "melting" endotherm. For this reason, the stainless steel DSC capsules were sealed under nitrogen while other conditions were kept the same as those used for the measurements in air. The results are also shown in Figure 2 for the fabric (curve c) and for the snippets (curve d). The reproducibility of these measurements were checked and found to be high. It can be seen from the figure that the second peak in the bimodal endotherm has been reduced and shifted, although not completely removed. This is because the degradation endotherm depends on the environment of an experiment. In general, different environments result in a different degradation endotherm; therefore, different overlapping for the total measured endotherm.

Results in Water

As noted by Wortmann and Deutz, the melting endotherm in the DSC curves, both in shape and peak size and peak temperature, varies significantly when a measurement is carried out in the presence of excess water, although identical experimental conditions are maintained. A common interpretation is that the variation is caused by the biological nature of wool. However, this variation was not observed when DSC experiments were carried out using silicone oil as a thermal medium both for the samples from a batch and for the samples from various batches of merino wool. In fact, a DSC experiment uses 5–10 mg of sample, containing thousands of wool snippets; the variation expected for a single wool fiber should have been well averaged.

In this present study, although strong bimodal endotherms similar to that published in Wortmann and Deutz's report⁵ were certainly observed, often singlet endotherms as shown in Fig-

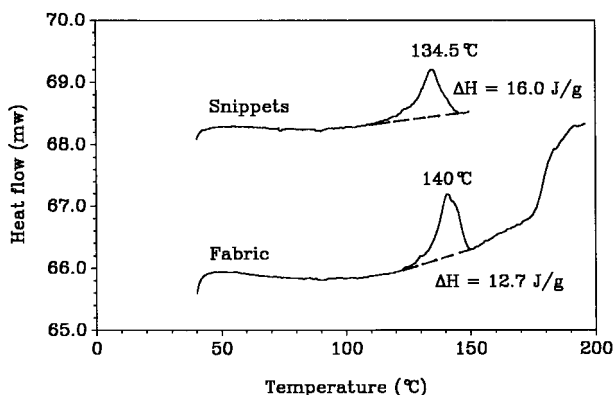


Figure 3 DSC curves for wool snippets and fabric immersed in excess water.

ure 3 were observed. This fact shows that even when a DSC measurement is carried out in excess water, the bimodal endotherm will not necessarily be observed, although all the merino wool samples always contain both ortho- and para-cortex.

The variation between individual DSC curves for wool measured in excess water can also be interpreted in terms of overlapping processes of the melting and thermal degradation. In water, both the melting point and thermal degradation are shifted to lower temperatures. These two thermal events, fortunately or unfortunately, occur over the same temperature range. Note that the degradation curve in water will not necessarily have the same shape and size as those in silicone oil. However, the thermal degradation is more sensitive to other subtle conditions of a wool sample or measuring conditions, e.g., different cleanliness of the wool surface, different scouring process, and different soaking period of the wool fiber in water prior to DSC measurement due to the interactive nature of water with wool, it occurs slightly differently in each individual experiment. This further causes different overlapping of the melting endotherm and the degradation endotherm. Therefore, the observed “melting” endotherm appears differently for each individual measurement. In fact, pronounced bimodal endotherms have been found more often when a DSC experiment is carried out for wool samples in excess water.

To evidence the above argument, the same experiments for the same samples were carried out as those used for Figure 3 but with longer soaking period (2 days) after the DSC capsules were sealed prior to measurements. A definite bimodal endotherm was observed for both the wool snippet

and fabric, as shown in Figure 4. This can be considered to be caused by the change in the thermal degradation endotherm, which in turn, results in different overlapping for the long soaked samples.

More evidence can be gained by a quantitative measurement of the endotherms. The melting enthalpy obtained from the DSC curves recorded in the presence of silicone oil, as shown in Figure 1, is about 8.6 J/g, which is consistent for various samples with different forms and regains; and the degradation enthalpy is around 11.3 J/g, which varies significantly for each individual run (the figures are calculated on 65% r.h 20°C conditioned wool basis). Summing the two enthalpies together, one obtains the total 19.9 J/g. This figure does fit in the range of the “melting” enthalpy obtained from the DSC curve recorded in excess water, which has been observed to vary from around 12 to 25 J/g.

Further evidence can be provided by using a lincoln wool fiber as an example. A batch of lincoln wool in our laboratory was found to have less variation in individual DSC curves measured in excess water. Experiments using silicone oil and water for the lincoln wool fiber were then carried out. As shown in Figure 5, the enthalpies for the melting and degradation of the lincoln wool fiber were 11.0 J/g and 9.0 J/g, respectively; and the “melting” enthalpy obtained in water was 19.8 J/g, indicating that the “melting” in excess water did represent the sum of the melting of α -form crystallites and degradation of other histological components in wool. The higher melting enthalpy of lincoln wool presumably results from its higher crystallinity as compared with merino wool. This explanation is supported by wide-angle x-ray dif-

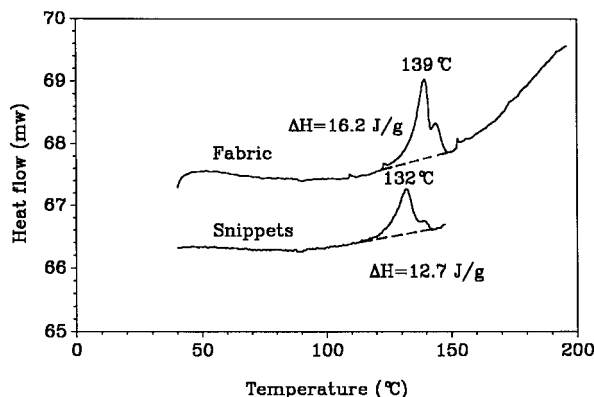


Figure 4 DSC curves for wool snippets and fabric soaked in excess water for 2 days.

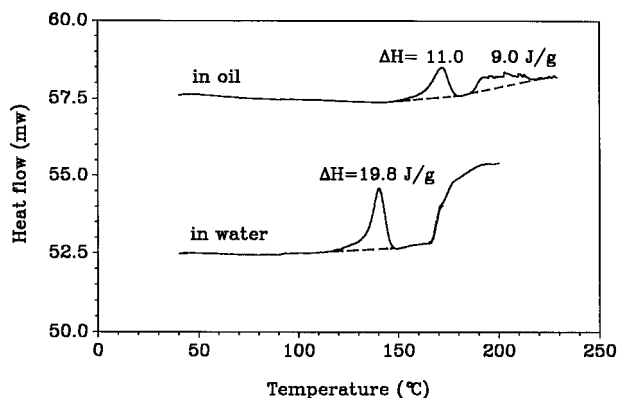


Figure 5 DSC curves for a Lincoln wool fiber measured using silicon oil and water.

fraction measurements, which show clearer α -crystalline pattern for Lincoln wool than for merino wool.

The present author would like to add further comments on the ortho- and para-interpretation as follows.

The correlation coefficient between the melting point and cystine content for the keratinous materials examined by Wortmann and Deutz was only 0.72, and the correlation is phenomenological in nature. It is well known that the melting point of a crystalline material depends on a number of factors, including chemical composition, molecular conformation as well as its crystal lattice structure. For instance, the melting temperatures for the crystal modifications of isotactic poly(propylene) vary from 145–175°C, although all the modifications have exactly identical chemical composition and molecular conformation. For example, in the area of wool, by stretching wool fiber, one obtains the β -crystalline form without changing the cystine content of the wool fiber. Melting of the β -form crystallites can not be observed at least until 350°C (dry samples) both for silk⁹ and for wool¹⁰ while the α -form crystallite has a melting point around 230°C for dry wool samples.^{2,10}

In addition, the cystine content used by Wortmann and Deutz was for the keratinous materials as a whole, not the cystine content for the crystalline phase. In fact, the reported differences between ortho- and para-cortical cells are largely due to the difference in the amorphous matrix surrounding the α -form crystallites and not solely the crystallites. Furthermore, even according to the correlation observed by Wortmann and Deutz,

the difference in the melting points of ortho and para is calculated to be only 1.7°C,⁵ which is insufficient to explain the 4–5°C difference observed gap between the peak temperatures. This is because the distance between the two peaks on the combined curve will usually be less than the difference for the two individual curves, in particular, when the two individual curves have a broad profile. For these reasons, the observed correlation between the melting temperature and cystine content for the keratinous materials examined produce little support to the ortho- and para-explanation of the bimodal endotherm for wool.

CONCLUSION

It is concluded that the often reported bimodal endotherm of merino wool is unlikely to result from the differential melting of α -crystallites in the domains of ortho- and para-cortical cells, but is more likely to originate from the overlapping between the melting endotherm of α -crystallites and the thermal degradation endotherm of other histological components in wool.

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