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THERMOMECHANICAL ANALYSIS OF MERINO WOOL YARNS

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There is a difference in structure across the wool fibre which is usually referred to as bilateral. The endothermic denaturation doublet of keratins has been observed by different authors for a variety of keratins and measuring conditions and mainly interpreted by different theories. Merino wool yarns have been analyzed by the thermomechanical analysis and at low stress two thermal transitions before melting have been identified. These two thermal transitions are in accordance with the onset temperatures of the denaturation doublet shown by the DSC both at temperatures lower than the thermal degradation temperature determined by TG. The DSC of fibrillated fibres by abrasion showed not a denaturation doublet but just only a denaturation peak. The two transitions of the TMA and the modification of the DSC curve by abrasion seems to confirm that abrasion removes the component which denaturates at lower temperature.

Keywords: *bilateral structure, denaturation, DSC, Merino wool, TG, TMA*

Introduction

Wool is formed by proteins some of which are natural block copolymers. The fine structure of wool fibre, which determines the tensile properties, consists of fibrils, with helical coiled molecules, embedded in the amorphous matrix. The fibrils and the matrix consist of polypeptides interconnected physically and chemically. The low-sulphur material with a simple regular structure and without cross-links forms crystalline fibrils, which are embedded in a matrix of more complicated and cross-linked high-sulphur material. The fibrillar protein forms first, and the low-sulphur parts of the natural block copolymer crystallise in parallel rods kept apart by the high-sulphur tails. Thereafter, the rest of the high sulphur protein is formed and the matrix is solidified. Nature joins the two constituents of this natural composite in a special way. The low-sulphur protein molecules in the fibrils have high-sulphur tails, which emerge from the fibrils at intervals and are cross-linked with the rest of the amorphous matrix [1].

Melting of the crystalline phase results in a discontinuous and rapid decrease in the mechanical performance (for example, stiffness and strength) of the material over a narrow temperature range. Softening of the amorphous phase, however, results in a continuous, slow decrease in fibre mechanical properties over a wider temperature range. It is therefore possible to characterize the structural behaviour of a material's crystalline and amorphous regions by monitoring its thermomechanical performance [2].

There is a difference in structure across the fibre, which is usually referred to as bilateral. The side with most reactivity is called the *ortho*-cortex and that with the least the *para*-cortex. The bilateral structure is associated with the assymmetrical keratinisation in the follicle, the para side being the one which keratinises first. Given the bilateral structure of wool, interest has been focused on the identification and the quantification of the two parts of the cortex [3]. The ortho-cortex has a substantial quantity of cystine incorporated in an intrachain fashion, with the result that it will swell more readily and be more receptive to dye than the more highly cross-linked structure suggested for the para-cortex.

Wortmann and Deutz [4] describe the different theories about the endothermic denaturation doublet of keratins. The 'helix/matrix' hypothesis was explained by Spei and his coworkers who claimed that the low-temperature peak should be attributed to α-helix denaturation, whereas the high-temperature peak originates in the matrix from cystine pyrolysis. Cao *et al*. [5] interpreted the lower temperature peak as originating from denaturation of the α-helical rather than from the melting of the crystalline material of wool keratin. These authors attributed the higher temperature endotherm to the thermal degradation of other histological components. The 'ortho/para' hypothesis was explained by Haly and Snaith [6] as well as Crighton and Hole [7], who ascribed the doublet to differences in the transition performance of the α-helical material in the ortho- and para-cortical cells. Wortmann and Deutz isolated ortho- and para-cortical

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cells from Merino wool. The high pressure DSC curves obtained from the isolated cell fractions are in good agreement with the results obtained of the whole fibre material. According to these authors, the results provide unequivocal evidence for the validity of the ortho/para hypothesis for the interpretation of the endothermic denaturation doublet of the keratins.

The aim of this work was to apply the thermomechanical analysis (TMA) the thermogravimetry (TG) and the differential scanning calorimetry (DSC) to a variety of Merino wool yarns in order to identify the components which denaturates at different temperatures.

Experimental

Material

Wool yarns were obtained from a Merino wool plain weave woven fabric of 345 g m^{-2}. Fibre fineness was 21 μm. The urea-bisulphite solubility was 36.24%, alkali solubility 21.76%, and pH of extracted water 6.8. Warp and weft yarns of 100% wool were removed from the fabric to be tested by TMA. Yarns were cut for TG and DSC analysis. Prior to testing all samples were conditioned in a standard atmosphere (22°C and 65%HR) during a minimum period of 48 h.

Abrasion treatment

Samples of the wool fabric were abraded using the Martindale Wear and Abrasion tester in accordance with the British Standard Method [8]. The abrasion test produces fabric rubbing, scraping and wearing against a wool reference fabric that 'wears out' the fabrics under testing [9]. At the end of the test the worn out wool fibres on the abrasive surface were collected and analyzed by TG and DSC.

Characterization

TMA

A Mettler-Toledo TMA/SDTA 840 was used for thermomechanical analysis. Warp and weft yarns were prepared in a special support for yarns to obtain samples 12.8 mm in length clamped with a copper staple. The staple-yarns were introduced into the analyzer and the analysis was performed under the following conditions: initial temperature: 25°C; final temperature: 300°C; heating rate: 5°C min^{-1}. Dynamic strengths were tested at two levels: 0.013–0.027 N (mean stress 0.3 MPa) and 0.25–0.55 N (mean stress 6.0 MPa); Frequency: 1/12 Hz; purging gas: nitrogen 30 mL min^{-1}.

TG

Trials were performed in a Mettler-Toledo TG50 unit using an aluminium oxide crucible of 70 μL. The following analytical conditions were used: initial temperature: 30°C; final temperature: 350°C; heating rate: 10°C min^{-1}; purging gas: nitrogen 200 mL min^{-1}.

DSC

Trials were performed in a Mettler-Toledo DSC821 unit. Micropunched (Ř 50 μm) aluminium pans of 40 μL were used. Conditions: initial temperature: 30°C; final temperature: 275°C; heating rate: 10°C min^{-1}; purging gas: nitrogen 50 mL min^{-1}.

Results

Results on original wool yarns

TMA

Samples of 12.8 mm in length of original wool warp and weft yarns underwent a TMA analysis at 0.3 and 6.0 MPa of mean stress with a periodical variation in stress at 1/12 Hz, from 25 to 300°C at a rate of 5°C min^{-1}. The TMA curve of warp and weft yarns at 0.3 MPa showed two changes of slope, the first being a sharp change near 210°C and the second less marked one at 226°C before fibre melting. The TMA curve at 6.0 MPa allows us to measure just one onset temperature at 213.2°C near the first transition indicated by the 0.3 MPa curve.

Figure 1a shows the TMA plot obtained at 0.3 MPa and Fig. 1b gives the mean dilatation curve. The first derivative corresponding to the slope of the mean dilatation curve was also plotted. This value corresponds to the instantaneous dilatation coefficient $\alpha = (dL/dT)/L_0$ /μm m^{-1} K^{-1}, dL being the infinitesimal increment in length, dT the temperature infinitesimal increment, and L_0 being the gauge length (12.8 mm) at room temperature. Before the first transition the value of the first derivative remains almost the same, whereas between the first and the second transition there is a sudden increase in the slope, which is illustrated by the step drawn by the α plot. After the second transition, the sudden increase in the slope due to fibre melting is also reflected by the α plot. Table 1 shows the two thermal transition temperatures of the Merino wool fibre: the onset temperatures of the dilatation curve T_{d1} and T_{d2}, and the onset temperatures of the instantaneous dilatation coefficient α, $T_{\alpha 1}$ and $T_{\alpha 2}$.

The structural differences between warp and weft yarns could account for the differences in the transition temperatures. Wool fibres in the warp yarn

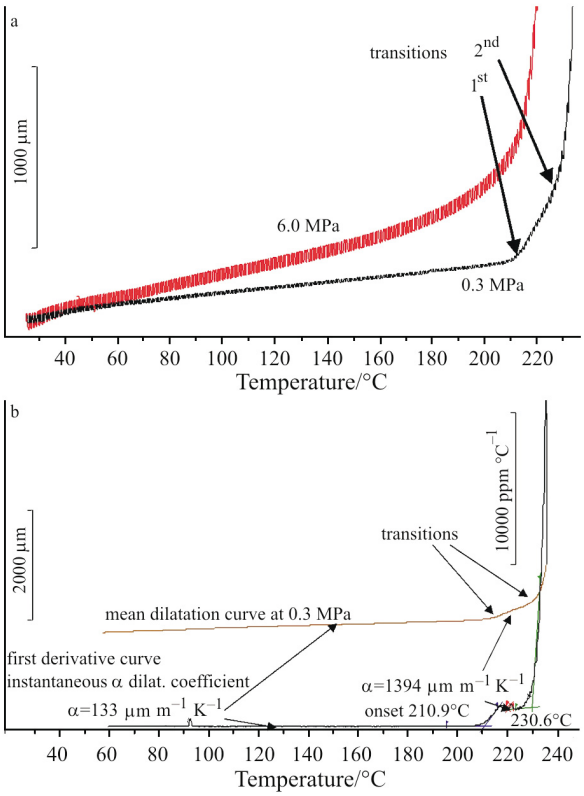

Fig. 1 a – TMA curves at 0.3 and 6.0 MPa of original wool warp yarns; b – mean dilatation curve at 0.3 MPa and plot of the first derivative corresponding to the instantaneous α dilatation coefficient

are more parallel and undergo more uniform stresses than the fibres in the weft yarns, with the result that parameters derived from the warp samples will be better estimators of fibre properties than those derived from the weft samples.

Given that the wool yarns are subjected to a periodical stress and given that the strains induced are measured by TMA, the elastic modulus is also measured. The elastic modulus can be split into two components: The first one in phase with strain is known as the storage modulus, the second one out of phase with strain is known as the loss modulus. A continuous increase in the storage modulus with temperature up to 200°C (maximum value) was observed. Thereafter a sharp decrease up to a stabilization step around 220°C is observed. It seems that all cells contribute to the modulus at 200°C whereas the sudden decrease and stabilization around 220°C should reveal some denaturation process of a fraction of cells while the non-denaturated ones are able to undergo mechanical stresses at this temperature. Afterwards a sudden decrease due to complete denaturation of cells is observed. The ratio between both modulus at 220 and 200°C should be related with the fraction of denaturated cells at 220°C (Table 2).

TG

The onset temperature at which the thermal degradation of keratin and other histological components begins is 232.84°C. Therefore the transitions observed at 200 and 220°C by the TMA do not correspond to a thermal degradation of cells but to a phase-transition or denaturation of them. The TG curve of approximately 6 mg of wool is shown in Fig. 2a. Up to 190°C the mass loss due to water evaporation was 7.48%.

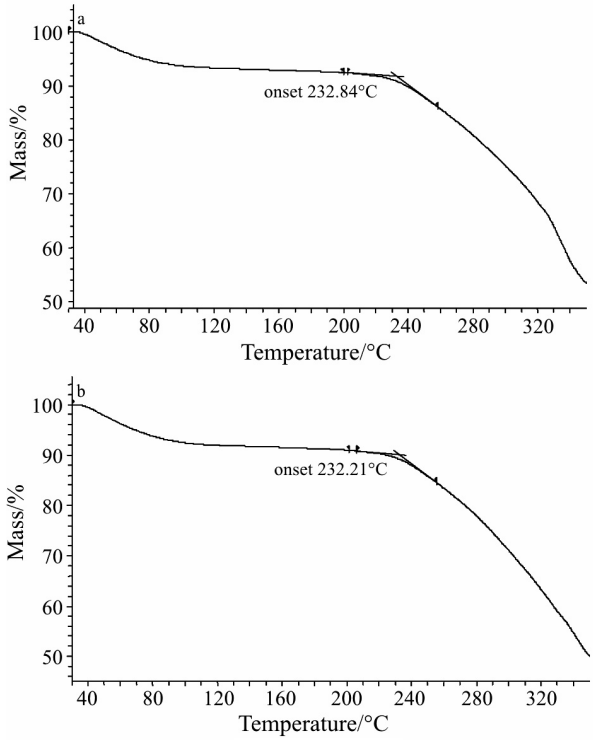

Fig. 2 TG curves of Merino wool fibre and Merino abraded wool fibre

Table 1 Thermal transitions of original Merino wool measured by TMA and DSC

Thermal transition		First transition/°C	Second transition/°C
onset temperatures of the TMA dilatation curve	Warp yarn	210.5	225.7
	Weft yarn	213.2	227.2
onset temperatures of the TMA dilatation coefficient α	Warp yarn	208.2	227.1
	Weft yarn	210.9	230.6
onset temperatures of the DSC denaturation doublet		215.9	227.4

Table 2 Storage modulus and instantaneous dilatation coefficient before the second and the first transition of the wool yarns

Thermal parameters		Before second transition	Before first transition	Relationship
storage modulus	Warp yarn	109 MPa (at 220°C)	216 MPa (at 200°C)	0.50
	Weft yarn	131 MPa (at 220°C)	227 MPa (at 200°C)	0.58
instantaneous dilatation coefficient α	Warp yarn	2090.7 ppm K^{-1} (at 218.3°C)	154.8 ppm K^{-1} (at 200°C)	–
	Weft yarn	1394.1 ppm K^{-1} (at 220.9°C)	132.6 ppm K^{-1} (at 200°C)	–
denaturation enthalpies		3.89 J g^{-1} (second doublet)	7.90 J g^{-1} (1^{st}+2^{nd} dbt.)	0.49

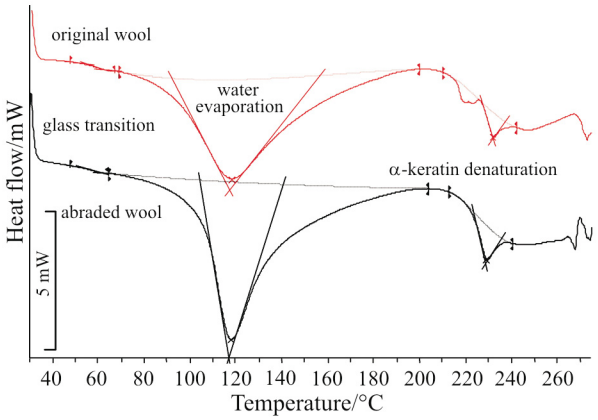

Fig. 3 DSC curves of Merino wool fibre and Merino abraded wool fibre

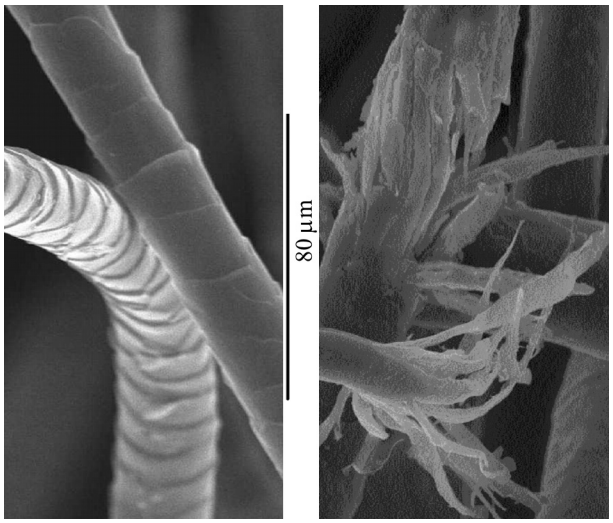

Fig. 4 SEM images of a – the original and b – the abraded Merino wool fibre

DSC

In order to identify the thermal transitions pointed out by the TMA a DSC curve of the wool yarn was made. The DSC curve of the original wool is shown in Fig. 3. It shows the T_g at 58.4°C thereafter a very prominent peak due to water removal with peak temperature at 117.9°C and evaporation enthalpy of 164.36 J g^{-1}. The peak evaporation amplitude at half peak height is 38.4°C. The DSC of the wool yarn shows a denaturation doublet with onset temperatures of 215.9 and 227.4°C and enthalpies of 4.01 and 3.89 J g^{-1}, respectively. The endset temperature of the denaturation processes is 236.1°C. The two transition temperatures observed on the TMA curve at 0.3 MPa are close to the onset temperatures of the denaturation doublet shown by DSC (Table 1), although the effect of the periodical stress induced by the TMA on wool yarns speeds up the first DSC transition from 215.9 to 210.5°C. No effect of the periodical stress is observed in the second transition. The relationship between enthalpies of the second doublet and the whole denaturation doublet are very similar to the relationship between the modulus at 220 and 200°C obtained by TMA (Table 2), which helps the hypothesis that the two thermal transitions observed by TMA at 0.3 MPa corresponds to the denaturation doublet observed by DSC.

Results on abraded fibres

The effect of the abrasion is shown by the photograph obtained by SEM at the end of the manuscript (Fig. 4). Owing to abrasion the fibre cuticle was destroyed and the cortex was fibrillated in the majority of the fibres. Consequently the external surface of the fibre was considerably increased. No TMA trials were possible to be performed with the abraded fibres.

TG

The onset temperature at which the thermal degradation of keratin and other hystological components begins is 232.21°C for the abraded wool samples. Up to 190°C the mass loss due to water evaporation was 9.12% (Fig. 2b). Owing to the removal of the external hydrophobic cuticle and to the increase in the external surface due to fibrillation by abrasion, the abraded wool absorbs more water than the original wool.

DSC

The DSC curve of the abraded wool sample of approximately 6 mg is presented in Fig. 3. The DSC curve shows the T_g at 56.6°C. Thereafter, a very prominent peak due to water removal with peak tem-

perature of 117.6°C is shown. The evaporation enthalpy is 195.88 J g^{-1}. The result is in accordance with the water content of the original and abraded fibre determined by TG. The amount of water absorbed by the abraded fibre is 20% higher than that absorbed by the original wool. Likewise, the water absorbed by the abraded fibre seems to be more strongly linked to the fibre than the water absorbed by the original fibre if the onset temperature of water evaporation (92°C for the original and 104°C for the abraded) is taken into account. The peak evaporation amplitude at half peak height is 23.2°C for the abraded wool fibre.

The DSC of abraded fibre shows a single denaturation peak with onset temperature of 223.5°C and 8.23 J g^{-1} of enthalpy. The endset temperature of the denaturation process is 235.1°C.

Considering that the abraded wool fibres showed fibrillated cells but a single denaturation peak with onset temperature 4°C lower than the onset temperature of the second denaturation doublet of the original wool, it seems reasonable to set up that abrasion has mainly removed the weaker cell units, those whose denaturation are produced when the first doublet appears.

Conclusions

The application of the different thermal analysis to original and abraded wool fibres allow us to draw the following conclusions:

- TMA: Two transition temperatures are observed in both warp and weft yarns, which is consistent with the onset temperatures of the denaturation doublet of original fibre observed by DSC. The contribution of the stress applied by TMA speeds up the first transition, decreasing its temperature by 5°C.
- The two transitions correspond to the denaturation of two fractions of cells that could be identified with the *ortho*-cortex and the *para*-cortex of the fibre. The relationship between denaturation peak enthalpies should be related to the paracortex fraction of the fibre. The same relationship is maintained when the storage modulus of the whole fibre (at 200°C) and the storage modulus of the fibre after the first transition (at 220°C) are compared.
- TG: The water absorption of the abraded fibre is 20% higher than the original fibre probably due to the increase in the external surface of the fibre. The thermal degradation of keratin and other histological components of the wool dried fibre take place at temperatures exceeding 232°C.
- DSC: The glass transition temperature of the original and the abraded fibre are practically the same. The enthalpy of water evaporation of the abraded fibre agrees with the amount of water absorbed determined by TG. The abraded fibre absorbs near 20% more water, which is more strongly linked to the fibre. The denaturation doublet observed in original wool fibre is transformed into a single denaturation peak in abraded fibre, with the onset temperature closer to that of the second denaturation peak of the doublet, although the whole denaturation enthalpy remains practically the same. The endset temperatures of the denaturation process are practically the same for both original and abraded wool fibres. The abrasion removes the component which denaturates at lower temperature. SEM photographs of original and abraded wool fibres reveal that abrasion removes the wool fibre cuticle and fibrillates the fibres increasing their external contact surface. After abrasion fibrillated cells are clearly observed.

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References

1 J. W. S. Hearle, J. Appl. Polym. Sci.: Appl. Polym. Simp., 47 (1991) 1.
2 J. Cao and H. Y. Bhoyro, Text. Res. J., 71 (2001) 63.
3 H. R. Peters, Textile Chemistry, Vol. I: The Chemistry of Fibres, Elsevier, Amsterdam 1963, pp. 269–277.
4 F. J. Wortmann and H. Deutz, J. Appl. Polym. Sci., 68 (1998) 1991.
5 J. Cao, K. Joko and J. R. Cook, Text. Res. J., 67 (1997) 117.
6 A. R. Haly and J. W. Snaith, Text. Res. J., 37 (1967) 898.
7 J. S. Crigthon and E. R. Hole, Proceedings of the 7th International Wool Textile Research Conference, Tokyo 1985, p. 283.
8 British Standard 5690-1979 Method 'Test for Determination of the abrasion resistance of fabrics'.
9 A. M. Manich, M. D. de Castellar, R. M. Saurí, R. A. L. Miguel and A. Barella, Text. Res. J., 71, 6 (2001) 469.

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