Thermal Analysis of Merino Wool Fibres without Internal Lipids

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Received 18 May 2006; accepted 3 August 2006
DOI 10.1002/app.25586
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Merino wool is made up of cuticle and cortical cells held together by the cell membrane complex (CMC), which contains a small amount of internal lipids (IWL) (1.5% by mass). IWL have been extracted from wool on account of their considerable dermatological interest owing to their proportion of ceramides. IWL have been extracted by different methods and solvents, methanol and acetone at laboratory and pilot plant levels. Thermal analysis of these extracted wool fibers is presented using thermogravimetry (TG) and differential scanning calorimetry (DSC). TG provides a measurement of the weight loss of the sample as a function of time and temperature. DSC gives information about possible structure modification of extracted wool fibers. Thermoporometry was applied to evaluate the pore size distribution of extracted wool fibers. The results showed that the extraction process increased the pore size distribution and the cumulated pore volume, which is consistent with some changes in the extracted wool CMC. Extracted fiber becomes more hydrophilic and absorbs a large amount of water. We can conclude that the lipid extraction of wool produced no relevant changes in the crystalline fraction when extracted with acetone. However, part of the amorphous keratin material was extracted with methanol, the rest of the crystalline material becoming more stable. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 545–551, 2007

Key words: internal wool lipids (IWL); differential scanning calorimetry (DSC); thermogravimetry analysis (TG)

INTRODUCTION

Wool is not exclusively a keratin protein; it also has an external lipid content (lanolin) and a small amount of specific internal wool lipids (IWL)(1.5%). These IWL arouse considerable interest because of their high ceramide content. In fact, IWL are rich in cholesterol, free fatty acids and ceramides, with smaller amounts of cholesteryl sulfate. They resemble membranes of other keratinic tissues such as human hair or stratum corneum from skin.[1,2]

This particular composition results in a highly ordered arrangement of lipids known as lamellar lipid bilayers. The intercellular lipids of the stratum corneum, especially the ceramides, play an important role in the barrier function of the human skin, preventing penetration of external agents and controlling the transepidermal water loss to maintain the physiological skin water content.[3,4]

In fact, the IWL composition, similar to ones present in the stratum corneum,[1,5] has been shown to be capable of forming liposomes with a stable bilayer structure.[6–8] Furthermore, it has been demonstrated that the topical application of IWL liposomes on intact and disturbed skins improves barrier skin properties.[9,10] Accordingly, IWL could be regarded as a new natural extract suitable for topical application and for incorporation into pharmaceutical or cosmetic formulations in the treatment and care of skin.

IWL have been extracted at laboratory and pilot plant levels using two organic solvents such as acetone and methanol. Analyses of wool extracts have been performed by TLC-FID, and chemical and mechanical evaluation of extracted wool has been carried out to determine residual grease, whiteness index, fiber diameter, fiber length, cleaning tests, alkaline solubility, bundle tenacity and drafting forces. Larger amounts of ceramides have been obtained when wool fibers were extracted with methanol versus acetone (0.20% of ceramides o.w.w. after a methanol extraction; 0.14% of ceramides o.w.w. by an acetone extraction). However, the improvement gained in the chemical and physical characteristics of the acetone extracted fibers is noteworthy. The superior fiber length obtained with a low alkaline solubility made this acetone extraction procedure the best option to facilitate further textile processing of the fibers extracted.[11]

Other mechanical and chemical parameters from extracted wool have been determined—residual grease, whiteness and yellowness indexes, fiber diameter, cleaning tests, alkaline solubility, abrasion resistance,

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pilling tests, and pore size—with the aim of obtaining more information about the industrial feasibility of these treated wools. The main difference observed is the high abrasion resistance in the case of the methanol extracted wool.[12] These results are related to the fact that CMC modification due to solvent extraction can increase the abrasion resistance of the fibers.[13]

Additional analyses of the extracted fibers have been performed. Parameters such as yield, fibril and matrix viscoelastic behavior, deformation work and breaking elongation have highlighted the effect of IWL on the fiber mechanical properties. An extraction of IWL has increased yield tenacity and decreased the elongation at break of the fibers, maintaining the feasibility of extracted wool for textile purposes.[14] We sought to optimize the specific processing operation without upsetting the balance of the protein-lipid domains of the composite structure of wool.

DSC is a method commonly used to determine crystallinity in polymers and involves measuring the melting enthalpy. Wool fibers have been studied by this technique in several papers.[15–19] There are currently difficulties in accurately measuring the melting transition of wool owing to the fibrous nature of the sample, (for exemple the level of cystine content could has influence in DSC analysis[19]), and to the moisture sensibility of the thermal transitions.[20] The differences in DSC parameters can be related to differences in the matrix material, that is the nonhelical parts of the intermediate filaments (IFs), the material between the IFs, and all other amorphous, morphological components.[19]

A number of researchers have studied the melting peak of α-form crystallites in merino wool. Some analyses of wool have been performed in an excess of water,[17–20] others in the absence of water,[16,20] and Cao et al. have used oil as a thermal medium.[15,21]

For Merino wool the endotherm is often bimodal. Wortmann and Deutz confirmed that ortho-cortical cells have a lower melting point than *para*-cortical cells,[18] which could account for the bimodal peak. Cao et al.[15] have investigated the origin of this bimodal endotherm and have presented an alternative interpretation, in which the bimodal peak arises from the overlapping of the melting endotherm of α-form crystallites with the thermal degradation of other histological components.

The aim of this work was to gain further insight into the extracted wool. Our study was performed using two thermal analysis methods: differential scanning calorimetry (DSC) and thermogravimetry (TG). The research was focused on the changes in the wool structure when IWL were extracted to better understand the bimodal endotherm peak behavior when other histological compounds were extracted from wool.

EXPERIMENTAL

Methods

Raw Spanish Merino wool samples supplied by SAIPEL (Terrassa, Spain) were used for solvent extraction. Wool was industrially cleaned in a process with five scouring becks for total degreasing. The cleaning sequence consisted of a washing at 35–40°C (1st beck), followed by a treatment with sodium carbonate at 40–45°C (2nd beck), sodium carbonate and ethoxylated nonylphenol at 50–58°C (3rd beck), ethoxylated nonylphenol at 50–52°C (4th beck), and a final rinsing with water at 45–47°C (5th beck). Finally, the wool was heat dried.

The extraction procedure consisted of a pump-forced reflow system. Wool samples (7 kg) were extracted and changed at 30 min, 1, 2, and 4 h and the 175 L of solvent (methanol or acetone) was maintained for 7.5 h. The extraction temperature was about 40°C for acetone extractions, and about 45°C for methanol extraction, in both cases being lower than the boiling points of both solvents. A kinetic control of both extraction processes was also carried out with different aliquots for analysis. Thereafter, solvents were distilled to obtain 11 L of lipidic extracts. Aliquots were dried and weighted, and lipid extraction percentages were determined.

The quantitative analysis of the internal wool lipids was performed by thin layer chromatography coupled to an automated ionisation detector as described in previous works.[5,22,23]

Differential Scanning Calorimetry (DSC) experiments were carried out without thermal medium, using two different pan preparations: one stainless steel pan (120 μL) was preheated at 200°C for 15 min to eliminate the possible tensions; before introducing the fiber sample into the pan and adding 50 μL of water during 6 days, water acts as a plasticizer; the other stainless steel pan (120 μL) had a lid with a hole, which permitted water evaporation. All investigations were conducted on a heat flux DSC instrument (DSC-821, Mettler Toledo). The heating rate used was 5°C/min, within a temperature range of 80–170°C in the preheated pan and 10°C/min, 25–275°C in the second preparation. The samples consisted of 6 mg short fiber snippets (~ 2 mm in length) cut from the different samples. Before the measurement, the samples were stored under standard room conditions (20°C, 65% HR) to ensure a constant water content.

As is well known, thermogravimetric analysis (TG) provides a measurement of the weight loss of a sample as a function of temperature, which enables us to reach the onset temperature of the thermal degradation of the fiber. All investigations were performed on a TG instrument (TG-50, Mettler Toledo). Samples consisted of short fiber snippets (~ 2 mm in

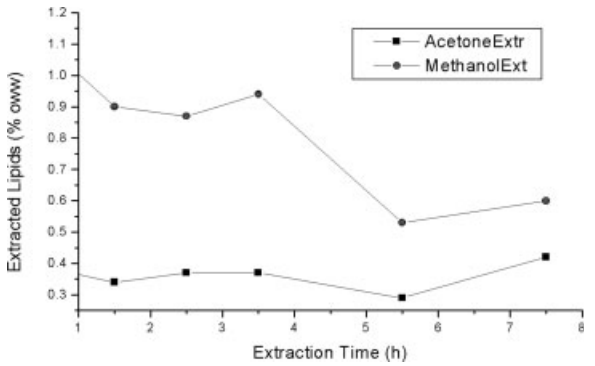

Figure 1 Kinetic graphic of the extraction of Spanish Merino wool with acetone or methanol. (Results of the lipid extracted are expressed in % on wool weight (% o.w.w)).

length) cut from the different parts of the wool samples. Around 6 mg of the sample were packed into a 70 μL TG pan. The heating rate used in this study was 10°C/min, within a temperature range of 25–300°C and a flow rate of nitrogen gas of 200 mL/min.

Thermoporometry is a thermal method based on the analysis of phase transformation of water confined in the pores of a material.[24] The surface areas obtained are very close to BET surface areas, which support the hypotheses which were made about the mechanism of fusion and solidification of a phase held inside a porous body. As far as an industrial or routine laboratory application is concerned, thermoporometry is a technique that is not very difficult to implement and that requires less time than the determination of a physical adsorption–desorption isotherm. This method can be applied to the determination of the area of materials whose pore radi are within the range 1.5–150 nm. Thermoporometry allows the determination of the surface area in the medium in which they are used, such as textile fibers in water. As these fibers swell, the BET surface area does not represent the surface area in the liquid medium, whereas thermoporometry does.[25]

Using the methodology described by Peronnet[26] and using a Mettler Toledo DSC, the pore size distributions were determined on raw wool. Changes in pore size distribution can be related to the effect of the lipid extractions. The samples were immersed in water for 1 h. After centrifugation at an angular speed to produce a radial acceleration of 1200 g for 15 min, the water was retained by the fiber including the water absorbed from the prevailing atmosphere, the water imbibed following immersion, and the moisture adhering to the fiber surfaces. Given that the imbibed water in the fiber is mainly located in the inner fiber pores, this kind of water was considered to be freezable pore water. The remaining water was considered to be extractable from the fiber by centrifugation. Samples of ~ 30 mg of centrifuged fiber were placed into a closed aluminum pan and then subjected to −20°C for 10 min to freeze the imbibed pore water. Subsequendly, the temperature was increased from −20 to 5°C at 0.5°C/min to melt the frozen pore water. The imbibed water of fibers was calculated by the centrifuge method[27] using two samples of 1 g and considering the variants on centrifugation time and speed described above. The fineness was measured by an Optical Microscopic Pyramid Axiophot ZEISS with a Digital Image System S.I. MIP 4.

RESULTS AND DISCUSSION

Raw Spanish merino wool was extracted at a pilot plant level to obtain lipid extract rich in ceramides, and the process was optimized: time of extraction and lipid saturation into the solvent were monitored with a kinetic control taking different aliquots in both extractions (Fig. 1).

As can be seen, percentages of lipid extracted using methanol (about 0.80% o.w.w) are higher than percentages using acetone (about 0.40% o.w.w); these results are consistent with a previous extraction procedure performed.[11] Bearing in mind that new wool is added at 30 min, 1.5 h, and 3.5 h with the same solvent, it can be observed that the solvent was enriched in the first 30 min; this behavior is more remarkable in the case of methanol where after 3.5 h of extraction the percentage of lipids becomes constant at 0.90% o.w.w. before undergoing a decrease of 0.60% o.w.w at the end of the process. With acetone, a constant amount of the lipid percentage obtained during the process (0.40% o.w.w) is observed. These results allow us to reduce the extraction time of further extractions of IWL.

The IWL composition of the final extracts was evaluated by TLC-FID following the methodology detailed in previous works.[5,22,23] A comparison between acetone and methanol extraction procedures can be seen in Figure 2.

According to the results shown in Figure 2, it seems that acetone has more affinity for the nonpo-

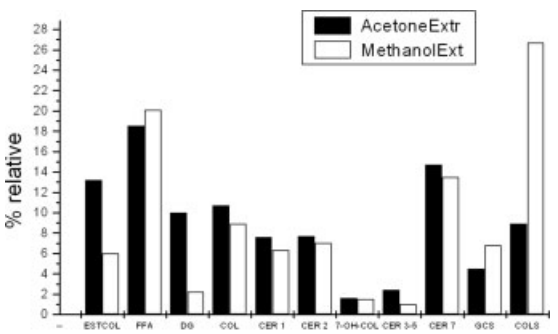

Figure 2 Detailed quantification of internal wool lipids of the final extracts obtained with acetone and methanol (expressed in % relative).

TABLE I
Relative Percentages of IWL After a Final Acetone or Methanol Wool Extraction

Extract	% o.w.w.	% lipids	% ceramides
Methanol	0.67	81.1	27.8
Acetone	0.32	91.5	32.5

lar compounds such as cholesterol ester (ColEst) and diglycerids (DG), whereas methanol has more affinity for polar compounds, in particular cholesterol sulfate (COLS). As regards the ceramide amount extracted, it seems that there is a slight increase in the case of acetone extraction (32.5% for acetone versus 27.8% for methanol), (Table I). The relative proportions of different ceramides are very similar in the two solvents, highlighting ceramide 7 (14%) and ceramide 1 and 2 (7% each).

A number of parameters were evaluated to determine the possible changes in the fibers at the mechanical and the chemical level after lipid extraction for comparison with nontreated raw wool: fiber diameter, whiteness index, residual grease, pilling rate, abrasion resistance, etc. The results obtained resemble those of the previous pilot plant study performed,[11,12] which confirms the feasibility of the extracted wool for further textile processing.

Some thermal analysis (TG and DSC) of the extracted wool fibers were performed. Thermogravimetry enables us to determine a value of the moisture loss of the fibers in addition to that obtained by conventional methods. The percentage of weight loss in the first step is due to the vaporization of water and the second step corresponds to the weight loss due to the decomposition of the protein fiber structure. In this case, a mixture of extracted wool at different extracted times was used.

The thermogravimetric results obtained are indicated in Table II. As can be seen, when IWL were extracted an increase in the water content took place, this effect being more accentuated with acetone extraction. Therefore, it seems that the lipid extraction favored the water absorption by wool fibers.

DSC commonly used to determine crystallinity in polymers involves the measurement of the enthalpy of melting. DSC curves present three thermal events: glass transition, water evaporation and denaturation. The first T_g observed, which normally ranges from

TABLE II
G Values and Relative Humidity for Extracted Wools

Wool	TGA (% step)	H_R (%)	Thermal degradation T_{onset} (°C)
Non-extracted	7.961	10.888	238.7
Mixture methanol-extracted	8.711	11.581	234.01
Mixture acetone-extracted	9.809	12.028	233.1

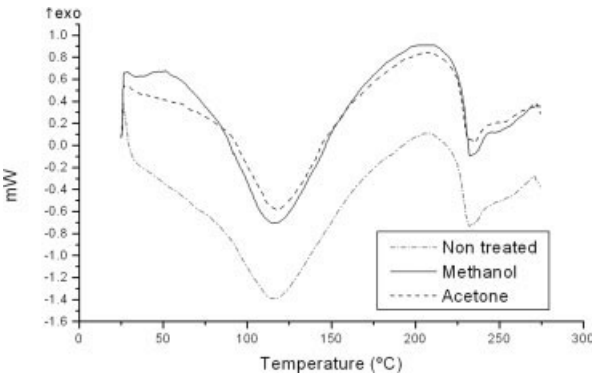

Figure 3 DSC curve for nontreated, methanol extracted 4 h, and acetone 4 h wool samples with perforated pan.

40 to 60°C (approx.) showing the glass transition, is difficult to be identified because the overlapping with the beginning of the big peak corresponding to water evaporation. This peak (T_W, ΔH_W) appears at around 120°C and is assigned to the evaporation water content of the sample. The peak, which is associated with the denaturation of the sample, appears around 230°C. This peak corresponds to the denaturation of the helicoidal material. Peaks are characterized by the peak temperature (T_D) and the area of the peak ($\Delta H_{D,}$ or denaturation enthalpy) (Fig. 3).

A DSC technique was used to study the influence of the absence of IWL on the extracted wool fibers. Two methodologies were employed to determine this influence: one with pans containing water, where the melting point of α-crystallites decreased to about 130°C. This phenomenon is explained by Flory's theory,[15] which suggests that the water molecules in wool interact with the polypeptide when the crystallites melt, and the result is this lower melting point, (Fig. 4); and the other with perforated pans, which permit the appearance of two peaks, one cor-

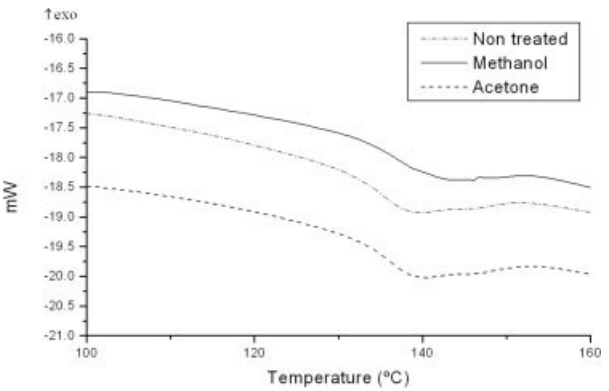

Figure 4 DSC curves for wool extracted by acetone for 4 h, methanol 4 h, and nontreated with prehot pan and water.

TABLE III
DSC Values for Wool Extracted by Methanol or Acetone at Pilot Plan Level

	Pre-hot pan + 50 μL water		Perforated pan			
Wool snippets	ΔH_D (J/g)	T_D (°C)	ΔH_W (J/g)	T_W (°C)	ΔH_D (J/g)	T_D (°C)
Non-extracted	11.69	138.49	74.72	116.68	11.16	231.59
Methanol ½ h	9.52	140.59	110.31	118.90	11.79	232.16
Methanol 4 h	10.95	141.37	234.77	115.92	13.92	232.32
Acetone ½ h	13.60	138.35	135.34	120.41	13.67	230.34
Acetone 4 h	12.55	138.12	179.74	119.44	14.07	231.34

responding to water evaporation (120°C), and the other to the denaturation (230°C) (Fig. 3).

Table III shows, in the case of the perforated pans, the amount of water present in the different samples (ΔH_W). The results indicate that there is a larger amount of water in the extracted wools than in the nonextracted wool as in the TG study. This effect is more marked when the extraction time is longer. When evaporation temperature (T_W) increases, the water interactions in the fiber are stronger; this is the situation for the acetone extracted wool: when IWL are extracted, the wool fibers absorb more water and the interactions between them are more consistent.

With the two types of pan preparations, the second peak was considered as the only one to calculate the melting enthalpy, but in Figure 3, it is possible to observe a certain bimodal peak. When IWL are extracted with acetone, the denaturation enthalpies (ΔH_D) are higher than the ones without extraction, although the temperature (T_D) is similar. Thus, it can be deduced that acetone extracts only IWL, without affecting the α-crystalline structure of the keratin.

In the case of methanol extraction, a different behavior was observed. The denaturation temperature T_D of the extracted fibers was slightly increased and ΔH_D was slightly decreased. This suggests that the methanol process alters the fiber structure in some way. The decreased ΔH_D could mean that methanol extracts part of the amorphous α-form keratin, whereas the high temperature could mean that the rest of crystalline material was more stable than that of the nonextracted wool. This phenomenon could be related to the high abrasion resistance obtained for these samples.[12]

The endothermic melting of α-form crystallines in wool keratin often appears to be bimodal. J. Cao proposed two interpretations to account for the origin of the bimodal endotherm[20]: first, this could be attributed to the differential melting of the α-form crystallines in the domains of ortho- and para-cortical cells, and second, it could be due to the overlapping of the melting endotherm of α-form crystallines and the thermal degradation of other wool histological components such as CMC. In the present work, weakly marked endotherms were obtained in all the samples studied with small enthalpy differences. Therefore, it seems that our results may lend support to the melting endotherm corresponding to the differential melting behavior of the α-form crystallines in the domains of ortho- and para-cortical cells as affirmed by Wortmann and Deutz[17,18] and by the results of Manich et al.[28]

The last part of our study was focused on the determination of pore size of treated wools to analyze the possible pore modification due to lipid extraction. The technique used was thermoporometry, which is based on the determination of the melting temperature of imbibed water for different pore sizes. Figure 5 and Table IV show the results obtained concerning fineness and pore volume for the raw wool, and extracted wools at 30 min and at 4 h with the two solvents.

It can be observed in Table IV that when IWL were extracted, the fibers imbibed an increased amount of water. This behavior was more pronounced with the extraction time, and the fineness of the extracted fibers remained unaltered. This behavior could be related to the high value of enthalpies from water evaporation (ΔH_W) obtained from the DSC curves when the lipids were extracted. Moreover, the TG values obtained seem to follow the same trend. All these results confirm the increase in water absorption when fibers are free of the hydrophobic domain constituted by internal lipids.

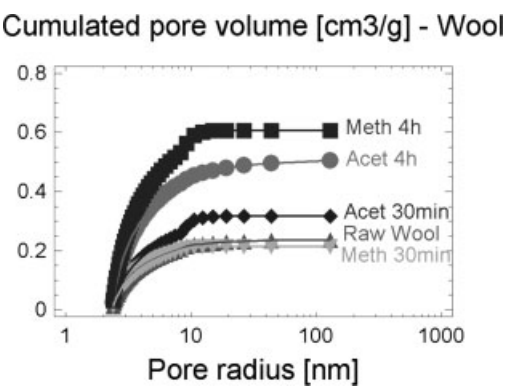

Figure 5 Graphic representation of cumulated pore volume of raw and lipid extracted wool fibers.

TABLE IV
Values of Fineness and Imbibed Water of Wool Fibres

	Non-extracted	Methanol ½ h	Methanol 4 h	Acetone ½ h	Acetone 4 h
Fineness (μm)	22.9	23.2	22.9	23.5	23.3
% Imbibed water	39.43	40.01	42.68	39.86	41.53

The intercellular lipids of the stratum corneum of human skin play an important role in maintaining a physiological transepidermical water loss gradient and in the movement of water molecules from inside to outside the skin. Likewise, when the IWL are extracted from the fibers, water molecules are more able to penetrate and to be absorbed in the protein structure of the fiber deprived of its lipid domain.

Figure 5 shows that the cumulated pore volume reaches a maximum of around 10 nm of pore radius for all samples, which suggests that the extraction process did not alter the pore size (around 10 nm of radius). However, when the fiber was extracted the amount of cumulated pore volumes detected increased (0.5cm^3/g for acetone extraction and 0.6 cm^3/g for methanol extraction versus 0.2 cm^3/g of nonextracted wool). These results indicate that there is an extraction of material from the Cell Membrane Complex of wool.

CONCLUSIONS

The solvent extraction conditions used in this work enable us to obtain yields of internal wool lipid extracts between 0.80% o.w.w in the case of methanol and 0.40% o.w.w with acetone. However, given that the solvent was suitably enriched in lipids, the extraction process can be reduced to 30 min for the same sample. As regards the evaluation of fiber modification due to internal wool lipid extraction, it may be concluded that the internal wool lipid extraction with non chlorinated solvents permits the re-use of the fibers in the subsequent textile process, and yields a by-product (IWL) with a high economic value in the cosmetic field.

In the absence of IWL, the extracted wool fibers absorbed more water. In the case of acetone extraction, a stronger bonding or interaction with the fiber may result. This behavior was demonstrated by the TG study and the DSC analysis with a perforated pan, where the amount of water increases when the extraction time is longer. Moreover, the cumulated pore volume of the extracted wool fibers increased, indicating that extraction of material from the Cell Membrane Complex occurred. As the hydrophobic material was extracted, the fiber became more hydrophilic.

The DSC curves show a small bimodal endotherm in both situations: non treated and extracted wools. Consequently, it seems that the bimodal peak of merino wool is not due to the overlapping between the melting endotherm of α-crystallites and the thermal degradation endotherm of other histological compounds such as internal lipids in wool. It may be concluded that the lipid extraction of wool produced no relevant changes in the crystalline fraction when extracted with acetone. However, part of the amorphous keratin material was extracted with methanol, the rest of crystalline material becoming more stable.

The authors are grateful to the technical support given by Mr. J. Carilla, Ms. A. López, and Mr. G. von Knorring. Thanks are also due to SAIPEL for supplying raw wool.

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