

Characterization of Secondary Structure Transformation of Stretched and Slenderized Wool Fibers with FTIR Spectra

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ABSTRACT

Characterizations of wool fibers were performed with FTIR testing technology for two categories of stretched wool fibers, i.e., the OPTIM™-Fine wool, and the stretched wool processed on TJGD-ERDOS 02 stretching equipment, developed at College of Textile Engineering, Tianjin Polytechnic University, Tianjin, China. It was observed that the two types of stretched wool fibers could be characterized by the IR transmittance peaks at $1620 \sim 1630 \text{ cm}^{-1}$ and $1510 \sim 1520 \text{ cm}^{-1}$. It was evidenced that upon stretching the secondary structure of the wool fibers transformed from alpha helix, the typical secondary structure of raw wool, to beta pleated sheet, the typical secondary structure of native silk, which was supported by the change in cross-sectional morphology and stress-strain curve.

INTRODUCTION

Fine wool fibers are highly desirable in wool textile industry due to soft hand, silk-like luster and touch, high tenacity and light weight yarn/fabric, which can be achieved by several ways such as chemical treatment, enzymatic treatment,^{1, 2} and mechanical stretching etc.^{3, 4, 14, 17 - 21} Both enzymatic treatments and chemical treatments would damage wool fibers

while imparting increased fineness by scale stripping, generating significant weight reduction and strength loss during the processing, though the former is environmentally friendly, and the latter is not. However, mechanical stretching technology may avoid fiber damage, generating light-weight yarns and fabrics in an environmentally friendly way, and it has been globally commercialized under the brand name of OPTIM™, initially created by CSIRO, Australia in 1992.^{3,4}

OPTIM™ technology/products are sold globally in two brands.^{3,4} OPTIM™ Fine fibers are stretched by 40-50% and then chemically permanently set to produce light weight yarns, yielding finer fibers of 3-3.5 microns reduced in diameter; OPTIM™ Max is designed to develop bulky yarns to generate a warmer end-product with reduced weight and modified insulating property. The fibers are 20-30% stretched, temporarily set, and then blended with normal wool to form bulky yarn/fabric upon relaxation/retraction of the stretched wool in hot water or steam.

Slenderized fibers from the mechanical stretching technology create novel wool fibers, and the changes

in wool property are highly associated with secondary structure transformation, which have been characterized⁵⁻¹³ by the well-established modern testing techniques, such as X-ray diffraction, infrared spectroscopy, Raman spectroscopy, differential scanning calorimetry. The evidences from these historical studies strongly support the view that the super molecular structure of wool fiber is transformed from alpha helix to beta form after stretching treatment, combined with pre-reduction treatment and post-oxidization treatment.

This study is focused on the characterization of stretched wool fibers with FTIR spectrogram, coupled with the change in secondary structure of wool fibers. The stretched wool fibers are from two sources: the OPTIM™ Fine wool supplied by a Japanese company, the stretched and permanently set wool produced on TJGD-ERDOS 02 stretching equipment, invented by the researchers at Tianjin Polytechnic University, Tianjin, P. R. China.

EXPERIMENT

The 66^s, 70^s and 80^s wool tops were subjected to stretching on the TJGD-ERDOS 02 stretching equipment respectively, permanently set with

chemical reagent and then tested on the FTIR spectrograph (Victor 22, Byukey), with raw 70^s wool as control, and the OPTIM™ Fine wool from Japan as bench mark. The apparatus used in this study for wool stretching is illustrated in *Figure 1*, with different stretching ratios used at the 6 stretching zones respectively.

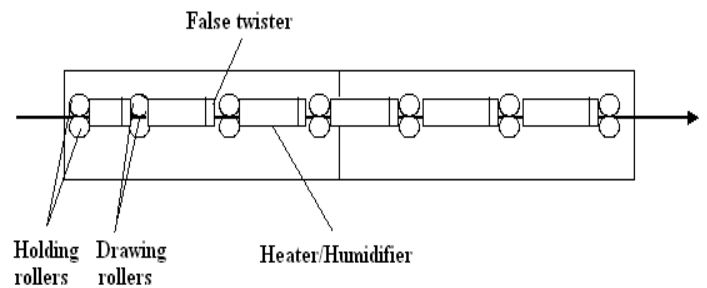


FIGURE 1. Illustration of TJGD-ERDOS-02 stretching equipment

The stretched wool fibers were produced based on the processing flow chart in *Figure 2*, where the fibers in wool top were stretched at wet conditions in the treating chambers.

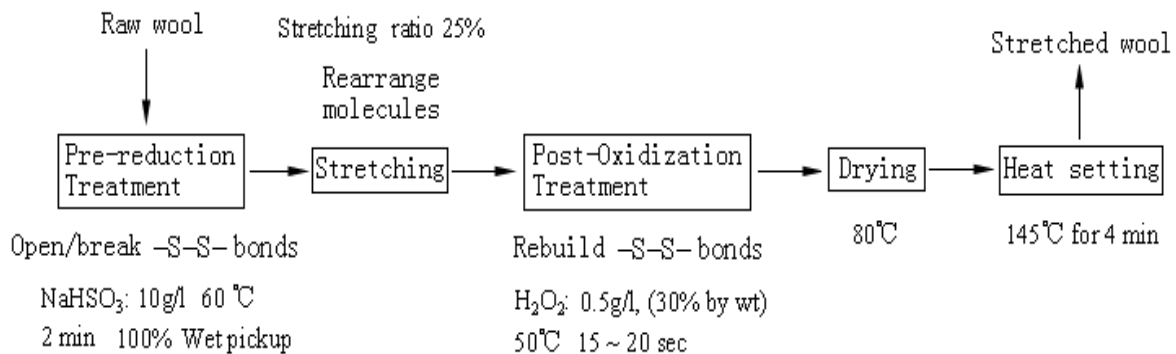


FIGURE 2. Processing flow chart for wool stretching on TJGD-ERDOS 02

The whole wool stretching treatment performed on the equipment of TJGD-ERDOS 2 was a process of reduction – mechanical stretching – oxidization, which could be described as:

Wool top → **Reduction** with NaHSO_3 → **Stretching** → Washing at tension → **Oxidization** with H_2O_2 at tension → Washing at relaxation → drying.

The reducing agent NaHSO_3 was used to break or detach the –S–S– bonds in wool structure, and thus to favor the wool fiber stretching and deformation. The similar reducing agent pre-treatment method was also used in the processing of commercial OPTIM-Fine fibers. The oxidization treatment was used to favor the reduced –S–S– bonds to rebuild new –S–S– bonds at new positions.

RESULTS AND ANALYSIS

Secondary structure and transformation

Primary structure of protein is sequence of a chain composed of 20 amino acids; secondary structure occurs when the sequence of amino acids are linked by hydrogen bonds. The regular configurations of protein macromolecules generally exist in three types, i.e., alpha helix, beta pleated sheet and beta turn. The principal structural units in the native wool fiber are successive turns of the alpha helix. The intrinsic stability of the alpha helix, and thus the fiber, results from intramolecular hydrogen bonds.

At the presence of mechanical tension and moist heat, wool can be stretched to a more extended beta form, indicating the potential of wool stretching and slenderizing. Upon stress relaxation in steam, the polypeptide chains recover to the less-extended alpha helical coil; the fiber and thus fabric shrinks, suggesting the importance of post setting treatment. Pretreatment may facilitate the extension of the alpha helical coil into beta sheet upon stretching. The

disulfide bridges, H-bonds, electrovalent bonds, etc., in wool fiber, form the hindrance to the movement of the molecular segments, and thus to the secondary structure transformation. The pretreatment, with reductant as major reagent, was expected to cleave off most of the crosslinks among wool macromolecules, providing the prerequisite condition for slenderized wool production with stretching technology. Polypeptide chains of silk have a very stable beta-pleated sheet structure, fully extended along the axis of the fiber. The alpha structure and beta structure are comparatively shown in *Figure 3*.

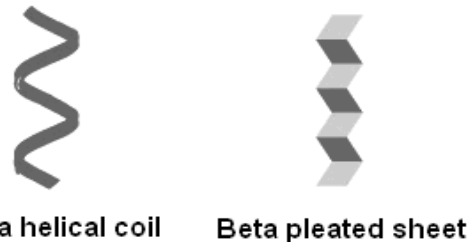


FIGURE 3. (Revised after Ref. 30)

An alpha helix is a tightly coiled, rod-like structure which has an average of 3.6 amino acids per turn²⁴ (*Figure 4*). The beta pleated sheet (*Figure 5*) is composed of two or straighter chains that are hydrogen bonded side by side; it may be formed from a single chain if it contains a beta turn, which forms a hairpin loop structure. The main component of wool fiber is hard keratin, having more contents of residual group of cystine. Both low-sulfur protein and high-sulfur protein exist in wool fiber, which play a key role in determining super-molecular structure of wool fiber.¹⁴ It is believed that in the low-sulfur protein of raw wool fibers, about 50% molecules exhibit α -helix structure in microfibrils, and the other 50% molecules exhibit the form of irregular coils. Most molecules exist in matrix as irregular coil in the

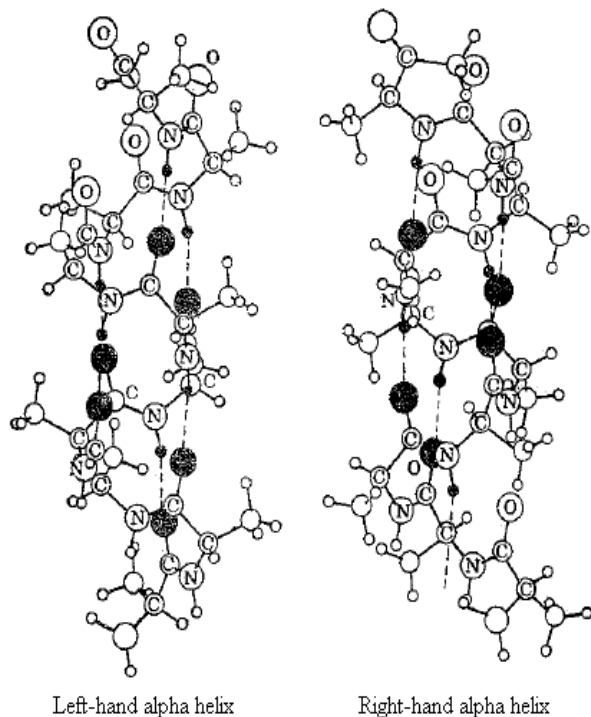


FIGURE 4. Alpha helix in secondary structure of wool (Ref. 15)

high-sulfur protein, and disulfide bonds linked low-sulfur protein molecules to high-sulfur protein molecules, therefore protofibrils in wool fiber are coupled with the matrix via S-S bonds. Moreover, there are interactions such as electrovalent bond, hydrogen bond, Van der Waals force, hydrophobic bond etc., among the protein molecules, which are sensitive to influence from water, exhibiting relatively high wet-heat plasticity.

Characteristics of FTIR spectroscopy of stretched wool fiber

All the wool samples, including the raw wool, stretched wool processed from TJGD-ERDOS 02 stretching equipment, and the OPTIM™ Fine wool from Japan were tested on FTIR spectrograph (Victor 22, Byukey) for the observation of the change in characteristic peaks. The sample powders were used for the FTIR tests and the characteristic spectra were

scanned in the wave number range of $4000\text{ cm}^{-1} \sim 500\text{ cm}^{-1}$ using KBr pellets.

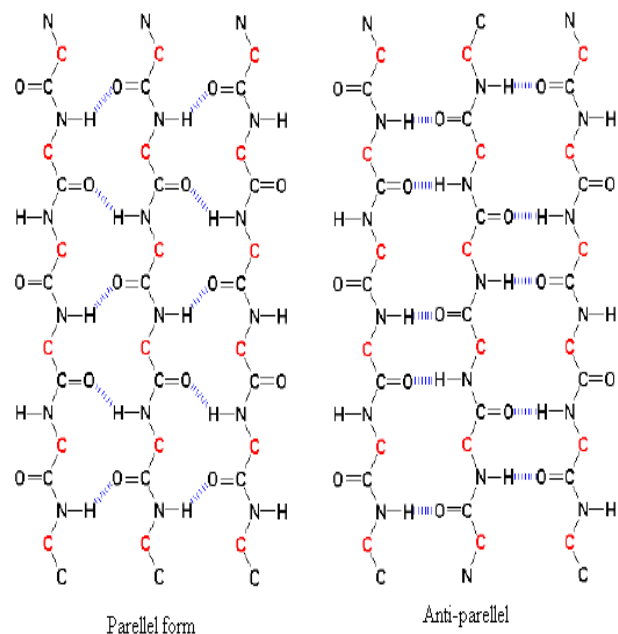


FIGURE 5. Beta-sheet in secondary structure of wool (Ref. 29)

Figure 6 depicts the IR spectra of raw wool and stretched wool, where the absorbency peak at $1620 \sim 1630\text{ cm}^{-1}$ is assigned to the elastic vibration peak of C=O bond, and the peak at $1510 \sim 1520\text{ cm}^{-1}$ is labeled as the bending deformation peak of C-N-H bond¹⁶, the peak positions of the two bonds shifted to lower wave-number positions in the stretched wool fibers compared to untreated wool fiber, which may be taken as a typical feature of the IR spectra of stretched wool.

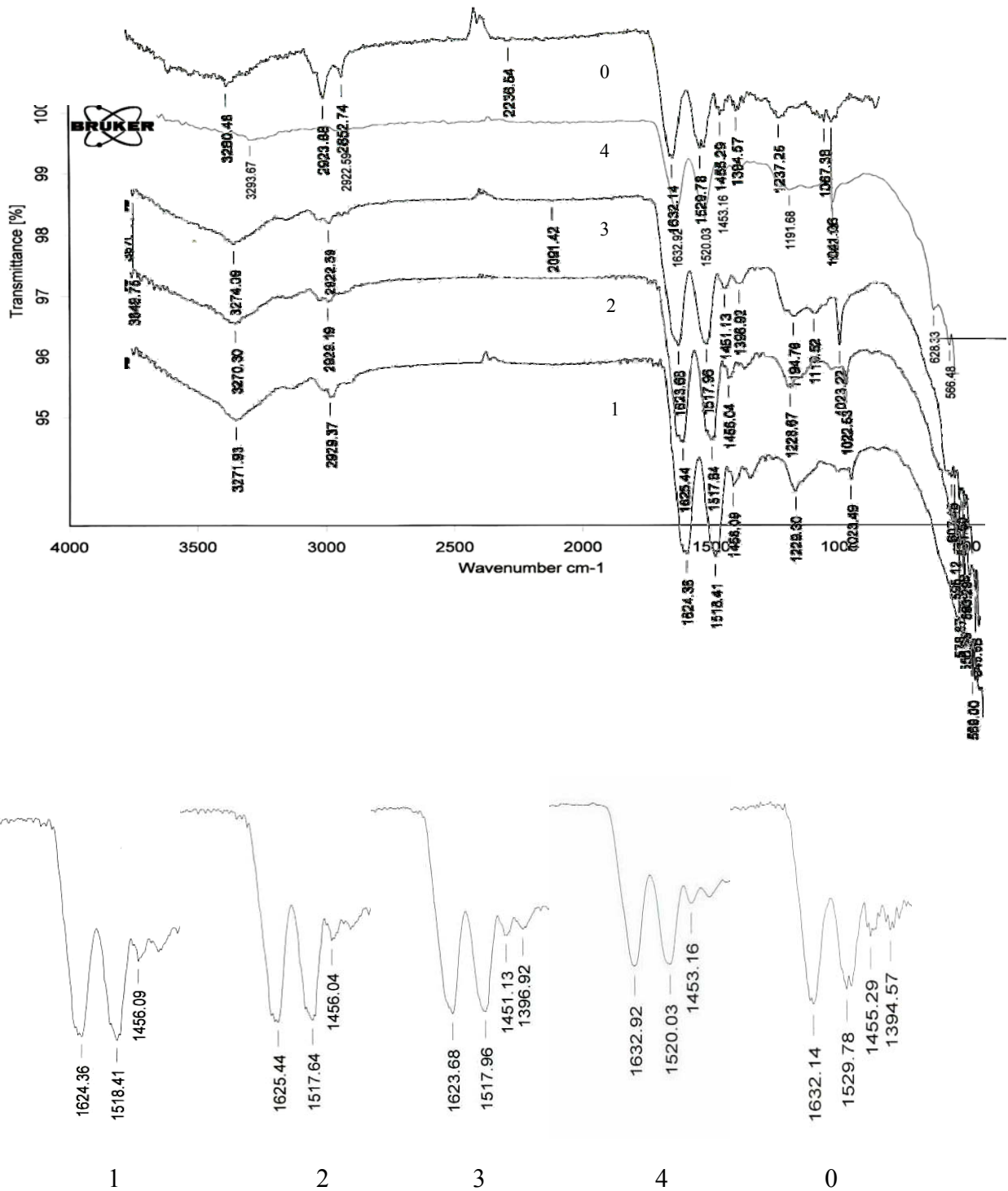


FIGURE 6. FTIR spectra of stretched wool against native wool: 0 — 70° raw wool; 1 — OPTIM™ Fine fiber from Japan; 2 — Stretched and permanently set 70° wool; 3 — Stretched and permanently set 66° wool; 4 — Pretreated, stretched and permanently set 66° wool.

The difference in peak intensity of the two characteristic peaks at $1510 \sim 1520 \text{ cm}^{-1}$ and $1620 \sim 1630 \text{ cm}^{-1}$ tended to disappear in stretched wool fibers, as can be observed in a silk fiber, in addition to the peak location change; the peak intensity at $1510 \sim 1520 \text{ cm}^{-1}$ in the IR spectra of the stretched wool increased drastically, even exceeded the intensity of the elastic vibration peaks of C=O at $1620 \sim 1630 \text{ cm}^{-1}$, indicating that the amount of the groups exhibiting or participating in the C–N–H bending deformation increased significantly. In the raw wool fiber, there is significant difference in the two characteristic peaks; however, this difference is almost unnoticeable in the IR spectra of stretched wool fibers. Therefore, less or no difference between the two peaks in intensity suggests better quality of stretched wool (finer and longer fiber). It thus could be inferred that, during the process of wool stretching, the secondary structure of wool fiber transformed from α -form to β configuration, and the protein molecules in the amorphous region (matrix) also participated in this process and formed the regular beta sheet structure. It was accordingly expected that, the regularity of the super molecular structure in the stretched wool is greater than that in unstretched wool.

As shown in *Figure 6*, the stretched wool fiber (No. 2, 3 and 4) processed on TJGD–ERDOS 02 stretching equipment showed similar IR spectrum feature to that of OPTIMTM Fine fiber, while great difference exists in the peaks at $1510 \sim 1520 \text{ cm}^{-1}$ between the other two samples. The 4# sample was pretreated but not fully set, therefore the intramolecular H-bonds in this sample were not sufficiently established, and the change in peak location between the two peaks was slight. However, this still indicated the increase in the regularity inside the fiber, due to the increase in the peak intensity at 1520 cm^{-1} caused by the secondary structure transformation from coiled alpha structure to pleated beta sheet upon stretching treatment.

In other words, compared to the raw wool fibers, the shapes of the characteristic peaks of the stretched wool fibers showed obvious change at the wave numbers of $1620 \sim 1630 \text{ cm}^{-1}$ and $1510 \sim 1520 \text{ cm}^{-1}$. In the IR spectrum of a raw wool fiber, there is greater difference between the peak intensity of the two foresaid peaks, while the peak intensities of the two peaks in the FTIR spectrum of a stretched wool fiber tends to be equal. As we know, a typical IR spectrum of silk fibroin, which is featured with the secondary structure of β -pleated sheet, shows no significant difference in the peak intensity of the two peaks of the amide group, while the α -helix exhibits different features. It is thus possible to identify the stretched wool fibers by taking advantage of the rule of the change in the intensity of the two foresaid peaks in a FTIR spectrum of a wool fiber.

Change in tensile curve after wool stretching processing

The characteristics of the stretched wool might change as well compared to the native wool, due to the change in super molecular structure. The stress-strain curves of a stretched wool fiber processed from TJGD-ERDS-02 stretching equipment and a raw wool fiber are schematically shown in *Figure 7*, which exhibits three distinct, approximately linear regions: Hookean, yield, and post-yield.²⁵⁻²⁷

In the Hookean region oa, the stress increases linearly with the increase in the strain from 0 to approximately 2% extension²², suggesting an elastic deformation in crystal structure of microfibrils, i.e., the extension of the bonds and the deformation of the bond angles. Beyond 2% extension, the fiber begins to yield, and this continues to around 30% extension. In this yield region, the alpha helices begin to unfold, mainly as the result of cleavage of the intramolecular H-bonds and intermolecular disulfide bonds. At around 20-30% extension, the wool stretching

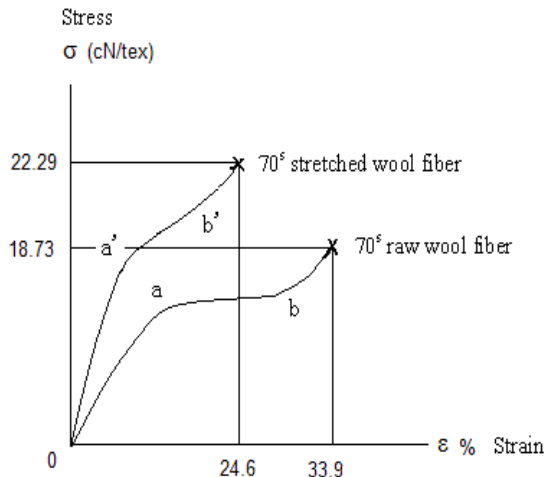


FIGURE 7. The schematic tensile curves of 70^s wool before and after stretching treatments: oa – Hookean region; ab – Yield region; bc: Post-yield region

reaches the post yield stage, where the stress in the fiber begins to increase rapidly with increase in fiber strain, indicating the re-establishment of the interactions among wool molecules. The alpha coils would fully extend to β strands at 70%-80% elongation. However, the β sheet would partially recover to α -helix when the external force is removed, if no measures are taken to set the structural arrangements.¹⁴⁻²³ Therefore, setting process is necessary to obtain permanently stretched wool fibers.

However, the Post-yield region in the tensile curve of the stretched wool is not obvious, compared to that of the native wool. After stretching and setting, most of alpha helix structure in wool fibers already transformed into beta pleated sheet and fixed, therefore the tensile capacity of the stretched-set wool decreased and it is hard to re-establish new crosslinks among the wool molecules in the post yield stage; the stretched wool fiber come to failure mainly due to the slippage of the molecular segments.

The tensile test results of the raw and stretched wool

fiber on the equipment of TJGD-GRDOS 2 and OPTIM Fine fiber were summarized in *Table I* for comparison.

It appeared that the stretched wool fibers showed higher tenacity but lower elongation at break, indicating the wool molecules tended to arrange in a regular way so that the tenacity of the whole fiber was increased, and thus the elongation capacity was decreased. The tenacity of the stretched wool fiber produced on the equipment of TJGD-GRDOS 2 was close to that of the commercialized stretched wool fiber OPTIM Fine.

TABLE I. Tensile strength comparison of different wool fibers

Sample ID	Elongation % @ break	Tenacity (cN/tex)
OPTIM FINE	19.3	23.69
70 ^s raw wool	33.9	18.73
70 ^s stretched wool	24.6	22.29
80 ^s raw wool	41.4	20.27
80 ^s stretched wool	26.2	25.59

Fiber tensile property test: YG001A Single fiber electronic tensile tester, specimen number 100, initial tensile force 300 mg, tensile test speed 12 mm/min.

Change in wool morphology after stretching and slenderization

The slenderized wool fibers after stretching exhibit irregular non-round cross-sectional configuration (*Figure 8*), responsible for the silk-like sheen and luster caused by the enhanced light refraction effect; the slenderization occurred after stretching was the direct consequence of the transformation of secondary structure from alpha coil to beta strand.

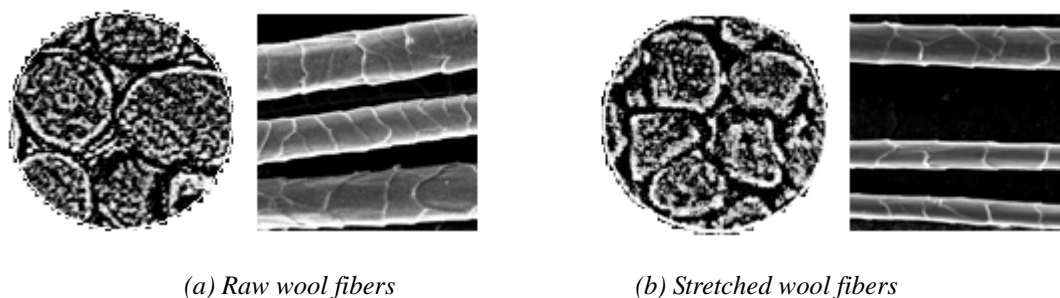


FIGURE 8. Microscope photos showing change in fiber morphology after stretching & slenderization

In fact, a wool fiber would be slenderized after stretching process, and the diameter of the stretched wool fiber would be reduced by 10-15% or so, while the stretched wool fiber would gain length of 20-35%, which is due to the extension of the natural crimp of the wool fiber, and the contribution from the reduction in diameter. The diameter values of the raw and stretched wool fibers are summarized in *Table II*.

TABLE II. Change in the size of wool fiber before and after stretching process

Sample ID	Ave. diameter/ μm	Stdev/ μm	CV/%
66 ^S Raw wool	20.77	4.68	24.24
66 ^S Stretched wool	17.56	4.26	22.53
70 ^S Raw wool	19.31	4.12	21.32
70 ^S Raw wool	17.27	3.95	22.78

Diameter test: Projection microscope method, specimen number 500.

CONCLUSION

FTIR spectroscopy has been used in this study to characterize stretched wool fibers in terms of secondary structure transformation. The two absorbency peaks of C–N–H bond and C=O bond occurred at lower wave number positions in stretched wool fibers compared to the unstretched wool fiber,

suggesting the transformation of secondary structure from alpha form to beta conformation. This feature could be used to differentiate stretched wool from native wool, and less difference in peak intensity between the C–N–H bond at $1510 \sim 1520 \text{ cm}^{-1}$ and the C=O bond at $1620 \sim 1630 \text{ cm}^{-1}$ means better processing quality of stretched wool. No difference occurred in super molecular structure between the stretched wool obtained on TJGD–ERDOS 02 stretching equipment and the OPTIMTM Fine wool from Japan, based on the analysis on the FTIR spectra of the two fibers. The Post-yield stage in the stress-strain curve of the stretched wool fiber is not obvious compared to the raw wool fiber, and the cross-section of the stretched wool turned to silk-like irregular configuration.

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