

Study of the Structure Transformation of Wool Fibers with Raman Spectroscopy

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ABSTRACT: Raman spectroscopy and tensile tests were used to investigate the structure transformation of stretched wool fibers with stretching ratios up to 110%. The typical bands analyzed in this article included the amide I region, the amide III region, the C—C skeletal vibration region, and the S—S and C—S bond vibration region. To investigate the variations of the crystallinity and orientation of the wool fibers, the density and birefringence of the fibers were also measured. The results showed that the secondary structure of the wool fibers was transformed from an α -helical structure to a β -pleated-sheet structure during the early stage of stretching. When the fiber was stretched more than 80%, the mechanism of stretching mainly relied on the slippage of

the peptides. Meanwhile, the pretreatment of the wool fibers with sodium bisulfite and the setting processing resulted in the reduction of the concentration of the S—S bonds. The results for the density and birefringence showed that the degree of crystallinity of the wool fibers decreased, whereas the degree of orientation increased during the stretching. The tensile behavior of the stretched wool also supported the $\alpha \rightarrow \beta$ microstructure transformation. The diameter results showed that the extent of slenderness was about 25.3% when the stretching ratio was 80%. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1–7, 2007

Key words: fibers; microstructure; Raman spectroscopy

INTRODUCTION

With the improvement of the standard of living, the demand for light-weight and comfortable fabrics increases quickly. However, wool fibers coarser than 21 μm in diameter are difficult to process into fine yarns to provide desirable lighter and softer characteristics. To achieve these features, artificial stretching slenderization for ordinary wool has been an alternative strategy for many fiber producers.^{1,2} To facilitate the application of this technique, it is necessary to understand the mechanism of the microstructure transformation of wool fibers during stretching to avoid serious damage to fibers and to improve the efficiency of slenderization.

Several well-established techniques have been used to analyze the structure transformation of wool fibers, including X-ray diffraction,^{3–6} infrared spectroscopy,^{7,8} Raman spectroscopy,^{9,10} and differential scanning calorimetry.¹¹ This evidence strongly supports the view that stretching results in the structure transformation of wool fibers from an α -keratin crystalline structure to a predominantly β -keratin crystalline structure. Church et al.¹⁰ analyzed the conformational changes of the peptide backbone of sodium bisulfite treated wool fibers during stretching by Fourier transform Raman

spectroscopy. They found that the transition from an α -helical structure to a β -pleated-sheet structure was most rapid during the early stages of stretching, and this conformational change mainly took place in the cortical cells. However, the maximum stretching ratio of the wool fibers in their experiments was 66%, which was too low to completely reveal the structure transformation of the wool during stretching.

The aim of this study was to explore the microstructure transformation of wool fibers after stretching by means of Raman spectroscopy and tensile testing methods. The maximum stretching ratio of the wool fibers was 110% in these experiments. To investigate the variations of the crystallinity and orientation of the wool fibers, the density and birefringence of the fibers were also measured. In addition, the diameters of the unstretched wool and the stretched wool were measured to show the extent of slenderization.

EXPERIMENTAL

Materials

The experiment was performed with Merino wool top (Shanghai Sanmao Enterprise Group Co., Ltd., Shanghai, China) with an average fiber diameter of 22.9 μm . The wool top was first pretreated in a sodium bisulfite solution with a concentration of 3% for 2 min to break some of the disulfide crosslinks in wool fibers and then stretched 30, 50, 80, and 110% longer than its original length in a 75°C steaming chamber with a laboratory

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stretching apparatus developed by us. After that, the stretched samples were set with two different setting agents for 2 and 3 min, respectively. Finally, the samples were rinsed three times with distilled water and baked at 140°C for 3 min in an oven. Thus, the stretched wool fibers were obtained.

For the further analysis of the fiber structure, all five samples, that is, the one unstretched wool fiber and the four stretched wool fibers, were rinsed with petroleum ether and ethanol before Raman spectroscopy analysis, density measurements, birefringence measurements, and tensile tests.

Experiments

A confocal Raman microscope with a 50× objective lens (Labram, DILOR/Instruments S.A.) was used for the acquisition of the Raman spectra. The excitation source was a He-Ne laser (632.8 nm) with a power of 6 mW; the laser beam was depolarized. Raman spectra were obtained with a resolution of 1 cm⁻¹. A single wool fiber picked from the prepared samples was placed on a glass slide, and both ends of the fiber were fixed with adhesive tape in a low pretension (100 mg). The laser beam was focused to a spot 1.5 μm in diameter on the single fiber, and multiple scans (200 scans) for one Raman spectrum were performed. The wavenumber range of the spectroscopy was 400–1800 cm⁻¹. For each sample, five fibers were measured and then averaged into a typical spectrum.

To understand the variation of the wool behaviors and verify the structure transformation of the wool fibers from another aspect, tensile tests of the unstretched and stretched single fibers were also carried out. The tensile experiment was conducted at a temperature of 20 ± 2°C and a relative humidity of 65 ± 2% with a 10-mm gauge length and a 10 mm/min extension rate.

The density of the fiber was measured by a density-gradient tube technique with a mixture of dimethylbenzene and phenoxin under standard test conditions to investigate the variation of the crystallinity following the stretching processes. Therefore, the tensile strength (GPa) and tensile modulus (GPa) of the fiber could be obtained. The birefringence measurements were also conducted with a polarized light microscope to investigate the variation of the orientation.

In addition, the diameters of the corresponding wool fibers were also measured with an optical microscope to show the extent of slenderization.

RESULTS AND DISCUSSION

Fundamental characteristics of the Raman spectra of stretched wool

The Raman spectra of the wool fibers stretched 30, 50, 80, and 110% are compared to that of unstretched wool

in Figure 1. The meanings of the captions in the following figures are the same as those in Figure 1.

For wool fibers, Raman investigations have mainly focused on the amide I, amide III, and C—C skeletal modes. The absorption peak of the amide I mode consists of the carbonyl stretching vibration with small contributions from the C—N—H in-plane bending and the C—N stretching vibrations. The corresponding Raman spectrum of amide I appears from 1650 to 1680 cm⁻¹. The intense band component at 1652 cm⁻¹ can be attributed to an α-helical conformation. The 1671-cm⁻¹ component has been assigned to a β-pleated-sheet conformation. This band component would also include a contribution from segments of disordered peptides. The band component observed at 1695 cm⁻¹ has been assigned to the amide group of the asparagine and glutamine side chains. The vibration of the amide III mode consists of the C—N—H in-plane bending and the C—N stretching. The corresponding Raman spectrum of amide III appears from 1230 to 1300 cm⁻¹. The intense band component at 1240–1250 cm⁻¹ can be attributed to disordered peptides. The 1230–1240-cm⁻¹ component has been assigned to a β-pleated-sheet conformation. A very weak band at 1260–1300 cm⁻¹ can be attributed to an α-helical conformation. The C—C skeletal mode has been assigned to a skeletal stretching vibration and appears in the region from 890 to 960 cm⁻¹.¹² In addition, the peak near 1450 cm⁻¹ can be considered the standard peak because it is largely associated with the amino acid side chains and thus not affected by the peptide backbone conformation.⁹ In addition, the bands near 513 and 665 cm⁻¹ can be assigned to the S—S bond and C—S band, respectively. The Raman characteristic bands and the assignments in the region of 400–1800 cm⁻¹ are shown in Table I.^{11,12} Each characteristic band of the wool fibers is illustrated in Figure 1.

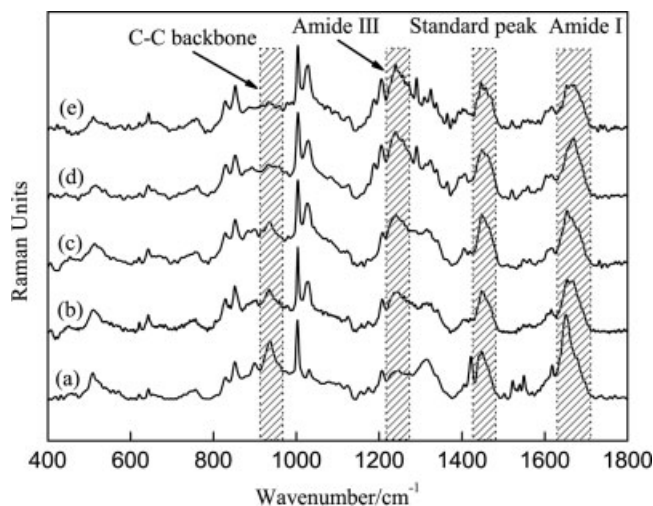


Figure 1 Raman spectra of wool fibers with different ratios: (a) 0, (b) 30, (c) 50, (d) 80, and (e) 110%.

TABLE I
Raman Characteristic Bands and Their Assignments

Band	Band position (cm^{-1})	Band assignment
Amide I	~ 1671	β -Pleated sheet + disordered
	~ 1652	α -Helix
	~ 1695	CONH_2
Amide III	1260–1300	α -Helix
	1240–1250	Disordered
	1230–1240	β -Pleated sheet
C—C skeletal	890–945	α -Helix
Others	~ 513	S—S
	~ 665	C—S

Transformation of the secondary structure

The Raman spectroscopy regions of amide I and amide III are particularly sensitive to changes in the protein secondary structure. In particular, the band shift depends on the microstructure transformation from an α -helix to a β -sheet. The amide I bands of the Raman spectra have been picked out correspondingly and are magnified in Figure 2.

It can be found through the comparison of these bands representing different stretching ratios that there are significant variations in the band shape, including the height of the peak and the peak position. According to Figure 2(a), the amide I peak for the unstretched fibers is located at 1652 cm^{-1} , whereas the peak of the wool fibers stretched 80% in Figure 2(d) shifts to 1672 cm^{-1} . It seems that the peak height of 1672 cm^{-1} rises whereas the peak at 1652 cm^{-1} falls down gradually with the increasing stretching ratio. The more the wool fiber is stretched, the higher the peak frequency is, and the broader the peak is. Because the peak at 1652 cm^{-1}

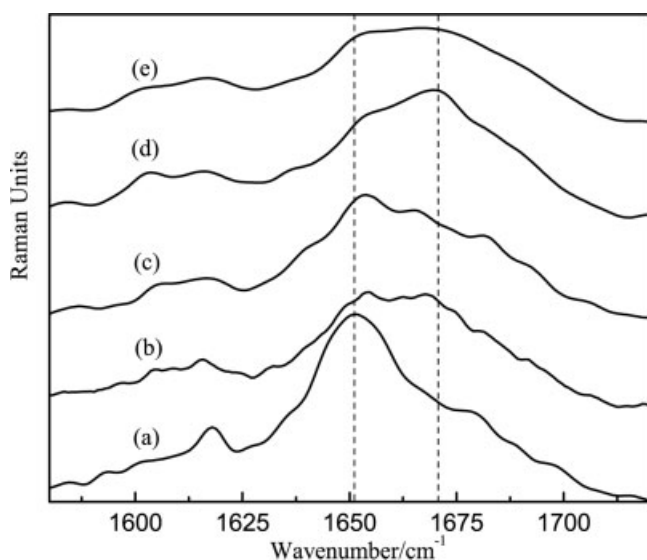


Figure 2 Comparison of the amide I region: (a) 0, (b) 30, (c) 50, (d) 80, and (e) 110%.

is characterized as the α -helical structure and the peak at 1671 cm^{-1} is assigned to the β -pleated-sheet conformation, the results in Figure 2 show that the stretching makes the secondary structure of the wool fibers transform from an α -helical conformation to a β -pleated-sheet conformation.

The characteristic bands of amide III in the range of $1200\text{--}1340 \text{ cm}^{-1}$ of Raman spectra can also indicate the transformation of the secondary structure, as the series of Raman spectra shows in Figure 3, which has been recorded from Figure 1 for the analysis of the various stretched wool fibers.

The peak near 1240 cm^{-1} for the unstretched wool fiber is not distinct, whereas those of the stretched wool fibers are relatively noticeable, and the intensity of the peak rises with the increase in the stretching ratio. The microstructure of the β -pleated sheet can be distinguished by the intensity of the amide III region at $1235 \pm 5 \text{ cm}^{-1}$ of the Raman spectrum.¹³ The results show that the β -pleated-sheet conformation of wool macromolecules is formed when the fibers are stretched 30%. This can be proved by the results of Church et al.¹⁰ Furthermore, there are no characteristic peaks for the α -helical conformation in the amide III region. In addition, the stretched wool produces a new band at 1290 cm^{-1} , which suddenly increases when the stretching ratio exceeds 80%. No previous assignment for this band in wool at related proteins has been reported, and the nature of the species responsible is at present unclear.

The Raman spectra for the C—C backbone vibration in the molecular chain of wool fibers are illustrated in Figure 4. The intensity of the band near 935 cm^{-1} , which is contributed to the α -helical conformation, decreases quickly after the wool fiber is stretched, and

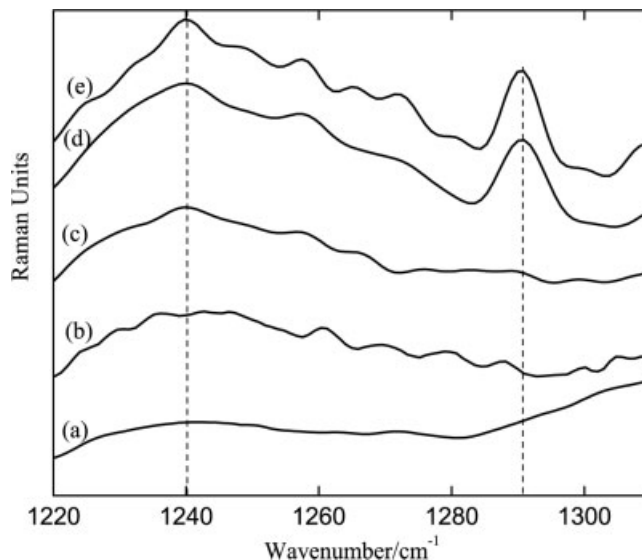


Figure 3 Comparison of the amide III region: (a) 0, (b) 30, (c) 50, (d) 80, and (e) 110%.

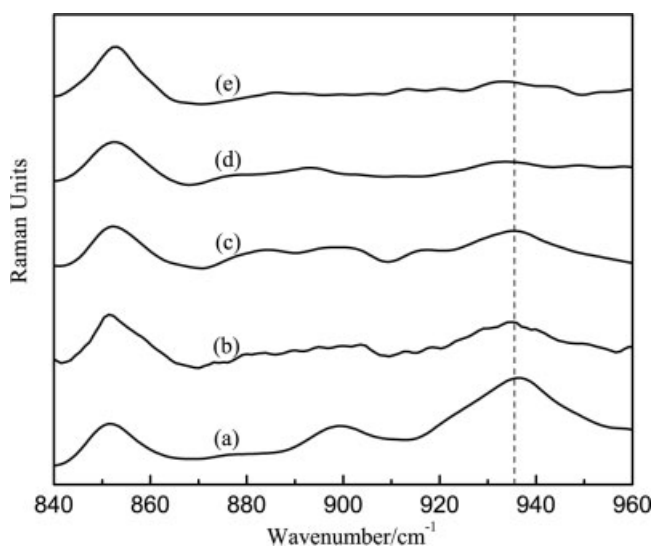


Figure 4 Comparison of the backbone vibration region: (a) 0, (b) 30, (c) 50, (d) 80, and (e) 110%.

the peak almost disappears when the fiber is stretched over 80%.

The quantitative transformation can be calculated by the curve-fitting method. The deconvolutions of the amide I region for the unstretched wool and the wool fibers stretched 110% are shown in Figure 5. The amide I regions of the spectra obtained from the remaining members of the series of stretched wool samples were analyzed in a similar manner.

Therefore, quantitative results for the five fibers were obtained. A plot of the amide I peak area as a function of the stretching ratio is shown in Figure 6. α denotes the conformation corresponding to the 1651 cm^{-1} band, and β denotes the conformation corresponding to the 1671 cm^{-1} band. The total area of the

microstructures is also shown in the figure. In addition, the densities of the wool fibers are also shown in the figure.

Significant shape changes in the complex peak area of amide I can be observed because of the peak change occurring at both the α -helical conformation and the β -sheet conformation. The peak area of the β -conformation increases gradually with the stretching ratio. However, the peak area of the α -conformation decreases with the stretching ratio. When the stretching ratio is more than 80%, both the peak area of the α -helical conformation and that of the β -sheet conformation almost remain constant. Moreover, the variation of the total area of the microstructure can be divided into two stages, that is, the decreasing stage followed by the constant stage. This result indicates that the main mechanism of stretching the wool fiber is the secondary structure transformation from α -helix to β -sheet. In addition, some of the α -helical conformations have been transformed to other conformations, including the disordered structure, which causes the reduction of the total area. However, the secondary structure transformation is almost finished when the stretching ratio reaches 80%. Therefore, the further stretching does not affect the contents of the α -helical conformation and the β -sheet conformation markedly. Because almost all the α -helical conformations have been transformed to the β -sheet conformations, the slippage between the peptides will be the main mechanism of microstructure transformation.

The results for the densities also support this point of view. Figure 6 shows that the variation of the wool density is similar to that of the total area of the microstructures. The density of the wool fiber decreases with the stretching ratio when the stretching ratio is lower than 80%. The density of the wool fiber stretched 80%

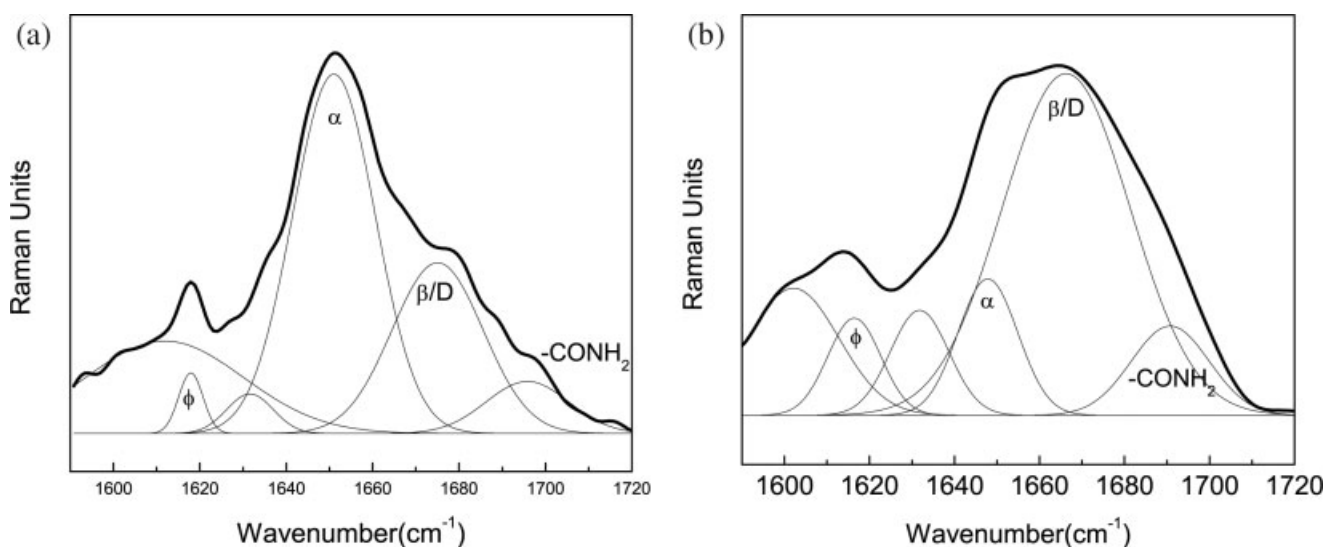


Figure 5 Deconvolution of the amide I region of the Raman spectra of the wool fibers: (a) unstretched wool and (b) wool fibers stretched to 110%.

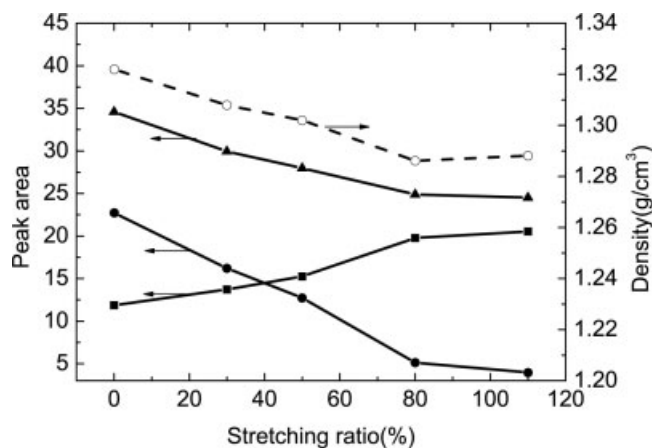


Figure 6 Plot of the peak area as a function of the stretching ratio: (■) α , (●) β , and (▲) $\alpha + \beta$.

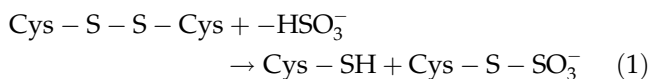
decreases 2.71% with respect to that of unstretched wool. However, the density of the wool fiber stretched 110% does not have pronounced variation from that of the wool fiber stretched 80%. Because of the positive correlation of the density and the degree of crystallinity of the fiber, the stretching makes the degree of crystallinity of the wool fiber decrease at low stretching ratios. At higher stretching ratios, the stretching does not affect the degree of crystallinity significantly.

According to the results, the main mechanism of stretching wool fibers can be divided into two processes. During the first stretching process, that is, with a stretching ratio lower than 80%, the stretching mechanism is mainly dependent on the secondary structure transformation from an α -helical structure to a β -pleated-sheet structure. When the fiber is stretched longer than 80% in the second process, the mechanism of the wool fibers may dominantly rely on the slippage between the peptides.

Characterization of the disulfide bonds

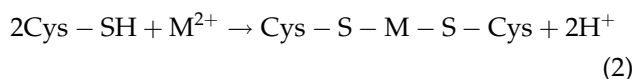
The cystine S—S bond plays an important role in the tertiary intermolecular structure of keratin. The peak near 513 cm^{-1} is assigned to the S—S bond, and the peak near 665 cm^{-1} stands for the cysteine C—S bond. The characteristic bands are shown in Figure 7, which illustrates two peaks of unstretched and stretched wool with various stretched ratios. The cystine S—S (near 513 cm^{-1}) band gradually decreases in intensity with an increasing stretching ratio, but the peak near 665 cm^{-1} for the C—S band is not noticeable. This means that the concentration of cystine S—S bonds in the stretched wool fiber is lower than that of the unstretched wool fiber. However, the concentration of C—S bonds in the stretched wool fiber does not change obviously. This may contribute to structural rearrangement as a result of partial disulfide bond rupture.

These disulfide crosslinks can form both between different peptide chains and within a single chain. The treatment of wool fibers with sodium bisulfite results in the cleavage of disulfide bonds and forms cysteine residues according to the following formula:



The breakage of disulfide has a significant effect on the mechanical properties of the wool fiber, which are expected to be highly dependent on the number and distribution of disulfide crosslinks.¹⁴ The cleavage of the disulfide bonds allows for more mobility both within and between the peptide chains, and thus the fiber can be stretched more easily.

After the stretching process, the wool fibers were set for the dimensional stabilization of the stretched fibers. The setting process can be expressed as the following formula:



It is evident from the formula that the metal ion M^{2+} has been introduced into the disulfide crosslinks during the setting process. Consequently, the number of disulfide bonds in the stretched wool fibers is lower than that of unstretched wool fibers. This is one of reasons that the intensity of the cystine S—S band at 509 cm^{-1} decreases after the fiber is stretched, as shown in Figure 7. However, the measured Raman spectra show that the setting process does not change the concentration of C—S bonds in the fibers.

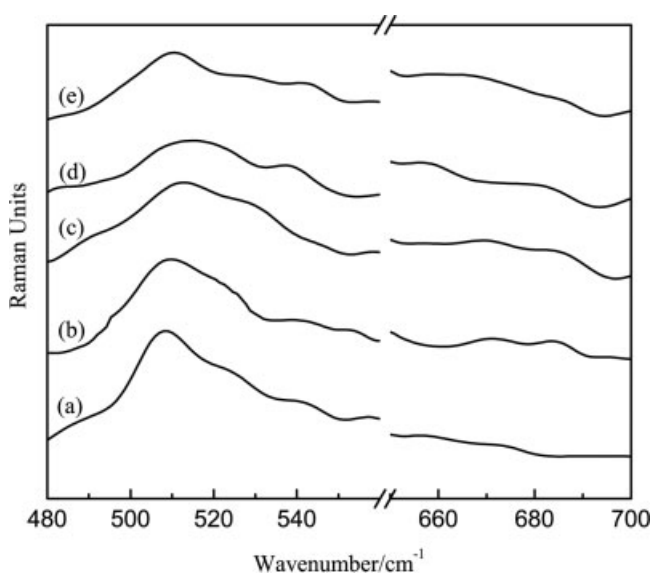


Figure 7 Comparison of the Raman spectra at $480\text{--}700 \text{ cm}^{-1}$: (a) 0, (b) 30, (c) 50, (d) 80, and (e) 110%.

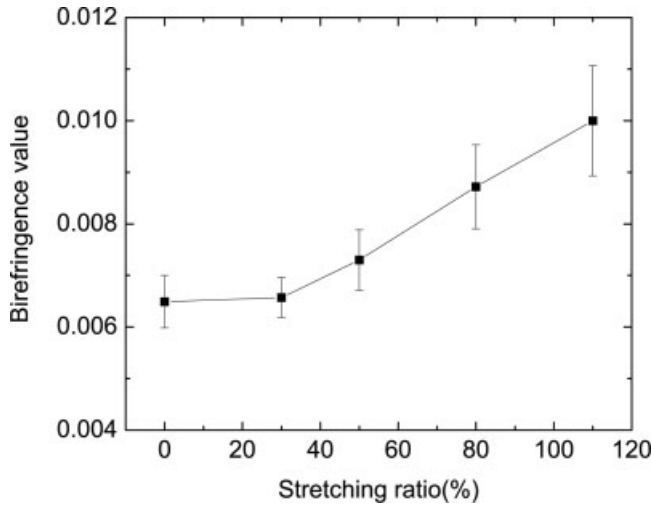


Figure 8 Birefringence as a function of the stretching ratio.

Variation of the degree of orientation

The variation of the birefringence value of the wool fiber is shown in Figure 8. The birefringence value of the wool fiber increases with the stretching ratio. The birefringence value of the wool fiber increases with the stretching ratio. The birefringence value of 30% stretched wool fiber is almost equal to that of unstretched wool. The birefringence value of 110% stretched wool fiber is 54.08% higher than that of unstretched wool. Because the birefringence value of the fiber is closely related to the degree of orientation, the stretching seems to increase the degree of orientation.

Tensile behaviors of the wool fiber

The typical tensile testing results for the wool fibers are shown in Figure 9 and Table II. For the unstretched

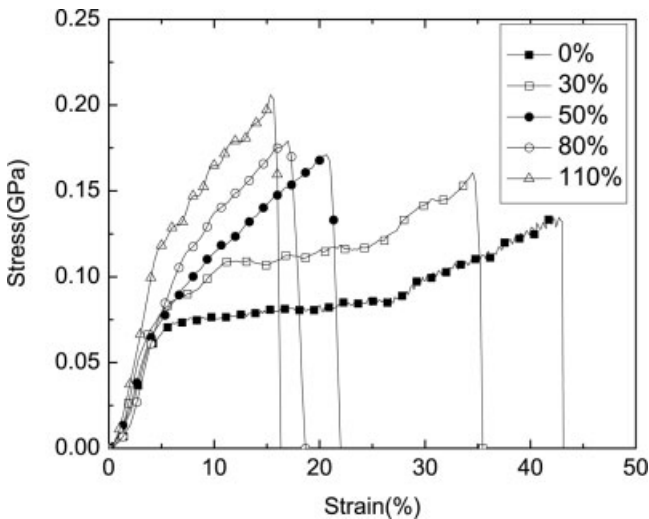


Figure 9 Stress-strain curves of stretched wool: (■) 0, (□) 30, (●) 50, (○) 80, and (△) 110%.

TABLE II
Tensile Behaviors of Unstretched and Stretched Wool Fibers

Stretching ratio (%)	Strength (GPa)	Modulus (GPa)	Elongation at break (%)
0	0.151 ± 0.037	2.88 ± 0.78	46.67 ± 4.52
30	0.161 ± 0.054	3.31 ± 1.20	34.53 ± 10.68
50	0.171 ± 0.056	3.63 ± 1.28	20.67 ± 7.53
80	0.179 ± 0.057	3.39 ± 1.31	17.00 ± 5.85
110	0.206 ± 0.066	4.51 ± 1.71	15.67 ± 4.30

wool, the stress-strain curve exhibits three distinct, approximately linear regions: Hookean, yield, and postyield. For 30% stretched wool, the stress-strain curve still exhibits three regions. For large stretching ratios, such as 50, 80, and 110%, the stress-strain curves can be divided only into two distinct regions, that is, Hookean and postyield regions, whereas the yield region disappears. The characteristics of the curve are similar to the tensile behavior of silk fibers, in which the secondary structure is mainly composed of β crystals. These results demonstrate further that there exists an $\alpha \rightarrow \beta$ transformation in wool stretching.

The tensile results in Figure 9 and Table II also show that the tensile behaviors of the stretched wool fibers depend strongly on the stretching ratio. With the increase in the stretching ratio, the strengths and modules of the wool fibers increase steadily, and this indicates that the stretching does not damage the wool fiber seriously. The average strength of 110% stretched wool fiber is 36.4% higher than that of unstretched wool. However, the elongations at break decrease with the stretching ratio because of the $\alpha \rightarrow \beta$ transformation. The average elongation at break of 110% stretched wool is only 15.67%, which is just 33.6% of that of unstretched wool. The $\alpha \rightarrow \beta$ transformation makes the α -helix concentration in the wool fiber decrease. There-

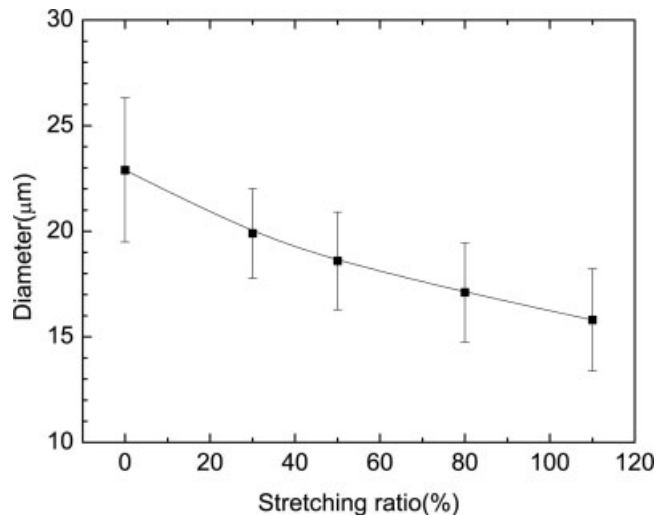


Figure 10 Diameter of stretched wool.

fore, the deformation ability of the stretched wool fiber decreases with the increase in the stretching ratio. As a result, the elongation at break of the stretched wool fiber decreases obviously.

Extent of slenderization

The diameter of stretched wool with various stretching ratios is shown in Figure 10. The results show that the diameter of the wool fiber decreases with the increase in the stretching ratio. When the stretching ratio is 80%, the average diameter of the fiber is 17.1 μm , which is 25.3% lower than that of the unstretched one (22.9 μm). The average diameter of 110% stretched wool is 15.8 μm , which is much finer than that of the original wool.

CONCLUSIONS

The microstructure of stretched wool fibers with a maximum stretching ratio of 110% has been studied with Raman spectroscopy and tensile tests. The characteristic bands of Raman spectra, used in the measurements, include the regions of amide I and amide III, the C—C skeletal vibration, and the S—S and C—S bond vibration. The density and birefringence of the fibers have also been measured to investigate the variations of the crystallinity and orientation of the wool fibers. In addition, the diameters of the unstretched wool and stretched wools have been measured to show the extent of slenderization.

The analysis of the amide I, amide III, and C—C vibration bands has revealed that the secondary structure of the wool fibers has been transformed from an α -helical structure to a β -pleated-sheet structure after stretching. The phenomenon has also been verified by the tensile test because the yield region of the stress-strain curve becomes small at stretching ratios from 0 to 50% and even disappears at larger than 50% stretching. This implies that the yield region corresponds to the transformation from α to β . Meanwhile, if the fiber

is stretched less than 80%, the stretching mechanism is mainly the secondary structure transformation. When the fiber is stretched more than 80%, the mechanism of stretching mainly relies on the slippage between the peptides. The variation of the density also supports the mechanism of stretching. The stretching decreases the degree of crystallinity of the wool fibers. The Raman spectra of the S—S and C—S vibration bands show that the setting process for recrosslinking cannot recover all the S—S bonds broken in the stretching pretreatment of the wool fibers with sodium bisulfite because of the effect of the metal ions, whereas the change in the C—S bonds is not significant in the stretched wool fibers.

The results of birefringence measurements show that the stretching tends to increase the degree of orientation. The diameter results show that the extent of slenderization is about 25.3% when the stretching ratio is 80%, and the diameter of wool decreases about 7 μm for a 110% stretching ratio.

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