Microstructural Transformation of Wool during Stretching with Tensile Curves

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ABSTRACT: The microstructural transformation of wool fiber during the stretching process was investigated by the tensile tests and TEM micrograph observation. The results showed that water breaks some of the hydrogen bonds in the fiber, whereas the sodium bisulfite solution breaks some of the disulphide crosslinks between the peptide molecules, then the wool fiber is easy to be stretched. Two types of transformations were found during the stretching process, that is, the slippage of molecule chains or micro-structural elements and the α→β transformation. The α→β transformation is dominant, in particular, during the low stretching rate process. In addition, the stretching slenderization tends to increase the tenacity of wool fiber and decrease its extension at break. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 816–822, 2007

Key words: stress–strain curves; wool fiber; microstructure transformation; slenderization

INTRODUCTION

Wool fibers coarser than 21 μm in average diameter are difficult to be processed into fine yarns, to provide desirable lightweight and comfortable softer fabrics. To achieve fine, soft, and lightweight features, artificial stretching slenderization of coarse wool has been an alternative strategy and the relevant techniques have been developed and employed.[1,2] However, to facilitate the application of this technique, it is necessary to understand the microstructure transformation mechanism of wool fibers during stretching so as to avoid fiber damage at large stretching rate (>80%) and to improve the efficiency of slenderization.

Previous studies[3–9] showed that the microstructure of wool fiber has transformed from an α-keratin crystalline structure to a predominantly β-keratin crystalline structure after stretching. However, for the case of large stretching rate, only the α-helix to β-pleated mechanism is not enough. As early as 1951, Pauling et al. [10] deduced the α-helical structure as the hydrogen-bonded conformations for the polypeptide chains in the wool fibers. The translation along the helical axis for one complete turn (3.7-residue) is 5.44 å and the value for one residue is 1.47 å. Pauling and Corey[11] also developed another secondary structure β-pleated sheet, and the vertical component of the axis of each residue is 3.07 å. Therefore, when the sec-

ondary structure of wool fiber is completely transformed from α-helix to β-pleated sheet, the maximum stretching rate is 109% longer than its original length. As a matter of fact, the practical stretching rate may be larger than 150%, which indicates that other mechanisms might occur during the stretching process. In our previous study,[12] the slippage between the molecules or microfibrils of the wool fibers was found by Raman spectroscopy. To further understand the mechanism, all information about the microstructure transformation during the stretching process should be recorded and analyzed. From this point of view, the tensile stress–strain curves might be useful.

It is well known that the mechanical properties of a fiber depend strongly upon its microstructure. On the contrary, the microstructure of a fiber can be characterized by its mechanical properties, including the tensile stress–strain curves. The aim of the present study was to explore the microstructure transformation during stretching of wool fibers by the tensile stress–strain curves.

EXPERIMENTAL

Stretching tests of wool fibers during slenderization

During the pretreatment processing, the wool fibers were first dipped in a sodium bisulfite solution to break some of the disulfide crosslinks in the wool fibers. Therefore, the process parameters, such as the concentration of sodium bisulfite, dipping time, and temperature, might influence the tensile behaviors of wool fibers in the sodium bisulfite solution. To analyze such effects, the Merino wool single fiber with an

average diameter of 22.9 μm (provided by Shanghai Sanmao Enterprise Co, Shanghai, P.R. China) was first clamped tightly with one pair of jaws, and then pretreated in an aqueous sodium bisulfite solution. The concentration of sodium bisulfite includes 1, 3, and 5%. The dipping time of wool fiber in the sodium bisulfite solution includes 10, 120, and 300 s. The temperature of the solution includes 30, 50, and 75°C. Then the fiber was stretched until its breakage. The load-extension curves of the single fibers were recorded and displayed simultaneously with a personal computer. The tensile experiment was conducted with a 10 mm gauge length and a 10 mm/min extension rate. The number of tensile test for each sample is 11. However, it is impossible to illustrate all of these curves in a figure. Therefore, the curve, which could represent the average properties of the samples, was selected and plotted in the figures.

To check the significance of the effect of pretreatment parameters on the tensile behaviors of wool fiber, the analysis of variance (ANOVA) was used. The one-way ANOVA can be divided into three steps as following:

1. The equality of variances which is one of the necessary conditions of ANOVA is tested using the Levene F method. If the F value is either very small or very large, we decided that the variances are unequal. Only when the variances are equal, the following tests can be continued.[13]
2. The fixed effects model is established. And the total variances were subdivided into the sum of squares within groups and the sum of squares between groups. Then the $F_{\text{statistics}}$ values can be calculated. The large value of F indicates that at least one of the terms in the regression equation has a significant correlation with the response variable.[14]
3. Multiple comparisons are further used to decide which groups are different. Many methods can perform the multiple comparisons, including LSD method, Bonferroni method, Tukey's method, S-N-K method, Scheffe method, Duncan method.[13,14] In this study, LSD method was used. If the simultaneous significance is larger than the level γ or the $100 \times (1-\gamma)\%$ confidence interval does not include zero, the null hypothesis that there is no difference between two groups may be rejected at level γ.

Tensile test of slenderized wool fibers

To investigate the effect of a stretching slenderization on the tensile behaviors of the slenderized wool fibers, the wool top was first pretreated in a sodium bisulfite solution with a concentration of 3% for 2 min and then stretched with various stretching rates,

including 30, 50, 80, and 110% in a 75°C steaming chamber. Then 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 slenderized wool fibers were obtained. The tensile tests of the wool fibers were conducted at a temperature of (20 ± 2)°C and a relative humidity of $(65 \pm 2)\%$ with a 10 mm gauge length and a 10 mm/min extension rate.

TEM observation

For TEM investigation, wool fibers were cut into smaller pieces (≈ 1 mm), washed three times in petroleum ether and ethanol, and then stained with 1% aqueous osmium tetroxide for 5 days, followed by 1% aqueous uranyl acetate, dehydrated, and embedded in Epoxy resin 812. The ultrathin sections (≈ 90 nm) were obtained with a diamond blade. The sections were picked up and examined in a HITACHI H-800 electron microscope operating at 175 kV.

RESULTS AND DISCUSSION

Stretching behavior of wool fibers in water and air

Figure 1 shows the stress–strain curves of single original wool fibers in water and air. A typical stress–strain curve of wool fiber exhibits three distinct, approximately linear regions, that is, Hookean, yield, and postyield. In the Hookean region, the stress occurs linearly with a rapid rise in the strain from 0 to about 5%. Beyond 5% extension, the fiber begins to yield, and this continues to around 30%. This process of yielding requires only a very small amount of additional stress. In this region, it has been considered that the α-helices begin to unfold and transform into
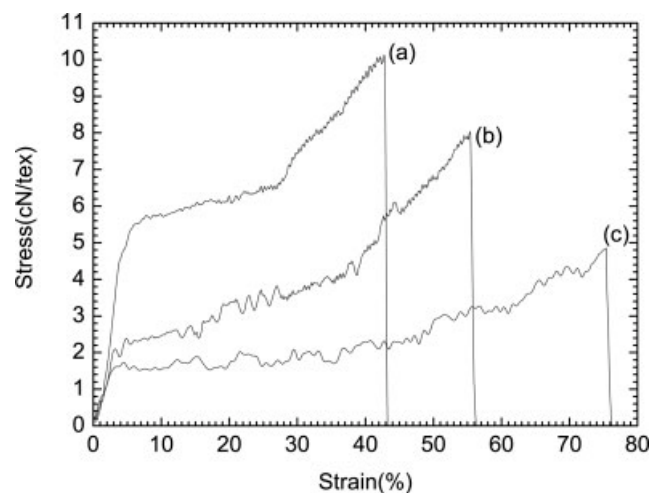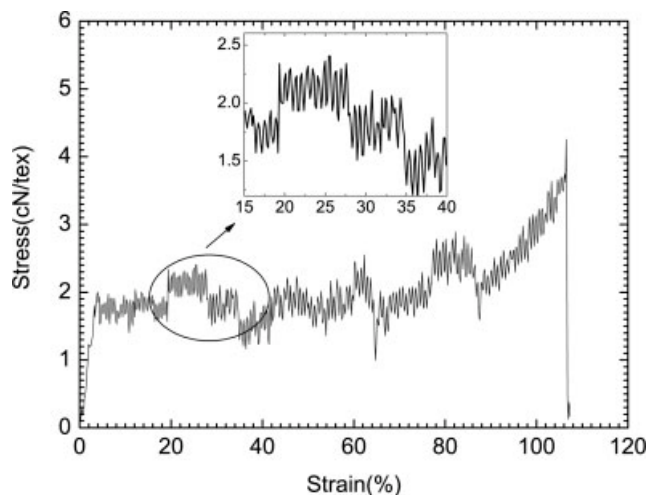

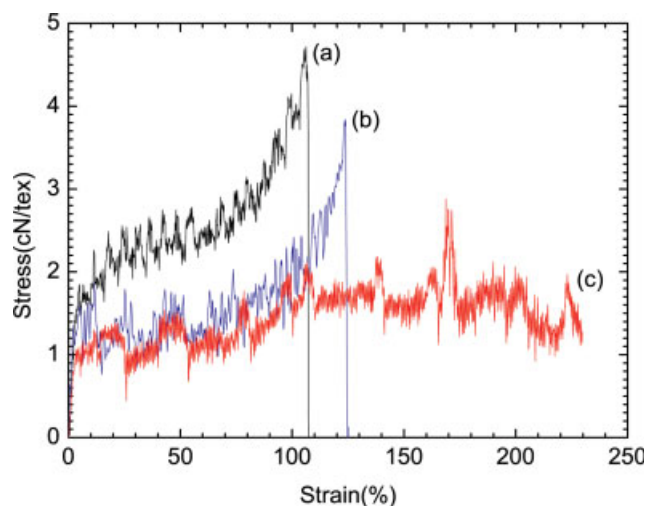**Figure 1** Stress–strain curves of wool in (a) air, (b) 20°C water, and (c) 80°C water.

the β-pleated sheets. At around 30% extension, the stress in the fiber begins to rise sharply with increase in extension. This has been interpreted as indicating the deformation of the β-pleated sheet crystals. In this study, we define the strain corresponding to the end of yielding region and the beginning of the postyield region as the Critical Strain (CS). Once the strain of fiber is larger than CS, permanent damage to the fiber might occur. Therefore, the stretching rate of wool fibers should be lower than CS. Obviously, many factors, including water, temperature, dipping time, and chemical solution, affect the value of CS. Results in Figure 1 show that the values of CS in 20 and 80°C water are ∼ 40 and 55%, respectively, which are apparently 30% larger than that in air. Water might break partial hydrogen bond in the wool, which makes the slippage and rearrangement of chain segments or chains more easily. In addition, high temperature is beneficial to the breakage of chemical bonds. However, it is impossible that the wool fiber is only immersed in water to slenderize to a desired diameter. A feasible method is to change the processing conditions, including the type of chemical solution, the concentration of solution, the dipping time, to vary the value of CS.

Stretching behavior in sodium bisulfite solution for fiber slenderization

A typical stress–strain curve of wool in the sodium bisulfite solution is shown in Figure 2. The wool was immersed in 5% solution at 50°C for 2 min, and then stretched. The stress–strain curve also exhibits the similar three regions as the same as aforementioned. The Hookean region covers the extension range between 0 and 5%, the yield region extends from


Figure 3 Stress–strain curves of wool with different concentrations of sodium bisulfite: (a) 1, (b) 3, and (c) 5%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

about 5 to 90%, and the postyield region ranges from about 90% extension to the breaking point.

In addition, the stress in the fiber varies acutely, and even forms several repeat courses of stress ascending and descending, namely stress descending → stress flatting → stress ascending. Such changes of stress reflect the microstructure transformation of wool fiber during stretching. The sodium bisulfite acts as a disulphide bond breakdown agent, which makes some of the disulphide bonds between different peptide chains, as well as within a single chain, to break. The breakage of disulphide significantly affects the mechanical properties of the wool fiber, which are expected to be highly dependent upon the number and distribution of disulphide crosslinks. Cleavage of

Figure 2 Stress–strain curves of wool in sodium bisulfite solution.
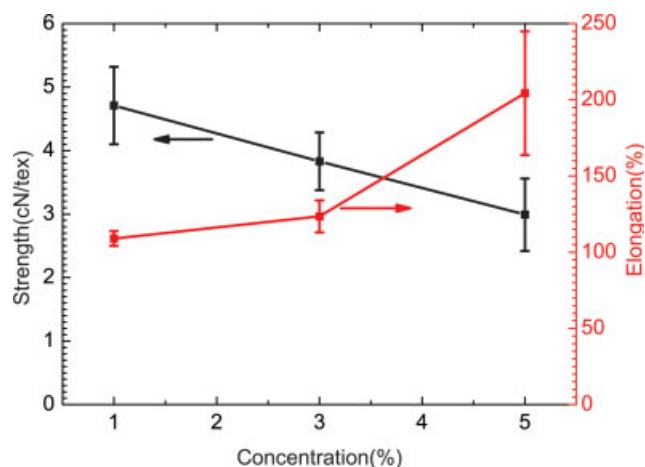
Figure 4 The effect of concentration on the tensile behaviors of wool. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
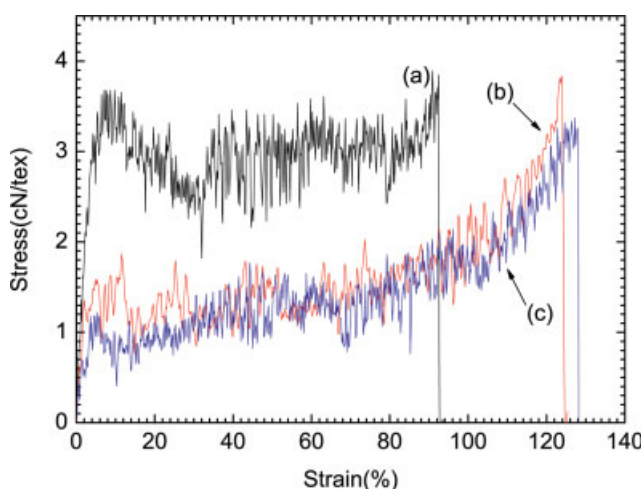
TABLE I
Multiple Comparison Result of the Concentration Effect

	Concentration (%)					95% CI	
	I	J	Mean difference (I−J)	SE	Significance	Lower bound	Upper bound
Strength (cN/tex)	1	3	0.8809*	0.2349	0.001	0.4012	1.3606
	1	5	1.7173*		0.000	1.2375	2.1970
	3	5	0.8364*		0.001	0.3566	1.3161
Breaking elongation (%)	1	3	−14.5182	10.3993	0.173	−35.7564	6.7200
	1	5	−95.3636*		0.000	−116.6018	−74.1254
	3	5	−80.8455*		0.000	−102.0837	−59.6073

* The mean difference is significant at the 0.05 level.

the disulphide bonds allows for more mobility within the peptide chains and the microstructure element. Thus the fiber can be stretched more easily. As a result, the stress in the fiber descends abruptly. After the breakage of the disulphide bonds, the slippages between the peptide molecules or between the microfibrils may occur. It makes the microstructure of the fiber rearrange, and the stress in the wool distributes again. Therefore, there is a stress flat and drop-down in the stress–strain curve. While the stress reaches a balance, the stress is shared with many peptides and begins to ascend.

Furthermore, the stress during the postyield region in the sodium bisulfite solution is lower than that in water, while the extension at break increases markedly even more than 100%. It is obvious that the extension exceeds that of the utmost limit in theory. As a result, the pretreated wool could be stretched easily. To maintain the integrality of the original wool, the breakage of disulphide and the slippage of the peptides should not occur drastically. Similarly the α-helices should not transform to the β-sheets drastically to keep its excellent elastic recovery. The

two aspects may be incompatible. Consequently, the effect of the concentration of the sodium bisulfite solution, temperature, and the dipping time on the stress–strain curve should be investigated.

Effects of stretching conditions on the tensile behaviors

Figure 3 shows the stress–strain curves of wool with 1, 3, and 5% concentration of the sodium bisulfite solution. The dipping time is 120 s and the temperature is 50°C. The effect of the sodium bisulfite solution concentration on the tensile behaviors of wool is shown in Figure 4. And the multiple comparison result is shown in Table I. The asterisk in Table I denotes that there is significant difference between the two groups. The solution concentration has a significant effect on the tensile curves of slenderizing wool fibers. The higher the concentration is, the more the stress repeats are, and the less the stress in the postyield region is. In addition, the wool fiber tends not to break in the 5% solution even when the strain is more than 230%. This indicates that the sodium bisulfite makes more disulphide bonds in fiber to break and lets the slippage of peptides become easier.
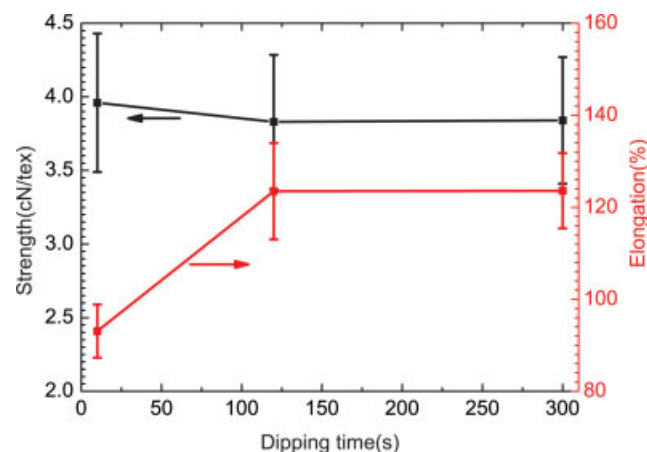

Figure 5 Stress–strain curves of wool with different dipping times: (a) 10, (b) 120, and (c) 300 s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6 The effect of dipping time on the tensile behaviors of wool. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Multiple Comparison Result of the Dipping Time Effect

|	Dipping time (s)					95% CI	
	I	J	Mean difference (I–J)	SE	Significance	Lower bound	Upper bound
Strength (cN/tex)	10	120	0.1300	0.1937	0.507	−0.2655	0.5255
	10	300	0.1209		0.537	−0.2746	0.5164
	120	300	−0.0091		0.963	−0.4046	0.3864
Breaking elongation (%)	10	120	−30.4182*	3.5804	0.000	−37.7302	−23.1061
	10	300	−30.5091*		0.000	−37.8211	−23.1970
	120	300	−0.0909		0.980	−7.4030	7.2211

* The mean difference is significant at the 0.05 level.

ANOVA results also indicate that the concentration influences the strength and breaking elongation of the wool fibers apparently. With the increase of the concentration, the strength of fiber decreases significantly, whereas the breaking elongation increases significantly except that the concentration varies from 1 to 3%. Therefore, the pretreatment process is obviously beneficial to the smooth stretching for the slenderization. However, too high solution concentration might cause fiber damage.

Figure 5 shows the tensile curves of wool fibers which are immersed in the sodium bisulfite solution for 10, 120, and 300 s, respectively. The sodium bisulfite solution concentration is 3%, and the temperature is 50°C. The influence of the dipping time on the tensile behaviors of wool fibers is shown in Figure 6 and Table II. Ten-second pretreatment is too short to make the sodium bisulfite penetrate into the wool, thus the modulus in the Hookean region is rather large. With continuous stretching, sodium bisulfite penetrates into the wool gradually. As a result, the stress in wool varies, and the curve is no longer smooth. Furthermore, the broken stress is close to the stress at the yield point, and no apparent postyield region appears in the tail part of the curve. While for 300 s, the fluctuation of the stress is more than that in short dipping time. Accordingly, the velocity of the wool tops during the pretreatment process should not be too large. The ANOVA results indicate that dipping time has no marked influence on the tensile behaviors of wool except that breaking elongation varies from 93 to 123% when dipping time varies from 10 to 120 s. And the tensile curve for 120 s is especially similar to that of 300 s, which means that 120 s is long enough for the sodium bisulfite to take action on the wool fibers.

The influence of the temperature on the tensile behaviors is shown in Figures 7 and 8 and Table III. Three distinct temperatures are 30, 50, and 75°C, respectively. The sodium bisulfite solution concentration is 3%, and the dipping time is 120 s. The ANOVA
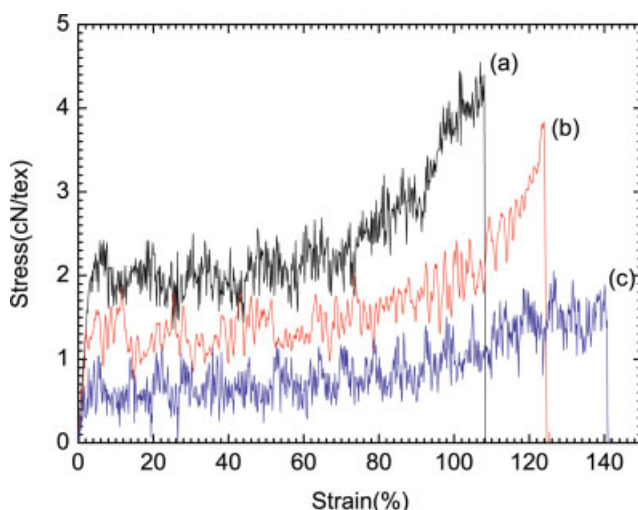
Figure 7 Stress–strain curves of wool with different temperatures: (a) 30, (b) 50, and (c) 75°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
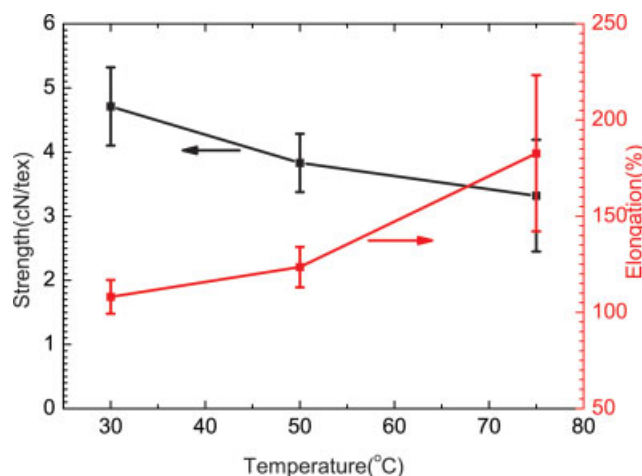
Figure 8 The effect of temperature on the tensile behaviors of wool. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Multiple Comparison Result of Temperature Effect

	Temperature (°C)		Mean difference			95% CI	
	I	J	(I–J)	SE	Significance	Lower bound	Upper bound
Strength	30	50	0.8118*	0.2334	0.002	0.3352	1.2884
(cN/tex)	30	75	2.6064*		0.000	2.1298	3.0829
	50	75	1.7946*		0.000	1.3180	2.2711
Breaking	30	50	−15.3546	11.2899	0.184	−38.4115	7.7024
elongation (%)	30	75	−74.5182*		0.000	−97.5752	−51.4612
	50	75	−59.1636*		0.000	−82.2206	−36.1066

* The mean difference is significant at the 0.05 level.

results show that the temperature influences the tensile behaviors of wool fibers apparently except the breaking elongation when the temperature varies from 30 to 50°C. The higher the temperature is, the lower the strength of the wool fiber is, and the higher the breaking elongation is. Therefore, the stretching slenderization should be performed at a relatively high temperature.

Stress–strain curves of the slenderized wool

To investigate the effect of the stretching on the tensile behaviors of the slenderized wool fibers, the tensile tests for the slenderized wool were performed. Figure 9 shows the stress–strain curves of the slenderized wool fibers with different stretching ratio. The tensile behaviors of the slenderized wool fibers are different from that of the original wool. For 30% stretching wool, the stress–strain curve still exhibits three regions. While for the large stretching ratio,

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

such as 50, 80, and 110%, the stress–strain curves can only be divided into two distinct regions, that is, no yield region. These curves are relatively similar to the tensile curves of silk in which the secondary structure is composed of the β crystals. It implies that almost all of the α-helices in wool have been transformed to the β-pleated sheets, which is the same as the previous findings.[3–9] In addition, the breaking stresses of the slenderized wool fibers increase with the stretching ratio, which indicates that the slenderization does not damage the wool fiber seriously. However, the extensions at break decrease with the stretching ratio because of the α→β transformation.

TEM analysis

The TEM micrographs of wool fibers are shown in Figure 10. The cracks are formed between the cuticle and cortex after stretching slenderization. This indicates that the slippage between the molecules does occur during stretching.

By the aforementioned analysis, we know that two types of microstructural transformations of wool fibers during stretching are found, that is, the slippage of molecules chains or microstructural elements and the α→β transformation.

CONCLUSIONS

The microstructure transformations of wool fibers during the stretching process have been analyzed using the tensile stress–strain curves. It is shown that water breaks some of the hydrogen bonds in fiber, whereas the sodium bisulfite breaks some of the disulfide crosslinks. Two types of microstructural transformations during the stretching were found, that is, the slippage of molecules chains or microstructural elements and the α→β transformation. The α→β transformation is dominant especially during the low stretching rate process. In addition, the stretching
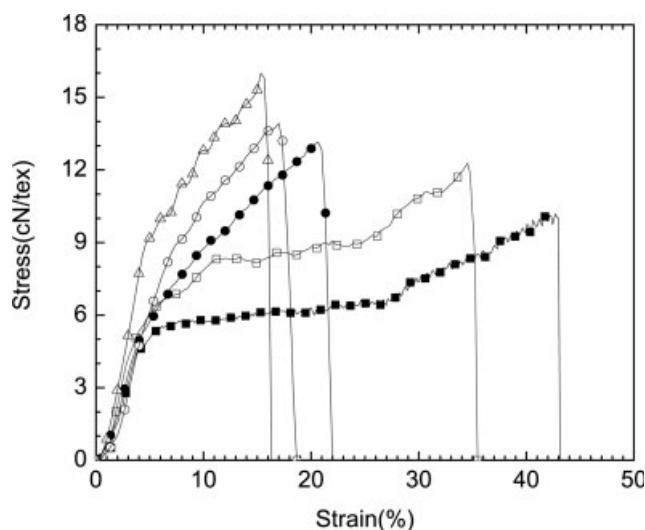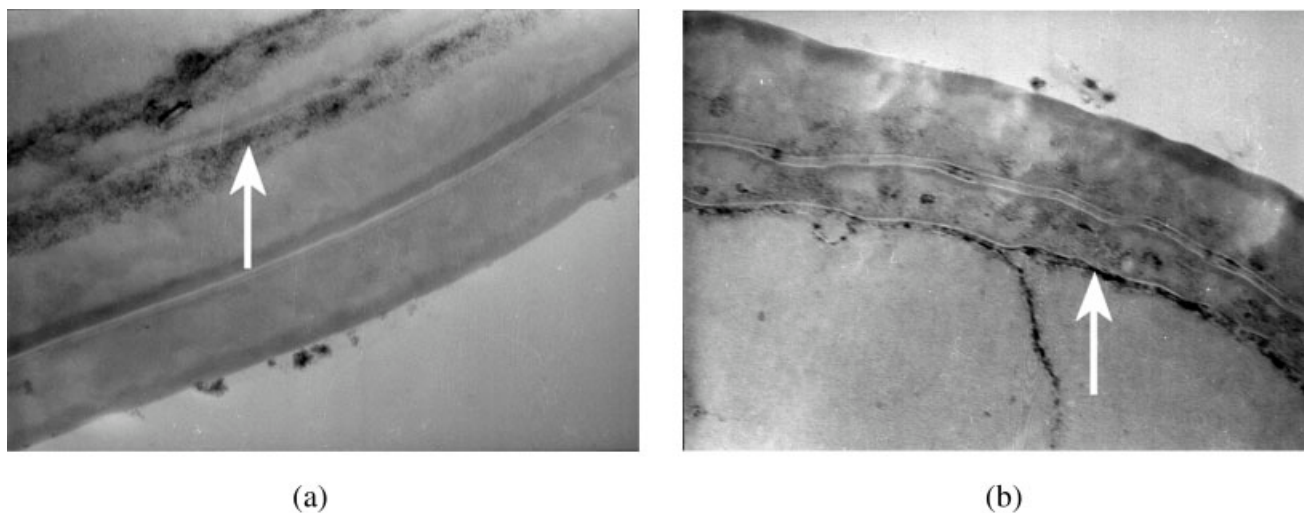
(a)   (b)

Figure 10 TEM micrographs of wool fibers: (a) unstretched wool and (b) 80% slenderized wool.

slenderization tends to increase the tenacity of wool fiber and decrease its extension at break.

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