Effect of Cyclic Stress while Being Dried on the Mechanical Properties and Thermostability of Leathers

by

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Abstract

Various mechanical processes are usually applied in leather making and using, which inevitably affect the structure and properties of leathers, such as mechanical performance and hydrothermal stability. Cyclic stress is very common in leather making, which may cause different changes to leather, compared with constant stress. However, very few results have been reported regarding the influence of cyclic stress on leathers. In the present work, cyclic stresses were applied to leather in drying. The influences of cyclic stress on the mechanical properties, hydrothermal stability and dry heat resistance of leathers were investigated. Also, the cross section of leather was observed with SEM, and the changes of hydrogen bonds in collagen fibers were characterized and discussed with the results of FT-IR. It was indicated that stress in drying leads to orientation of collagen fibers and increased mechanical strength. A balance is set up between tensile strength and elongation at break of leathers with the action cyclic stress. Longer stretching leads to higher tensile strength and lower elongation at break. Meanwhile, stress in drying may prevent the formation of hydrogen bonds inside collagen fibers and change the weaving structure of collagen fibers, resulting in decreased hydrothermal stability of leathers. Cyclic stress may provide leathers with better dry heat resistance than constant stress. Also, a simplified model of collagen fibers movement was introduced, to establish a relationship between processing and properties of leathers from viewpoint of collagen fiber structure.

Introduction

Leather is a composite with three-dimensional collagen fiber matrix, which endures various mechanical processes in leather making.[1] The effects of mechanical processes on the structure and properties of collagen fibers cannot be neglected.[2, 3, 4] One of the most important mechanical operations in leather making is drying, from which excess water is removed and leather acquires its final texture, consistency and flexibility under heat and force.[5]

Stress in drying changes the aggregate state and weaving structure of collagen fiber in leather,[6,7] causing significant changes to leather performances, such as mechanical properties. Stress also leads to orientation of collagen fibers along the direction of external force,[8] and collagen fibers gradually shape with water removal. As a result, leather acquires increased tensile strength, decreased elongation at break and poor flexibility.[9] Lower drying rate and temperature will result in better mechanical properties.[10, 11] After the release of force, leather will obtain some permanent set, which is the main cause of leather area yield. Higher tensile ratio can bring greater leather yield,[9] but stretching should not be overdone (over 10%), otherwise poor leather properties may be the result.[10]

Meanwhile, drying will affect the thermal stability of leather, which is mainly related to hydrogen bonds in collagen and the aggregate state of fibers.[12, 13] So the factors that affect the hydrogen bonds and the aggregate state of collagen will also affect the thermal stability of leather. For example, water removal in drying reduces the free volume for the movement of collagen α-chain,[14] and provides closer distance for collagen groups with opposite charge to form more stable chemical bonds, thus greatly improving leather thermal stability. Longer heat treatment will enable bovine collagen fibers to gain better dry heat shrinkage resistance.

We previously reported the effect of stress in drying on collagen thermal stability and mechanical properties of leather dried at constant forces.[15-17] In fact, there are many cyclic stresses in leather processing, which may cause different changes to the structure and properties of leather. For example, milling is physical process in which leather is tumbled in a drum. It is

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efficient for separating the sticky collagen fibers and improving tensile strength and elongation at break.[18] In this work, cyclic stresses were applied in drying process. The mechanical properties and thermal stability of the collagen fibers were investigated and the relationship between structure and properties of the fibers under cyclic stress was discussed. The results may be beneficial for tanners to better understand the relation between structure and properties of collagen in leathers, as well as to optimize mechanical processes in leather making.[19, 20]

Experimental

Materials

Bovine wet blue was purchased from local tannery. Then it was glutaraldehyde (50% aqueous solution, Shanghai chemical reagent factory, China) retanned, neutralized, and MK (a commercial fatliquoring agent produced by TFL Co. Ltd., Germany) fatliquored in a five-drum tanning machine (DJD-350, Wuxi Derun Light Industry Machinery factory, China). The obtained crust leathers were then stretched with a self-made iron tensile device, which can be placed in the oven (Guangming medical Instrument Factory, China) in drying. The sketch of self-made tensile device is shown in Figure 1.

Methods for the Preparation of Leather Samples

Each sample experienced a specific cyclic stretch + release drying with stretch at a specific direction. All samples were dried for 4h at 45°C and ambient pressure despite the difference in cyclic stretch + release mode, while the cyclic stretch were all 15% strain even though the direction may differ. There are three kinds of cyclic stresses, i.e., parallel to the backbone (X), vertical to the backbone (Y), and alternating in two directions (XY). And there are 7 stretch and release modes: 45 min stretching + 10 min release, (45-10); 30 min stretching + 10 min release, (30-10); 30 min stretching + 30 min release, (30-30); 20 min stretching + 10 min release, (20-10); 15 min stretching + 30 min release, (15-30); stretched for 4 hours without release; and the control without stretching in drying(control). The way to name the samples is to add stretching direction to stretch and release mode. For example, if a sample was stretched 30 min parallel to backbone before a 10 min release, it would be marked as X 30-10. Similarly, XY 30-10 represents that stress alternates in two directions. After drying, samples were equilibrated at 25°C under 60% RH for 24 h. Then samples were ready for subsequent study.

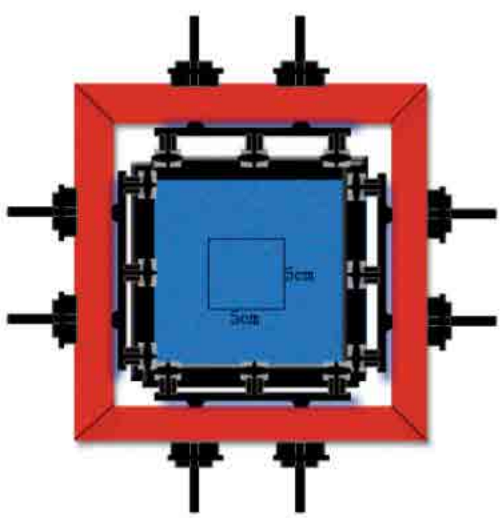

Figure 1. Sketch of self-made tensile device.

Characterization

Mechanical Properties

The mechanical properties of leather samples were studied with a Universal electronic testing machine (Sans Metering Technology Co. Ltd., Shenzhen, China). Dumbbell shaped leather samples were cut from the standard test areas as described in GB/T 1040.3-2006. The stretching ratio was 100 mm/min and stress-strain curve was automatically given by the computer. Each test was conducted three times with the average reported.

Hydrothermal Shrinkage

Samples of 50mm×2mm were cut along X direction, and then gradually heated in glycerin from 30°C to 170°C. The shrinkage ratio was calculated by equation (1).

$$R_1(\%) = (L_0 - L_1)/L_0 \times 100 \quad (1)$$

Where, L_0 is the length before shrinkage; L_1 is the length after shrinkage; R_1 is the shrinkage ratio.

Dry Heat Shrinkage

Leather samples were split into 3 layers to get thin leather sheet. Collagen fibers were extracted from the middle dermis layer. BX51 polarizing microscope (OLYMPUS Co. Ltd) was employed to observe the set variation of leather sheet and collagen fibers during the two-step heating with the first stage, from 30°C to 205°C at the heating rate of 20°C /min and the second, from 205°C to 325°C at heating rate of 10°C /min. The area (S) of leather sheet and length (L) of collagen fibers were recorded at each temperature and the equations for calculating the shrinkage rates were shown as follow:

$$R_2(\%) = (S_0 - S_1)/S_0 \times 100 \quad (2)$$

$$R_3(\%) = (L_3 - L_2)/L_2 \times 100 \quad (3)$$

Where S_0 and S_1 are the areas of leather sheets before and after heating, respectively; L_2 and L_3 are length of collagen fibers before and after heating. R_2 and R_3 represent the shrinkage ratios of leather sheet and collagen fiber, respectively.

TG Thermal Analysis

After the thermal analyzer (NETZSCH Co. Ltd., Germany) was calibrated, samples were placed on the crucible and heated from 25°C to 800°C at the heating rate of 10°C /min in N_2. The TG curve was automatically given by the computer.

Scanning Electron Microscopy (SEM) Observation

A field emission scanning electron microscopy (SEM), JSM-7500F, made in Japan was employed to observe the morphology of cross section parallel to the backbone (X direction) of samples. Before SEM observation, gold spraying was conducted to increase the conductivity of the specimens.

FT-IR Analysis

Collagen fibers, combined with KBr, were ground evenly in an agate mortar, and pressed into transparent tablets in mold. Then FT-IR-8700 made by Shimadzu Co. Ltd., Japan, was employed to scan at the range of 600 - 4000 cm^{-1}.

Results and Discussion

Hydrothermal Shrinkage

Leather consists of collagen fibers. Higher crosslinking degree in collagen means more stable structure and higher shrinkage temperature of leathers. When being heated, collagen with unstable chain structure and more scattered aggregate state will shrink firstly, while the stable and sticky collagen fibers will shrink later. Larger space for fibers to shrink will result in greater shrinkage ratio. It is clear, from Figure 2(a), that stress in drying causes little effect on shrinkage temperature, while greatly increases the hydrothermal shrinkage ratio (over 22%). Longer stretching and less releasing leads to higher shrinkage ratio, which means poorer hydrothermal stability. This is probably because stress, though causing little influence on collagen chain structure, still dramatically changes the weaving structure of collagen fibers. Stretching may provide more space for collagen fibers to shrink. So long time of stretching causes more ordered arrangement of collagen fibers and easier slippage across each other when being heated.

Figure 2(b) shows the hydrothermal shrinkage curves and shrinkage ratio of Y stretched leather. It is observed that Y stretching decreased the hydrothermal shrinkage ratio (below 22%). This is probably because the samples were cut parallel to backbone, meaning vertical to the direction of force in drying. As there is dramatic shrinkage caused by removal of excessive water and stretching in X direction, less space is available for collagen fibers to shrink, resulting in lower shrinkage ratio. However, the mode of stretching and releasing shows complex pattern on the shrinkage ratio. This is mainly due to the complicated structure of leather and collagen fibers.

Figure 3 shows the hydrothermal shrinkage curves (a) and shrinkage ratio (b) of XY stretched leather. It is clear that stress alternating in two directions (X and Y) increases the shrinkage ratio of leathers, exceeding 32%. Cyclic stress could lead to lower shrinkage ratio than constant stretching and stretching for a long time in drying will result in higher ratio. This is because alternating stress not only leads to the orientation of collagen fibers, but also separates fibers. Once leathers have enough time to recover in cyclic stress, they get less space to shrink.

Dry Heat Shrinkage Resistance

Dry heat shrinkage resistance is important for leathers because they may have to endure high temperature process (over 200°C) in shoe making. Figure 4 shows the dry heat shrinkage curves of XY stretched collagen fiber (a) and leather sheet (b). The dry heat resistance is closely related to the aggregate state and weaving structure of collagen fibers. It is illustrated that stress in drying slightly affect the dry heat resistance of collagen fibers, while

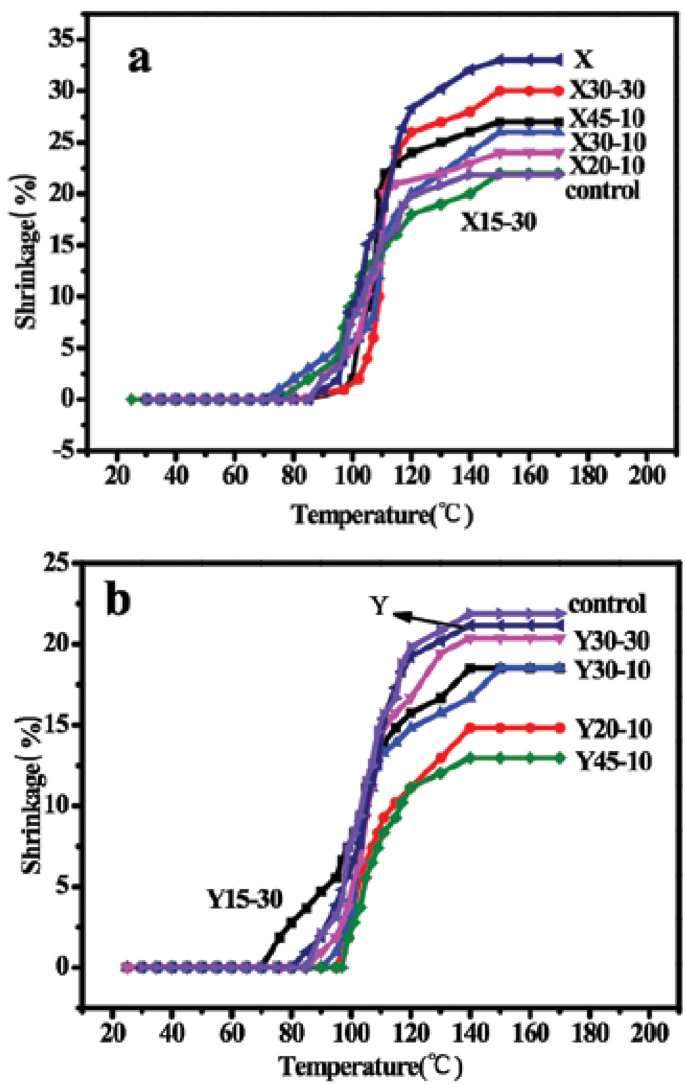

Figure 2. Hydrothermal shrinkage curves of X (a) and Y (b) stretched leather.

significantly affect that of leather sheets. The longer the stress is applied, the less the dry heat resistance of leather would be. Little difference of shrinkage ratio at very high temperature can be observed for collagen fibers, but very high shrinkage ratio (over 60% at 250°C) for leather sheets. Stress leads to little changes to the internal structure of collagen fibers, but significant changes to the weaving structure of leathers. Biaxial stress leads to orientation of collagen fibers on one hand and separates fibers and causes more space for fibers to shrink on the other hand.

Thermal Degradation

Thermal degradation is an efficient way to investigate internal structure stability of collagen fibers. Higher degradation temperature refers to better degradation resistance and more stable structure. Figure 5 shows the TG (a) and DTG curves (b) of cyclically stretched leather. The degradation curves of all samples in Figure 5 tend to overlap each other, with only the stretched leather having slightly decreased pyrolysis temperature, which indicates that stress could only cause very limited change to the chain structure of collagen fibers. The result is similar to that of dry heat shrinkage for leathers.

FT-IR Spectra

Figure 6 shows the FT-IR spectra of leather experienced different modes of stretching while being dried. The absorption peak of collagen fibers from stretched leather moved toward the higher frequency, closer to the absorption peak of free hydroxyl group at 3570-3700cm^{-1}, which indicates that stress in drying may prevent the formation of some hydrogen bonds inside collagen, probably because stretching causes larger distance between collagen fibers. So, as a result, stretching in drying leads to poor thermal stability.

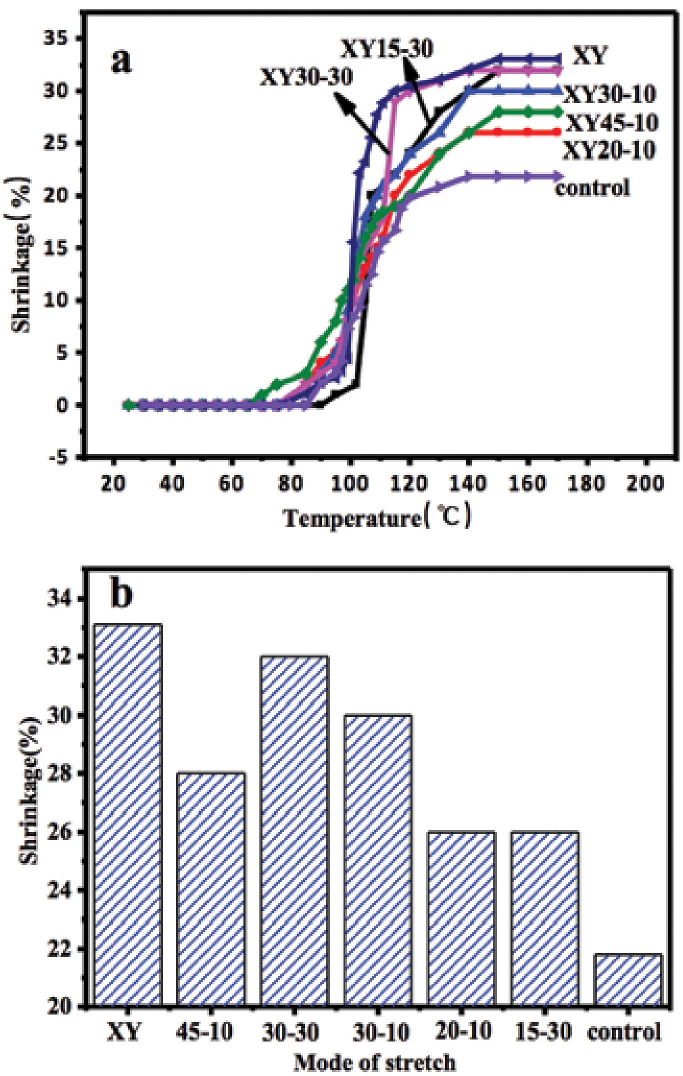

Figure 3. (a) Hydrothermal shrinkage curves and (b) shrinkage ratio of XY stretched leather.

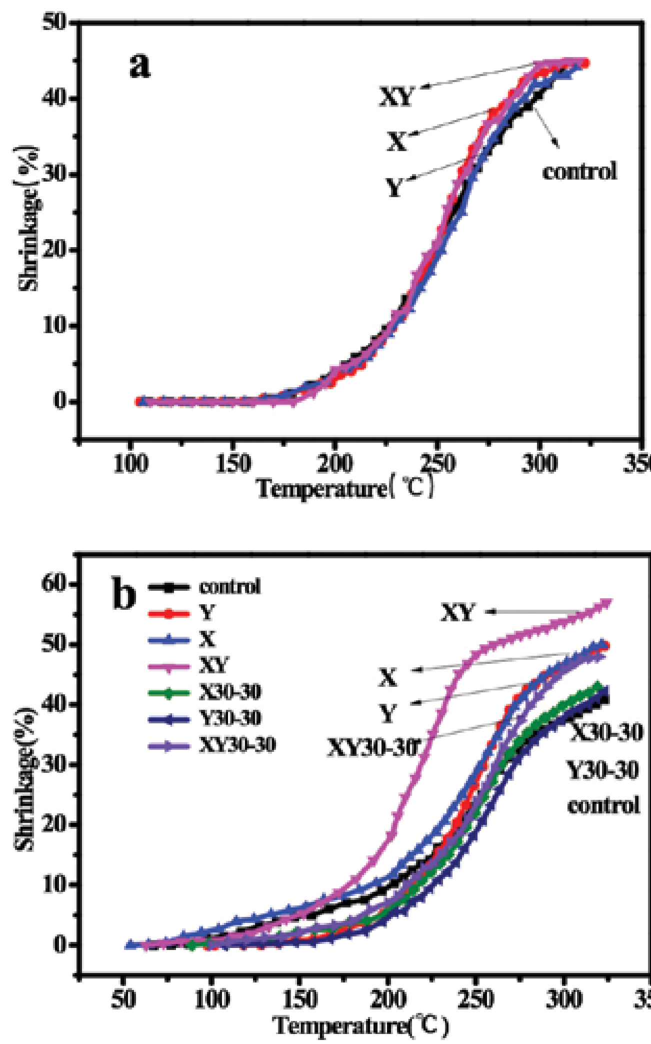

Figure 4. Dry heat shrinkage curves of (a) XY stretched collagen fiber and (b) leather sheet.

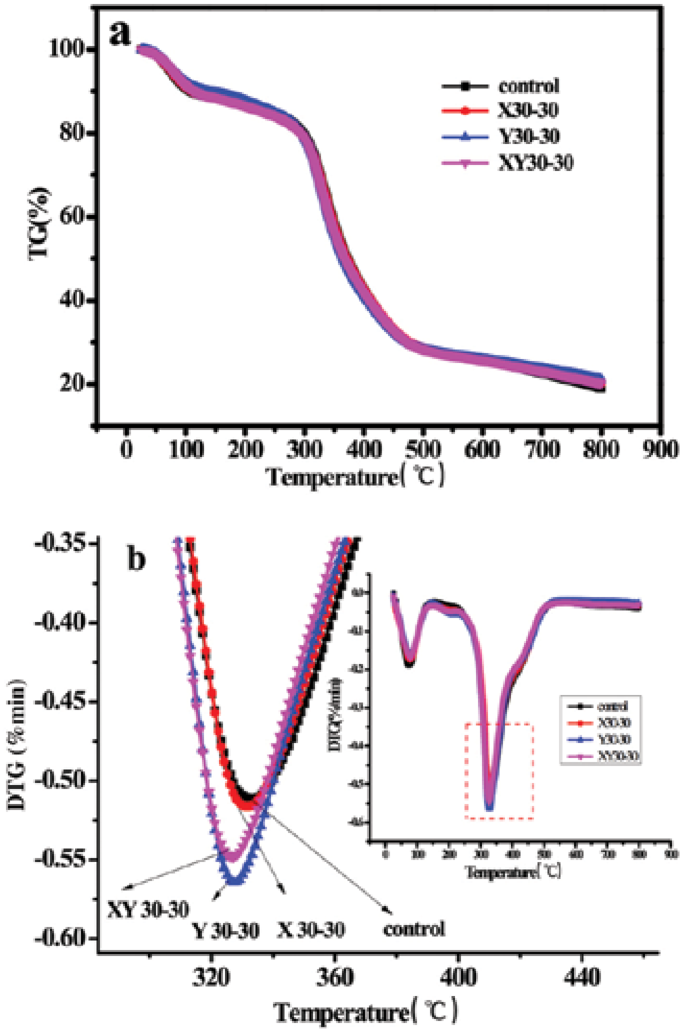

Figure 5. (a) TG and (b) DTG curves of cyclically stretched leather.

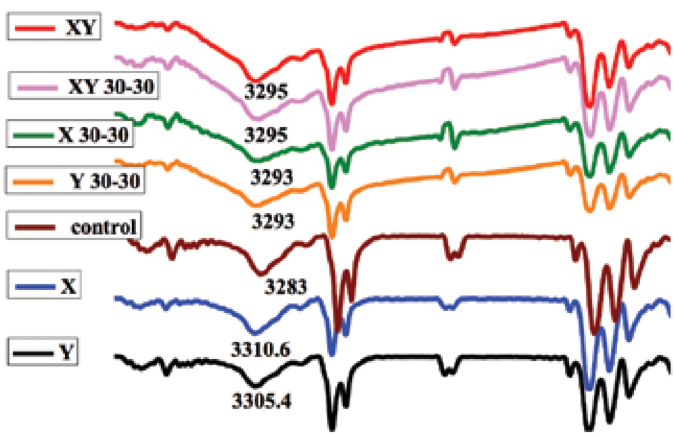

Figure 6. FT-IR spectra of leather experienced different modes of stretching in drying.

SEM Images

Figure 7 shows the SEM images of cross section of different leather samples. While the collagen fibers in control sample interweave in an irregular way, collagen fibers along the parallel (X) direction show more obvious orientation along the direction of stretching (force). The orientation and structured morphology were caused by stress. For vertically (Y) stretched leather (Figure 7c), fibers stick to each other and have large gaps. The vertical (Y) stress which leads more fibers to arrange in Y direction, instead of in direction of X and thickness. When excessive water was removed from collagen matrix, it becomes more difficult for fibers to slip across each other. Therefore, in leather making, further mechanical softening is commonly required after drying.[18] Figure 7(d), (e) and (f) show that intermittent cyclic stress produced inadequate collagen fibers orientation as constant stress does, but it would greatly loose collagen fibers, thus enabling fibers to slip across each other easily. For instance, Y 30-30 in Figure 7(e) gains many gaps between the sticky collagen fibers. It is the result of stretching and releasing, and the XY 30-30, which experienced both insufficient stretching in both directions of X and Y has limited orientation and gaps.

Effect of Stress on the Mechanical Properties

Tensile strength and elongation at break are important for leathers, which determine its value and field of application. Proper softness is also needed for high grade leathers. The quantitative assessment of softness can be based on measurement of the gradient of stress-strain curve in elastic deformation phase.[9] Smaller gradient refers to more flexible leather. Figure 8(a) shows the stress-strain curves of X stretched leather. It is clear that drying could significantly improve the tensile strength of leather and reduce the elongation at break and softness. Constant stress results in the greatest effect on mechanical properties of leather, while cyclic stress enables leathers to obtain balanced tensile strength and elongation at break. Long time of drying and short time or release provides higher strength but

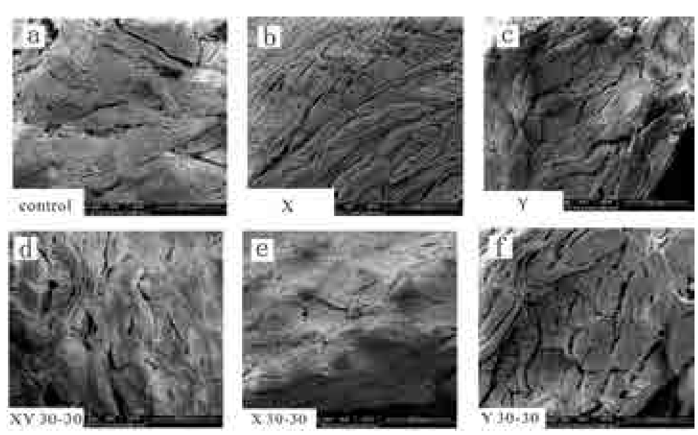

Figure 7. SEM images of cross section of different leathers. (a, control sample; b and c, constant stress; d, e, and f, cyclic stress. Cross section parallels to the backbone.)

worse elongation and softness. This is probably because of joggling, which creates orientation of collagen fibers as shown in Figure 7 (b), thus fibers obtain higher resistance to deformation and destruction. While the leather undergone cyclic stress has time to release and recover, it has less orientation than constantly stretched leather, shown in Figure 7 (e).

By contrast, Y stress cannot offer leathers with significantly increased tensile strength, but can maintain the softness, and slightly increase the elongation at break, found in Figure 8(b), simply because fibers orientation along Y direction cannot provide resistance to deformation in X direction. As also could be found, constant stress brought reduced elongation at break, but cyclic stress brought slightly increased elongation. This may be attributed to the anisotropic nature in the alignment of the fiber bundles of bovine hide in which the fibers tend to align in one direction (parallel to the backbone)[9] and are therefore, more resistant to stretch in the direction. What is interesting, as can be seen from Figure 8 (b), all curves nearly overlap at the initial

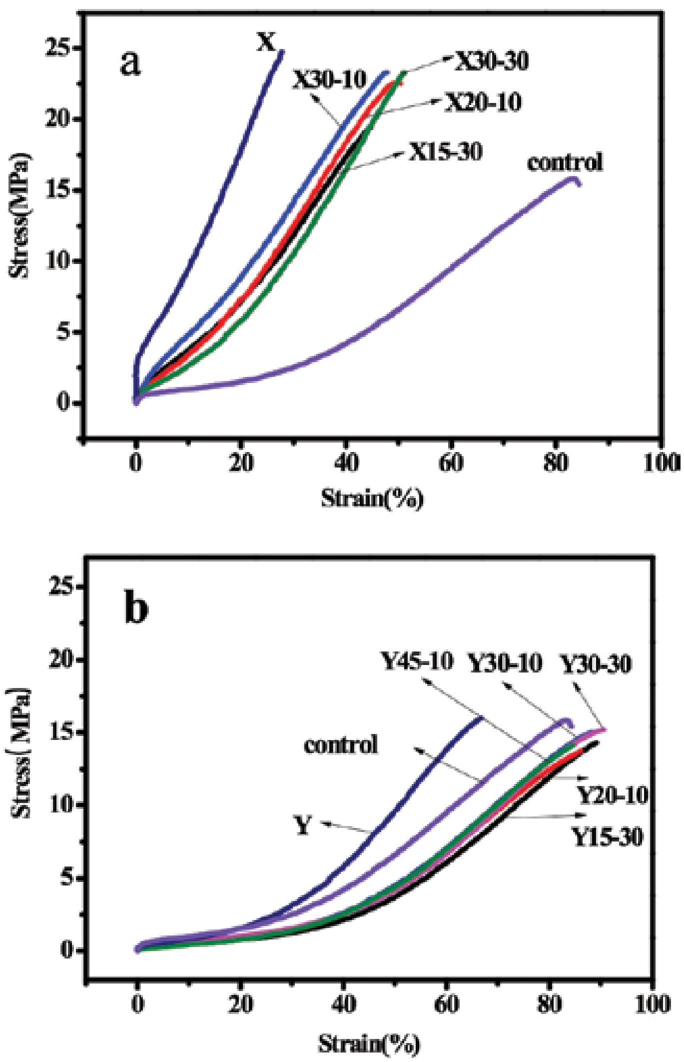

Figure 8. Stress-strain curves of (a) X and (b) Y stretched leather.

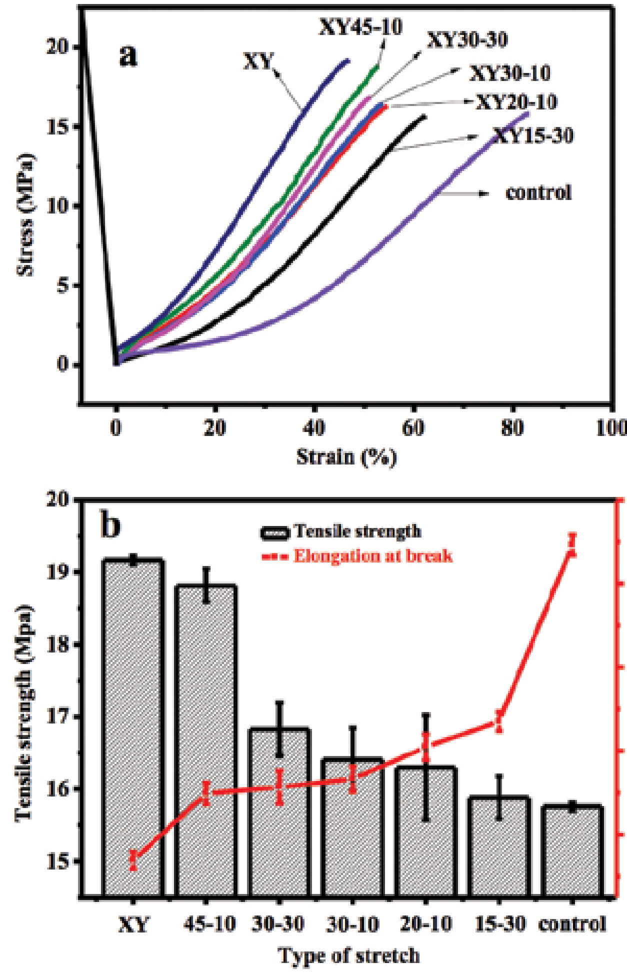

Figure 9. (a) Stress-strain curves, (b) tensile strength and elongation of XY stretched leathers.

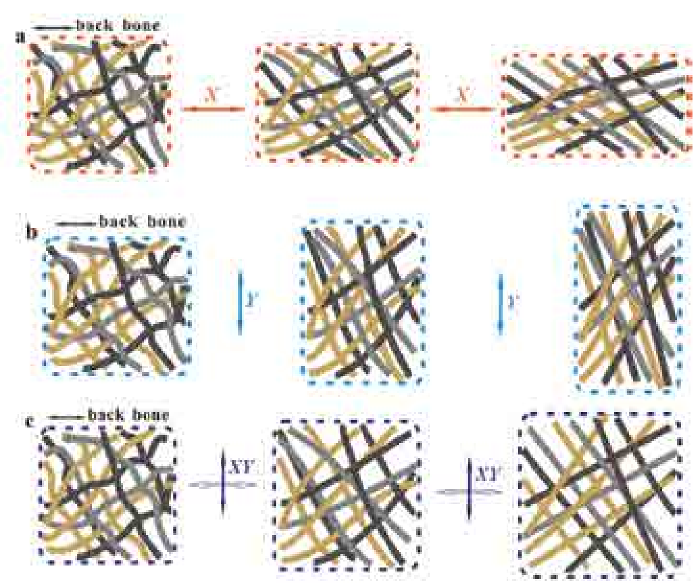

Figure 10. Sketch of fiber orientation in cyclic (a) X stress, (b) Y stress and (c) XY stress.

stage (before 10% strain). This is due to dramatic shrinkage of collagen fibers caused by water evaporation and tight three-dimensional weaving structure of leather matrix. Fibers along the thickness direction and vertical (Y) direction will prevent excessive shrinkage in X direction. Y stress can also cause shrinkage of fibers in X direction, though relatively limited.

Biaxial stretching is an effective way to increase leather yield, which determines the income for tanneries. Therefore, it is commonly applied to leather in drying. Figure 9 (a) shows the stress-strain curves of leathers stretched with alternative stress. It is observed that these curves have similar trend but more even distribution than those in Figure 8 (a). Tensile strength is between 15-20MPa and elongation at break between 40% and 80%,[5] mainly related to the orientation and dispersion. In cyclic stress, tensile strength increases with increasing the stretching time, but elongation at break and softness increase with increasing the releasing time. More release means less orientation and more time and space for fibers to recover, as shown in Figure 7. Therefore, this may benefit tanners to produce leathers with designed mechanical property by carefully controlling the time of biaxial stretching and releasing.

Sketch of Fiber Orientation in Cyclic Stress

According to the results of SEM images and mechanical properties mentioned above, the fibers movement and orientation in cyclic stress was proposed as shown in Figure 10. Arrow appoints the direction of force (stress) in drying. When leather is subjected to uniaxial stress, along direction either (X) parallel to the backbone or (Y) perpendicular to backbone, collagen fibers, originally curled and loosened, are extended along external force (stress). As stretching goes further, they will orient along the force (stress) direction, which greatly increases the length of the force direction and decreases the length of the direction vertical to force direction. However, collagen fibers could gain increased final length and more uniform distribution in the whole matrix when being subjected to alternating forces.

Conclusions

Stress when leathers are dried may prevent the formation of some hydrogen bonds inside collagen and change the weaving structure of collagen fibers, resulting a decreased hydrothermal stability of leathers. Cyclic stress may offer leathers better dry heat resistance than constant stress. Different from constant stress, cyclic stress would lead to orientation of collagen fibers and increased mechanical strength. There is a balance between tensile strength and elongation at break by separating fibers. The final strength of leathers is closely related to the mode and time of stretching in drying. Leathers could be produced with designed mechanical property by controlling the times of stretching and releasing when the leathers are dried.

Acknowledgments

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