

THERMAL SHRINKAGE EFFECTS ON THE MECHANICAL BEHAVIOR OF LEATHERS*

by

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ABSTRACT

Thermal shrinkage will take place when leathers are heated to a high temperature, usually resulting in a decrease in its value and utility. In this paper, changes in mechanical behaviors by thermal shrinkage of leathers are studied systematically for the first time, and the influencing mechanism of thermal shrinkage on the mechanical behaviors of leathers are investigated and analyzed. The results indicate that, by thermal shrinkage, the aperture ratios of leathers are decreased and such mechanical properties of leathers as elastic modulus, tensile strength, and elongation at break are increased. The improvement in mechanical behaviors by hydrothermal shrinkage is at the cost of loss of utility and economic value of leathers. The results indicate that shrunken leathers may have a host of new applications because of their excellent mechanical behavior.

RESUMEN

Encogimiento térmico ocurre cuando los cueros son calentados hasta alcanzar alta temperatura, resultando un decremento en su valor y utilidad. En este trabajo, cambios en comportamientos mecánicos por encogimiento térmico se estudiaron sistemáticamente por primera vez, y el mecanismo de encogimiento térmico que influye en el comportamiento mecánico de los cueros fue investigado y analizado. Los resultados indican que, por contracción térmica, las fracciones de apertura en los cueros son reducidas y tales propiedades mecánicas del cuero como el módulo de elasticidad, la resistencia a la tensión, y la elongación a la rotura son incrementadas. Los incrementos en los comportamientos de las propiedades mecánicas son al costo de pérdidas en capacidad de utilización y valor económico de los cueros. Los resultados indican que cueros contraídos [térmicamente] podrían tener numerosas y novedosas aplicaciones por su excelente comportamiento mecánico.

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INTRODUCTION

Leather is a kind of natural biopolymer material transformed from raw skins or hides through a series of processes, including soaking, degreasing, liming, deliming, bating, pickling, tanning, retanning, fatliquoring and finishing, etc. Leather goods are popular because they often provide a very comfortable feeling to the people who wear them. Leather has played a very important role in the world's economy and in people's daily lives. Shrinkage will take place when skins or leathers are heated to a certain temperature.¹ Raw skins will shrink at 60 degree centigrade, and the shrinkage temperature for fully chromed tanned leathers may reach even higher than 120 degree centigrade.² When thermal shrinkage takes place, both the area and the volume of the leather is reduced and the service performance is lost. A high thermal stability is, consequently, important and needed for leathers.

In the meantime, thermal shrinkage will also lead to changes in mechanical behavior of leather. To understand the changes in mechanical behavior by thermal shrinkage may help to improve leather making technology in order to produce leathers with high thermal stability and excellent mechanical behavior. It also does well for us to know the thermal shrinkage mechanism and the structure of leathers. Studies of the changes in mechanical behavior of skins or leather due to thermal shrinkage, however, have not been reported before.³⁻⁴ With regard to the thermal shrinkage mechanism of leather, it is thought that collagen chains in leather may move more quickly when being heated, resulting in the destruction of cross linking between peptide chains and causing more easy movement between peptide chains. Thermal shrinkage of leathers is the macroscopic performance of this movement and destruction. It is also thought that the thermal shrinkage of leathers is virtually the melting denaturalization of some crystalline regions in the collagen. It is an irreversible transformation.

In the present paper, pigskin wet blues were neutralized and fatliquored with different kinds and various amount of fatliquoring agents to obtain different samples. The samples were then soaked in water for more than 24 hours and heated in glycerol to be contracted. The stress-strain curves of the samples before and after thermal shrinkage were obtained and compared. Such mechanical properties as tensile strength, elongation at break, and initial elastic modulus of the samples before and after thermal shrinkage were studied and discussed. The influence of hydrothermal shrinkage on the mechanical behavior of leather was investigated. Results indicate that thermal shrinkage may improve the tensile strength, the elongation at break and the initial elastic modulus of leathers greatly. On the other hand, the rigidity is increased and the area is diminished. Consequently, the utility and economic

value of leather is greatly reduced by hydrothermal shrinkage. The improvement in the mechanical behavior thus is at the cost of loss of utility and economic value of the leather.

EXPERIMENTAL

Main Material and Apparatus

Pigskin wet blues were kindly provided by Decision Chemical Co. Ltd, China. Ammonium bicarbonate, analytical pure, was from Tianjin Sitong chemical Co. Ltd. Sodium acetate, analytical pure, was purchased from Wuchang chemicals plant. Formic acid, analytical pure, was made by No.1 Tianjin chemical reagent company. TGR retanning agent and MK, SF fatliquoring agents were all industrial grades and kindly provided by TFL (Together For Leather) leather chemicals Co. Ltd, and Decision chemicals Co. Ltd, respectively. Sulfites fish oil and sulfated castor oil were industrial grade and provided by Henan institute of leather and plastics, China. The water bath constant temperature oscillator, THZ-82, was made by Fuhua instruments plant, Jiangsu, China. The tanning machine, DJDΦ350, was purchased from Dongbeitang leather machinery plant, Xishan, China. A Computer-controlled electronic universal testing machine, CMT6000, was made by Sans testing machine Co. Ltd, Shenzhen, China.

Procedure:

Sampling: All the samples were from the same part, i.e., the center of shaved pigskin wet blues.

Weighing: The samples were accurately weighed and the weight was used as the calculation base in subsequent processes.

Neutralization: 0.6 wt% of ammonium bicarbonate and 0.5 wt% of sodium acetate was used in the neutralization process with a float of 3.0 at 38 degree centigrade. After 90 min of neutralization, the pH of the float was around 5.5-6.0.

Washing: The samples were water washed for 5 min, with a float of 3.0 and at 20 degree centigrade.

Retanning: 5 wt% of retanning agent (TGR) was used in retanning, with a float of 3.0 and at 40 degree centigrade. The retanning lasted for 90min in all.

pH adjusting: About 1 wt% formic acid of the pigskin wet blues was added to adjust the float pH to around 4.0. About 30min was needed.

Washing: The samples were water washed again for 5 min, with a float ratio of 3.0 and at 20 degree centigrade.

Fatliquoring: After having been neutralized and retanned, the samples were fatliquored. Different kinds and various amount of fatliquoring agent were used as shown in the section of “results and discussion”. The float was 3.0 and the temperature was controlled at 55-60 degree centigrade. The samples were drummed for around 90 min before the addition of formic acid. About 1 wt% formic acid was needed to adjust the float pH to around 4.0 in 30 min. The samples were washed with water again for 5 min. After being air-dried, the samples were skated and conditioned in air with a relative humidity of 65% and at 25 degree centigrade.

Hydrothermal shrinkage

Before hydrothermal shrinkage test, the samples with dimension of 2 X 50 mm X mm were soaked in the distilled water for more than 24 h. The samples were then immersed in glycerol and heated from room temperature at a heating rate of 5°C/min. The samples shrink during the heating. When the length of the samples did not change anymore, the samples were taken out and air dried. They were then staked and air-conditioned with a relative humidity of 65% and at 25 degree centigrade before mechanical tests.

Mechanical behaviors of the samples

A computer-controlled electronic universal testing machine, CMT6000, was employed to study the mechanical behaviors of the samples. A standard dumbbell-shape cutter was used to get the sample specimens. The specimens were stretched at a speed of 100mm/min. The procedures were according to standard GB/T 508-1998.

Determination of aperture ratios

The aperture ratios of the samples were determined according to reference 2. The samples were cut to strips with length of 20 mm and width of 2~3 mm. Samples of about 5 mg were accurately weighed with an analytical balance. The samples were put into a 100 mL volumetric flask. The volume of volumetric flask 100 mL was referred as V_0 . Methylbenzene (with the volume V_1) was added through a burette till the scale mark of the volumetric flask. The flask was left standing still for 24 h. The methylbenzene penetrated into the pores of the samples gradually and the liquid level dropped. More methylbenzene (with the volume of V_2) was added to reach the scale mark. Pour the methylbenzene and samples out and wipe the samples' surface carefully with filter paper. Put the samples into the volumetric flask again and add methylbenzene (with the volume V_3) till the scale mark. The aperture ratio was calculated as follows:

$$Ra = \frac{V_1 + V_2 - V_3}{V_0 - V_3} \times 100\%$$

RESULTS AND DISCUSSION

Mechanical behaviors

The stress-stain curves of different samples before and after thermal shrinkage are shown in Figure 1. It should be noted that, in Figure 1, all the samples were fatliquored with different kinds and various amounts of fatliquoring agent. Samples of a, b, and c were fatliquored with sulphited fish oil, sulfated castor oil and BK fatliquoring agent, respectively. The amount of fatliquoring agent used was 20 wt% of the pigskin wet blue. Samples of d, e, and f were all fatliquored with MK fatliquoring agent, with the amount of 20 wt%, 10 wt%, and 5 wt% of the pigskin wet blue, respectively. From Figure 1, it should be found that, for all the samples studied here, regardless of the amount and kinds of fatliquoring agents used, the trend is the same. By thermal shrinkage, the mechanical behaviors of leathers were improved greatly. For example, the initial elastic modulus (the tangent slope in the initial stage of the stress-strain curve), the tensile strength, and the elongation at break are increased after thermal shrinkage.

The changes in mechanical behaviors of leathers because of thermal shrinkage are illustrated in Table 1. From Table 1, it may be found that such mechanical behaviors of leathers as the initial elastic modulus, the tensile strength, and the elongation at break of the samples increase remarkably by thermal shrinkage, which is to say that the mechanical behavior is improved greatly by thermal shrinkage. On the other hand, we know that the area and volume of leather is decreased by thermal shrinkage. By hydrothermal shrinkage, the distance between collagen fibers is reduced. Some cross-linking may take place between the collagen fibers, resulting in an increase in intermolecular forces and consequently increasing the mechanical behaviors of the leather. Subsequently, the tensile strength and the initial elastic modulus of the samples are increased by thermal shrinkage. With regard to the increase in the elongation at break of leathers, it may be the case that the intermolecular forces may be due to hydrogen bonds or polar interactions among collagen molecules. There are plenty of polar groups such as amino, hydroxyl, carboxyl and peptide groups on collagen molecules. Hydrogen bonds may be formed between collagen fibers because of the existence and interaction of these groups. When thermal shrinkage takes place, the distance between collagen molecules decreases and extra cross-linking may be formed. Hydrogen bonding is not a normal chemical bond. It is an electron- shared bond and can be regarded as a weak covalent bond, meaning that the energy needed to break it is small.⁵ There are such covalent bonds as C-C, C-N, and C-O in the backbone of collagen peptide. The bond energies for these covalent bonds are 365 kJ/mole, 305 kJ/mole, and 358 kJ/mole, respectively.⁶ Compared with the energies of these covalent bonds, hydrogen bond energies are much smaller, and are in the range from 4 to 25 kJ/mole.⁶

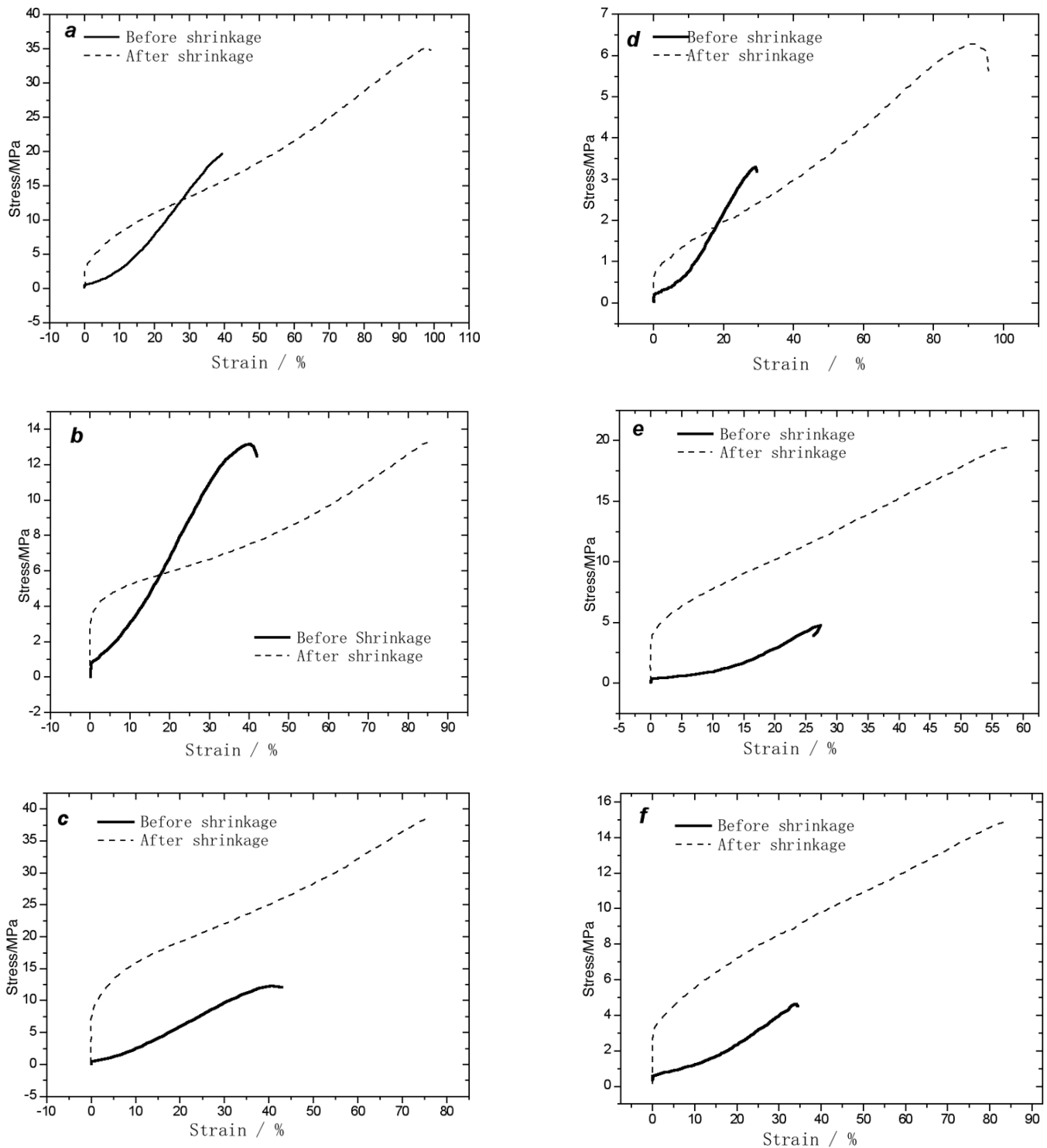


Figure 1. – Stress-strain curves of samples before and after thermal shrinkage.

Hydrogen bonds normally exist in a system of interconnections. They are additive and contribute greatly to the overall stability of systems such as the polypeptide polymers.⁷ Collagen is also a polypeptide polymer. Although hydrogen bond is very weak, its function cannot be neglected, because many hydrogen bonds may be formed between collagen fibers. Therefore, the initial elastic modulus and the tensile

strength are improved by thermal shrinkage. On the other hand, because this kind of extra cross-linking is weak, it may be broken easily when the samples are stretched and heated. The elongation at break is increased as a result, when being over-stretched. The decrease in the original length may contribute to the overall increase in elongation at break as

TABLE I

Mechanical behavior of leather samples before and after thermal shrinkage

Sample No.	E / MPa		σ_b / MPa		ϵ_b / %	
	Before shrinkage	After shrinkage	Before shrinkage	After shrinkage	Before shrinkage	After shrinkage
<i>a</i>	17.0	57.0	19.8	35.4	40.3	110.8
<i>b</i>	13.0	32.7	13.2	13.3	42.0	86.0
<i>c</i>	21.5	115.5	12.4	38.7	43.4	77.8
<i>d</i>	3.5	11.0	3.3	6.3	29.4	95.7
<i>e</i>	6.5	77.3	4.8	19.6	27.5	62.0
<i>f</i>	5.1	37.7	4.8	15.0	35.7	85.2

TABLE II

Aperture ratios of different samples before and after thermal shrinkage

Sample No.	Aperture ratio / %	
	Before shrinkage	After shrinkage
1	63.0	31.9
2	57.1	20.0
3	51.5	18.9
4	48.0	15.2
5	46.4	9.0
6	60.0	10.3
7	45.3	9.8
8	58.3	10.8

well.

Under thermal shrinkage, while the elastic modulus and the rigidity of leather are increased, the softness of leather is decreased. The result is that the shrunken leather may not be suitable for use as clothing material and the use value for clothing is lost. Although the mechanical behavior of leather is improved by thermal shrinkage, the leather may not be suitable for use in the traditional clothing field. Furthermore, the economical value is greatly diminished because of the reduction in area and volume. Even if the shrunken leather could be used in clothing, it would be greatly limited from the viewpoint of the economy. The comfortableness that leather clothing may provide is lost because of the decrease in softness. Therefore, in order to increase the economic value and the use value of leather products, many more studies should be done to improve the thermal stability, to reduce the thermal shrinkage ratios, and to increase the thermal shrinkage temperature. As the mechanical behavior of leather is improved by thermal shrinkage, new application fields

should also be explored for shrunken leathers.

Aperture Ratios

Changes in the aperture ratios of leathers by thermal shrinkage are shown in Table 2. It should be noted that sample 1 is the control sample without fatliquoring. Samples numbered 2-5 are fatliquored by the MK fatliquoring agent, with the fatliquoring amounts of 5 %, 10 %, 15 % and 20 % of the pigskin wet blues in weight. Samples numbered 6-8 are fatliquored by sulphited fish oil, sulfated castor oil, and BK, respectively. The amount of fatliquoring agents used here are all 20 % of the pigskin wet blues in weight. From Table 2, it can be found that, for all the samples studied, no matter whether they have been fatliquored or how much fatliquoring agents were used, the aperture ratios decreased to a great degree because of thermal shrinkage. For all the samples, the aperture ratios were 45 %-63 %. After thermal shrinkage, the aperture ratios decreased to 10%-30%. It is not difficult to understand the reason why the aperture ratios decreased so remarkably by thermal shrinkage. For leathers to be shrunken, the whole volume and area of the samples are reduced, and the distance between molecule chains is made shorter. Spare space in the samples decreases, and the aperture ratios are decreased as a result.

Collagen fibers will tend to tropism toward the force direction when the samples are stretched. Before thermal shrinkage, the aperture ratios of the samples are large, and there is much more space for collagen molecules to move when the samples are being stretched. The initial elastic modulus of samples before thermal shrinkage is small, as indicated in Figure 1 and Table 1. After thermal shrinkage, however, the aperture ratios of the samples decrease, and there is less space for collagen molecules to move while being stretched. Therefore, the elastic modulus was increased. When a force great enough is applied to the samples, the extra forces formed by thermal shrinkage, including hydrogen bonds between the collagen molecules, may be destroyed, and the aperture ratios are increased. Much more space is provided for the collagen

molecules to move and an obvious increase in elongation will occur. Also, the contribution of the decrease in the original length of the shrunken samples to the entire elongation at break should also be considered.

CONCLUSIONS

With thermal shrinkage the mutual forces between collagen molecules increase, while the aperture ratio decreases. The mechanical behavior, including the initial elastic modulus, the tensile strength, and the elongation at break of leather are all increased by thermal shrinkage. The improvement in mechanical behavior by hydrothermal shrinkage is at the cost of loss in utility and economic value of the leather. Studies should be performed to find new applications for (thermally) shrunken leather because of their excellent mechanical behavior.

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REFERENCES

1. Keyong Tang, Jie Liu, Fang Wang, et al. Dry heat resistance of hide and leather, *JALCA* **98**, 168-172, 2003.
2. Leather research section of Northwest Institute of Light Industry, Leather Analysis. Beijing: Light Industry Press, China 1996.
3. Keyong Tang, Fang Wang, Jie Liu, et al. Preliminary studies on the thermal degradation kinetics of cattlehide collagen fibers, *JALCA* **99**, 401-408, 2004.
4. Tang, Keyong, Wang, Fang, Liu, Jinglong, et al. Influence of sweat on hide and leather, *JS LTC* **91**, 30-35, 2007.
5. The hydrogen bond network, <http://polymer.bu.edu/Wasser/robert/work/node12.html>
6. H. Clark Metcalfe, John E. Williams, Joseph F Castka, et al. Modern Chemistry, New York : Holt, Rinehart and Winston, 1986 p168.
7. Role of Hydrogen Bonding on Protein Secondary Structure, <http://www.sas.upenn.edu/~caramboc/protein%20lesson.pdf>