Effect of Thermocycling on the Properties of Goat Skin Leather[#]

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Abstract: The pickled goat skins were tanned by chrome powder, aluminum salt, wattle extract and chestnut extract, respectively. The samples were thermocycled in a container held at different temperature with a dwell time of 5 h. The thermal stability, water vapor permeability and dimensional stability of the samples were characterized before and after thermal treatment. The effect of thermocycling on the properties of different tanned samples was discussed. It was found that the thermocycling at moderate temperature (50 ºC) exerted little influence on the xerothermic shrinkage temperature (Txs) of the tanned collagen fibers. The thermal treatment at higher upper limit temperature (100 ºC and 150 ºC) decreases the Txs and results in an impaired thermal stability. The decrease in xerothermic shrinkage ratio after thermocycling at higher temperature, however, is probably the result of the irreversible shrinkage of the weak parts in collagen fibers during the thermal treatment. The water vapor permeability was decreased after the thermal treatment, likely due to the reduction of the amount of hydrophilic groups of collagen macromolecules as well as the decrease of the pore ratio of the leather. The dimension of tanned leather samples was also decreased to some degree. Treatment at high temperature damaged the dimensional stability of the specimens.

Key words: collagen; thermocycling; properties

1 Introduction

Leather is a biomaterial made of collagen fibrous protein. In order to avoid putrefaction, collagen is usually industrially modified by tanning. The essence of leather tanning is to introduce extra strong and stable cross-links between adjacent collagen molecules so that the hydrothermal and mechanical properties of collagen fibers can be improved. In principle, the tanning efficiency of a tanning agent is critically dependent on its ability to form interfibril cross-links with great strength and extensiveness. The nature and strength of these crosslinkages vary considerably depending on the type of tanning material employed.

It is important to evaluate the impact of environment factor on the structure and properties of collagen materials. Examination of the literature suggests that factors that influence the temperature of denaturation (shrinkage) include: the content of imino acid of collagen and their hydroxylation and position in the chain[1], the content of water in the material[2], the pH[3], the nature of heating medium[4], the ionic environment[5], salt type and salt concentration[5], tanning/retanning[6] and ageing[7], etc. Leather products are sometimes used in environment with periodically varying temperature, which exert great influence on the structure and properties of collagen other than the constant one. However, little research work has been done to understand the influence of periodically varying temperature on the performance of leather product. In the present work, two metal complexes (chromium powder and aluminium salt) and two vegetable extracts (wattle extract and chestnut extract) were applied as tanning agents to endow the

[#] Supported by the National Natural Science Foundation of China (20676126, 20604026) and Natural Science Research Plan of Henan Province (2009A430016).

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collagen with extra crosslinking. The samples were thermocycled at different temperature for different cycles. The thermal stability, water vapor permeability, and dimensional stability of the samples were characterized before and after the thermal treatments, aiming to understand the effect of thermocycling on the properties of tanned collagen.

2 Experimental

2.1 Materials and Chemicals

Pickled goatskins were supplied by Heitian Mingliang Leather Co., Ltd., Xinxiang, China. Chrome powder (Cr_2O_3 content of 25% and basicity of 33%), wattle extract and chestnut extract, commercial grade, were supplied by Sichuan Decision Chemicals Co., Ltd., Deyang, China. The other chemicals, $Al_2(SO_4)_3$, NaCl, $NaHCO_3$, and sodium acetate are all analytical reagents.

2.2 Preparation of Tanned Samples

Tanning processes were carried out by using laboratory-scale tanning drums (DJDϕ350 tanning drum, Xibeitang Leather Machinery Company, Xishan, China). The tanning agents used are chrome power, $Al_2(SO_4)_3$, wattle extract and chestnut extract. Standard laboratory tanning conditions are applied for each tanning agent.

2.3 Thermocycling

All the samples were conditioned in a desiccator with relative humidity of 65% (controlled with 36.7 wt% H_2SO_4) for at least two weeks to a constant weight. The samples were thermocycled in a container held at 0~50, 0~100, 0~150, and -20~150°C with each dwell time of 5 h. One to four cycles of the thermocycling were applied to each sample.

2.4 Thermal Stability

The thermal behavior in this paper was characterized by the shrinkage temperature and the shrinkage ratio in the air dried state, in which state the structural properties of collagen and its supermolecular architecture are of great importance.[4,8] All the samples were conditioned in a desiccator with relative humidity of 65% (controlled with 36.7 wt% H_2SO_4) for at least two weeks to a constant weight. A single collagen fiber was separated carefully from the leather matrix. The XT5A optical microscope equipped with a heating platform (Beijing Keji Dianguang Instrument Factory, China) was used to characterize the xerothermic behavior of the collagen fibers. All measurements were conducted in air from room temperature to 350ºC at a heating rate of 5ºC/min. The length of the collagen fiber was recorded during the heating. A typical xerothermic shrinkage curve of shrinkage ratio vs. temperature is shown in Fig. 1. To distinguish it with hydrothermal shrinkage temperature, the xerothermic shrinkage temperature is abbreviated as Txs, which is defined as the peak point of differentiate curve of shrinkage ratio to temperature. The xerothermic shrinkage ratio (SR) was calculated as follows:

$$SR = \frac{L_0 - L_1}{L_0} \times 100\%$$

Where SR is the shrinkage ratio, L_0 is the original length of the fiber, and L_1 is the length after shrinkage.

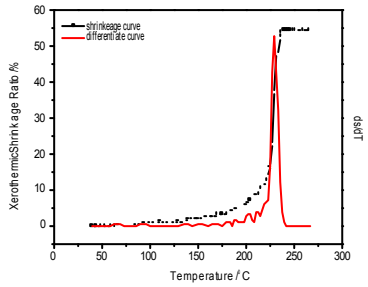

Fig. 1 A typical xerothermic shrinkage curve of collagen fiber

2.5 Water Vapor Permeability

All the samples were conditioned in a desiccator with relative humidity of 65% (controlled with 36.7 wt% H_2SO_4) for at least two weeks to a constant weight. Water vapor transmission rate (WVTR) was measured by permeation cup method. Fill the stainless steel cup (body diameter of 45.0 mm and top diameter of 30.0 mm) with 50 mL distilled water. The leather sample was mounted to the top of the cup. An O-ring was used to hold the sample in place. After taking initial weights of the test cup, the cups were placed in a desiccator cabinet with 98 wt% H_2SO_4. Weight loss measurements were taken by weighing the test cup with an electronic scale after 24h of incubation. WVTR was calculated as follows:

$$WVTR=(w_1-w_2)/At\ (mg/(10cm^2\cdot 24h))$$

where w_1 is the weight of the cup before test (mg), w_2 is the weight of the cup after 24h of incubation (mg), A is the area of exposed film (7.07 cm^2), and t is the time of experiment (h). There were at least three repetitions per experiment.

3 Results and Discussion

3.1 Xerothermic Stability

The leather samples were thermocycled at 0~50°C, 0~100°C, 0~150°C and -20~150°C for different cycles. A single collagen fiber was carefully separated from the matrix and the xerothermic stability was characterized. The xerothermic shrinkage temperature (Txs) and shrinkage ratio are presented in Fig. 2 and 3.

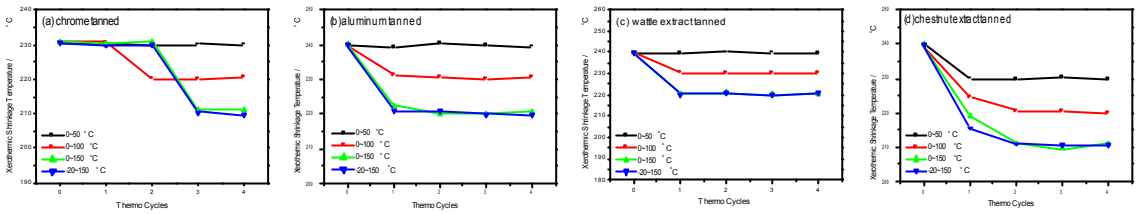

Fig. 2 Xerothermic shrinkage temperatures of tanned collagen fibers before and after thermocycling

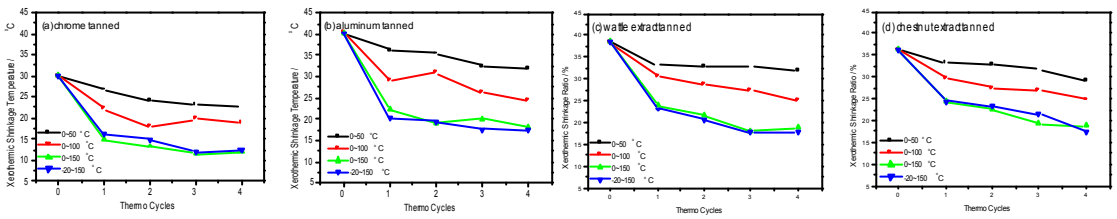

Fig. 3 Xerothermic shrinkage ratios of tanned collagen fibers before and after thermocycling

It is seen that, in general, thermocycling at 0~50°C exerts little influence on Txs of the tanned collagen fibers but decreases the xerothermic shrinking ratio to some degree. Decreased shrinkage ratios are usually related to an improved thermal stability. It is deduced that the thermal treatment in this moderate temperature zone may result in a more uniform structure of the samples, and therefore, a lower shrinkage ratio. The thermocycling at higher upper limit temperature (0~100 ºC, 0~150 ºC and -20~150 ºC) change both Txs and shrinkage ratio obviously. A fall in Txs indicates an impaired xerothermic stability. It is seen that thermocycling at higher upper limit temperature leads to a weaker xerothermic resistance of collagen fibers. It is well known that hydrogen bonds are electrostatic and their stability strongly depends on temperature. When treated at the dramatically varied temperature, part of the hydrogen bonds in the collagen fiber network may be destroyed and recomposed. On the other hand, supplying external heat to collagen transfers kinetic energy to it. This externally applied energy causes an increase in molecular movement which increases the rate of collision between adjacent molecules and thus increases the rate of reaction. The thermocycling may bring about oxidative degradation of the collagen and cause breaks in the backbone chain of the molecule and changes to the chemical composition of the side chains[9]. These may lead to a reduction in Txs. However, a dramatic decrease in the shrinkage ratio is also found for all the samples after the thermal treatment at 0~100 °C, 0~150 °C and -20~150°C (Fig. 3). A lower shrinkage ratio is usually related to the improved thermal stability, which is obviously inconsistent with the decreased Txs. It is deduced that part of the weak links in the collagen may shrink during the treatment at high upper limit temperature. Due to the fact that the denaturation (shrinkage) of protein is irreversible, the already partly shrunk collagen fibers, which have shorter length, would shrink less during the xerothermic stability characterization and show a reduced shrinkage ratio.

Among the four tanning agents investigated, chromium-tanned collagen fibers seems having better resistance to thermocycling than the rest three tanning agents. The Txs shows little change for chromium-tanned samples treated at all temperature for 1 cycle (Fig. 2a). Only after being treated for more than 2 cycles, does Txs decrease dramatically.

3.2 Water Vapor Permeability

Water vapor permeability is an important property of leather to make successful breathable materials. Fig. 4 shows that the thermocycling results in a dramatic decrease in water vapor transmission rate (WVTR). It is seen that WVTR of all the samples decreases with the increase of upper treating temperature. Furthermore, there is a steady decrease in WVTR with the thermo cycles. It is known that, in a controlled environment, the dominant parameters that may influence the WVTR include the crystallinity, the amount of hydrophilic groups and the pore characteristics of the material, e.g. pore volume, pore size, pore size distribution and pore microstructure. It is deduced that the amount of polar groups of collagen macromolecular chain may decrease due to the potential reaction during the treatment at high temperature, which is obviously not in favor of the adsorption and diffusion of water vapor molecules throughout the samples. Furthermore, the less stable structure of collagen may shrink during the thermal treatment, leading to a reduced pore ratio of the matrices and, therefore, a reduction of water vapor transmission rate.

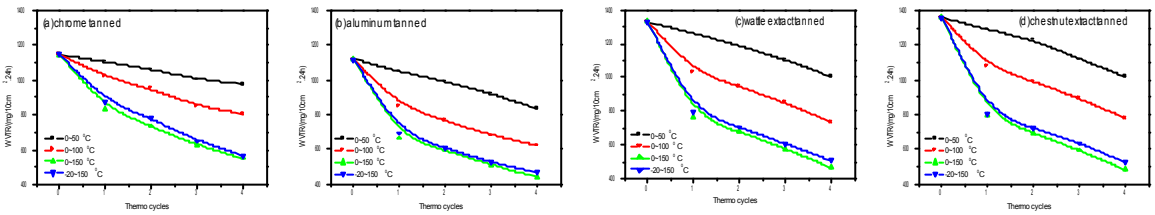

Fig. 4 Water vapor transmission rates of tanned leather samples before and after thermocycling

3.3 Dimensional Stability

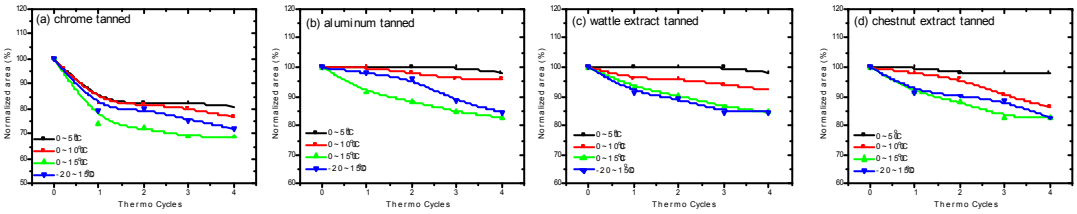

Fig. 5 Normalized sample areas of tanned leather samples before and after thermocycling

Products with a stable dimension are required in many applications. The area of each sample was measured before and after thermocycling and the normalized areas are illustrated in Fig. 5. It can be seen that a steady decrease in the area of the leather matrices was found after thermocycling, especially after being treated at higher upper temperature. It is deduced that the shrinkage of the weak parts of tanned collagen fibers during the thermal treatment results in a decreased sample dimension. This is accordant to the decrease in water vapor transmission rate discussed above.

4 Conclusions

The influence of thermocycling on the properties of tanned leather samples has been investigated. The thermal treatment at moderate temperature does not change the xerothermic shrinkage temperature of collagen fiber obviously, while decreases the xerothermic shrinkage ratio to some degree. The thermal treatment at higher temperature impairs the xerothermic stability of the samples. Part of the weak links in collagen macromolecular chains may shrink during the thermocycling and results in the decrease in shrinkage ratio of collagen fibers. The thermocycling treatment decreases the water vapor permeability. Water vapor permeability decreases continuously with the thermo cycles. The dimensional stability of the samples is also impaired after thermocycling treatment.

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