Water Absorption Mechanism of Goatskin Collagen Fibers#

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Abstract: Goatskin collagen fibers were tanned by chrome, glutaraldehyde and chestnut extract, and the chrome-tanned sample was fatliquored with emulsified chlorinated paraffin, granulesten and sulphitated granulesten. The water adsorption behaviors of the different tanned and fatliquored goatskin collagen matrices were systematically studied. The water absorption mechanism at different temperatures was also investigated and discussed. Gravimetric analysis was used to obtain water absorption capacity of goatskin collagen fibers. It was found that the water absorption process of collagen fibers can be divided into two individual stages: pre-stage, water absorption capacity reaches or close to the maximum rapidly; after 2-4 hours of adsorption, water adsorption reaches equilibrium level with a lower adsorption rate. Particularly, the water absorption capacity of un-tanned and chestnut extract tanned samples decrease in the second stage. In all the tanned samples investigated, chestnut extract tanned sample has the largest water absorption capacity, while emulsified chlorinated paraffin fatliquored one shows the largest capacity in all the fatliquored samples. Water absorption capacity does not increase with the increase of temperature. Samples show the largest absorption capacity at 20 ºC and the smallest at 40 ºC, while in between at 0 ºC and 30 ºC.

Key words: collagen fibers; water absorption mechanism; tanning; fatliquoring

1. Introduction

Collagen is the most abundant protein in higher vertebrates [1]. It is the major structural component of the connective tissue matrix and an extracellular matrix protein that has an essential role in maintaining the architecture of multicellular organisms as well as having important industrial uses as leathers, sutures, implants and prosthesis. Collagen sequences are characterized by the repetition of triplets of the Gly-X-Y. The positions X and Y of triplets are frequently occupied by iminoacids (Pro and 4R-Hydroxy-2S-proline (Hyp)) [2].

It is well known that collagen is the main composition of skin and leathers. Goatskin has high

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concentration of Type I collagen, around 85% of the dry biomass. It has a strong interaction with water on the numerous hydrophilic groups, such as hydroxyl, carboxyl and carbonyl groups. Hydration properties of protein including water adsorption, wettability, water keeping capacity and swelling. Nomura and his co-workers identified four regimes in the hydration of collagenous tissue from changes in the dynamic mechanical parameters with water content. They suggested that the first water which was associated with structural water sorbed by collagenous tissue, is incorporated into the triple helix, and that the bound water subsequently imbibed is associated with the polar side chains and is located in the interhelical regions within the collagen fiber, and finally the free or freezable water constitutes, with the mucopolysaccharides, the interfibrillar matrix gel [3]. Triple-helical domains in collagenous and non-collagenous proteins contain significant amounts of the unusual imino acid Hyp(hydroxyproline). There are three distinctive carbonyl groups per tripeptide unit. Carbonyl groups from Hyp residues have two hydration sites whereas only one gyration site appears for carbonyl groups of glycine. The hydroxyl group from Hyp residues has both hydrogen-bond donor and acceptor properties. Thus, double hydration would be expected [4]. It is demonstrated that Hyp residues play a critical role in stabilizing the triple-helical conformation, both in collagen [5] and in synthetic peptides with collagen-like sequences [6]. In the presence of excess water, a polymer may become swollen, exhibiting major changes in mechanical and chemical properties. Water can plasticize the polymer matrix or form stable bridges through hydrogen bonging, resulting in an anti-plasticizing effect [7]. At present, most of the computational studies on collagen-like peptides have been focused on iminoacid-rich sequences [8].

Leather is an intermediate industrial product with numerous applications in downstream sectors. It can be cut and assembled into shoes, clothing, leather goods, furniture and many other items of daily use [9]. Tanning is the most convenient and efficient way to increase the usability of leathers. Different kinds of tanning agents used in leather-making may provide leathers with different properties and styles. In the fatliquoring process, oils/fats are employed as oil in water emulsion known as fatliquoring agent. Fatliquoring agent may be anionic, cationic or non-ionic [10]. Accordingly, different tanning agents and fatliquors have the various influences on the water absorption capacity of leathers respectively.

In the paper, the water adsorption behaviors of different tanned and fatliquored goatskin collagen matrices were systematically studied. The water absorption mechanism at different temperatures was also investigated and discussed.

2 Experimental procedure

2.1 Main materials and apparatus

Pickled goatskins were supplied by Hetian Mingliang Leather Co., Ltd., Xinxiang, China. Chrome powder and chestnut extract, commercial grade, were supplied by Decision Chemicals Co., Ltd., China. The other chemicals, NaCl, $NaHCO_3$, K_2SO_4 and sodium acetate are analytical reagents.

2.2 Procedures

Goatskin collagen matrices were tanned and fatliquored in tannery machine, DJDΦ35, Xishan Northeast Tangkuang moutain Leather Machinery Factory. The sample's porosity was measured using the appropriate method. The samples were cut into pieces of 40mm×20mm after drying to constant weight. Then put the small pieces dip in water, and note the weight of small sample under a certain interval of time and temperature.

3 Results and discussion

3.1 The difference of porosity

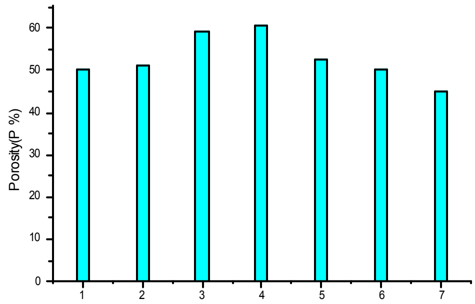

Fig. 1. Porosity of different samples, 1(untanned), 2(chrome tanned), 3(glutaraldehyde tanned), 4(chestnut extract tanned), 5(emulsified chlorinated paraffin fatliquored), 6(granulesten fatliquored), 7(sulphitated granulesten fatliquored)

The porosity of different samples is presented in Fig. 1. As a natural polymer matrix composite, leather has many unique properties due to the plenty of natural microporous in fibers. Leather porosity mainly depends on the original organizational structure of collagen fibers. The combination of tannin and filling also affects the real density of leathers in tanning and fatliquoring process. Fig. 1 suggests that chestnut extract tanned sample and emulsified chlorinated paraffin fatliquored one has the biggest porosity among all the tanned samples and fatliquored samples, respectively. Tanning increases the porosity of the sample, whereas the porosity of fatliquored samples is lower than the corresponding chrome tanned one. This may be because of the different tanning mechanism, as well as the amount of tanning agents and fatliquoring agents used in the experiment.

According to Kelvin equation [11],

$$RT\ln(\rho_r / \rho_o) = 2\gamma V / r \tag{1}$$

The smaller the capillary diameter is, the higher the additional pressure value is and the more beneficial will have on capillary effect. The speed for collagen fibers to adsorb water is determined by the diameter and the density of capillary. The speed of water adsorption among different samples just had a little difference according to Fig. 2 and Fig. 3. It indicated that tanning and fatliquoring process did not affect the diameter of capillary obviously. The surface area of sample mainly depends on the porosity when the diameter of capillary is constant. The surface area of sample determines the water adsorption capacity.

3.2 The water adsorption capacity of goatskin collagen matrices at different temperatures

Plotting all of the date for each sample in the experiment revealed that tanning and fatliquoring reduced the water adsorption capacity of goatskin collagen matrices. From the curves of Fig. 2 and Fig. 3, the process of water adsorption may be divided into two stages: pre-stage, water absorption reaches or close to the maximum rapidly; after 2-4 hours of adsorption, water adsorption reaches equilibrium with a lower adsorption rate. Chestnut extract tanned sample has the largest water absorption capacity in all the tanned samples investigated, while emulsified chlorinated paraffin fatliquored one shows the largest water adsorption capacity in all the fatliquored samples. In the second stage, the water adsorption capacity of un-tanned sample and chestnut extract tanned one show a downtrend phenomenon.

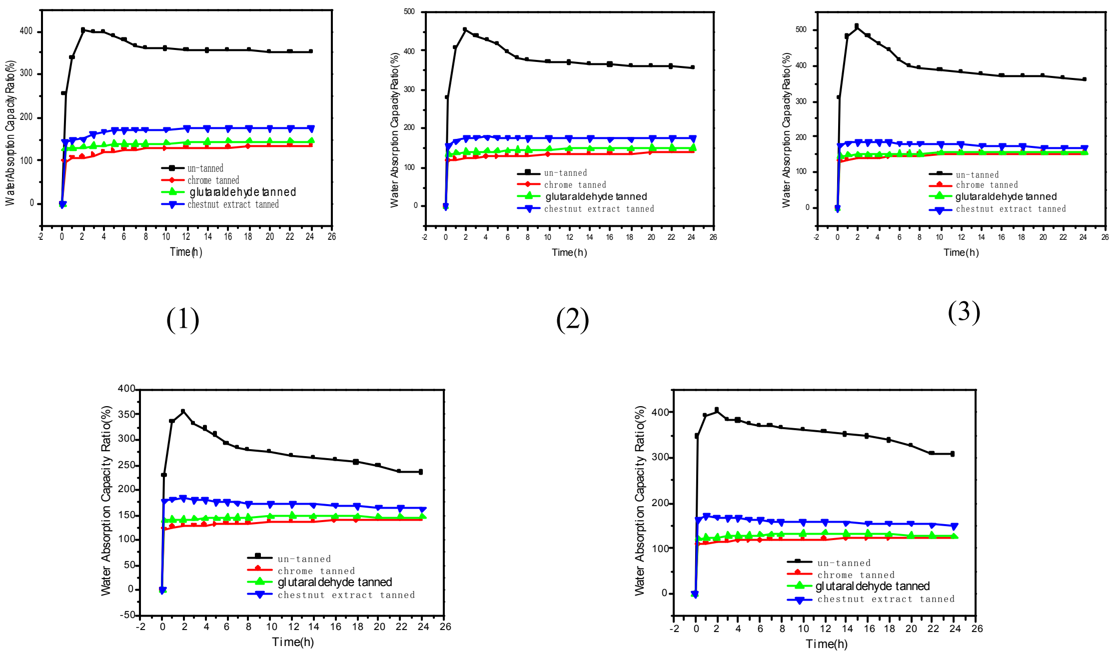

Fig. 2 Water adsorption curves of un-tanned and tanned samples at different temperatures, (1) 0 °C, (2) 10 °C, (3) 20 °C, (4) 30 °C, (5) 40 °C

The differences of water adsorption capacity between un-tanned and tanned samples are presented in Fig. 2. In the process of tanning, tanning agents penetrated into the collagen fibers and destroyed part of inner polar action or hydrogen bonds, to combine with the collagen fibers in a special way and played an important part in the stabilization of collagen fibers structure. Tanning increased the degree of crosslinking of collagen matrices. The structure of collagen fibers was changed. It is not easy for tanned collagen matrices to swell. The water adsorption capacity of samples was subsequently reduced. The water adsorption capacity of un-tanned sample was reduced in the second stage. It may be due to the changes in the structure of sample after water swelling, which resulted in swollen, solvent, dispersed and dissolved of collagen.

The difference in combination stability between tanning agent and collagen fibers mainly depends on difference of tanning mechanism. The cross-linking between goatskin collagen matrices and chrome complexes was formed mainly by two or more points coordination between chromium(III) complexes and carboxyl on the collagen side chain. In all the single tanning agent methods, chrome tanning is the most stable and popular one. The mechanism of chestnut extract tanned is mainly hydrogen-bond combination, and glutaraldehyde tanned is mainly covalent combination. The combination stability between tanning agent and collagen fibers of glutaraldehyde tanned and chestnut extract tanned samples are weaker than chrome tanned one. It is indicated that chrome tanned sample has the smallest capacity in all tanned samples investigated, which is consistent with the above illumination. Hydrogen-bond combination mechanism of chestnut extract tanning determined the downtrend phenomenon of sample in the second stage.

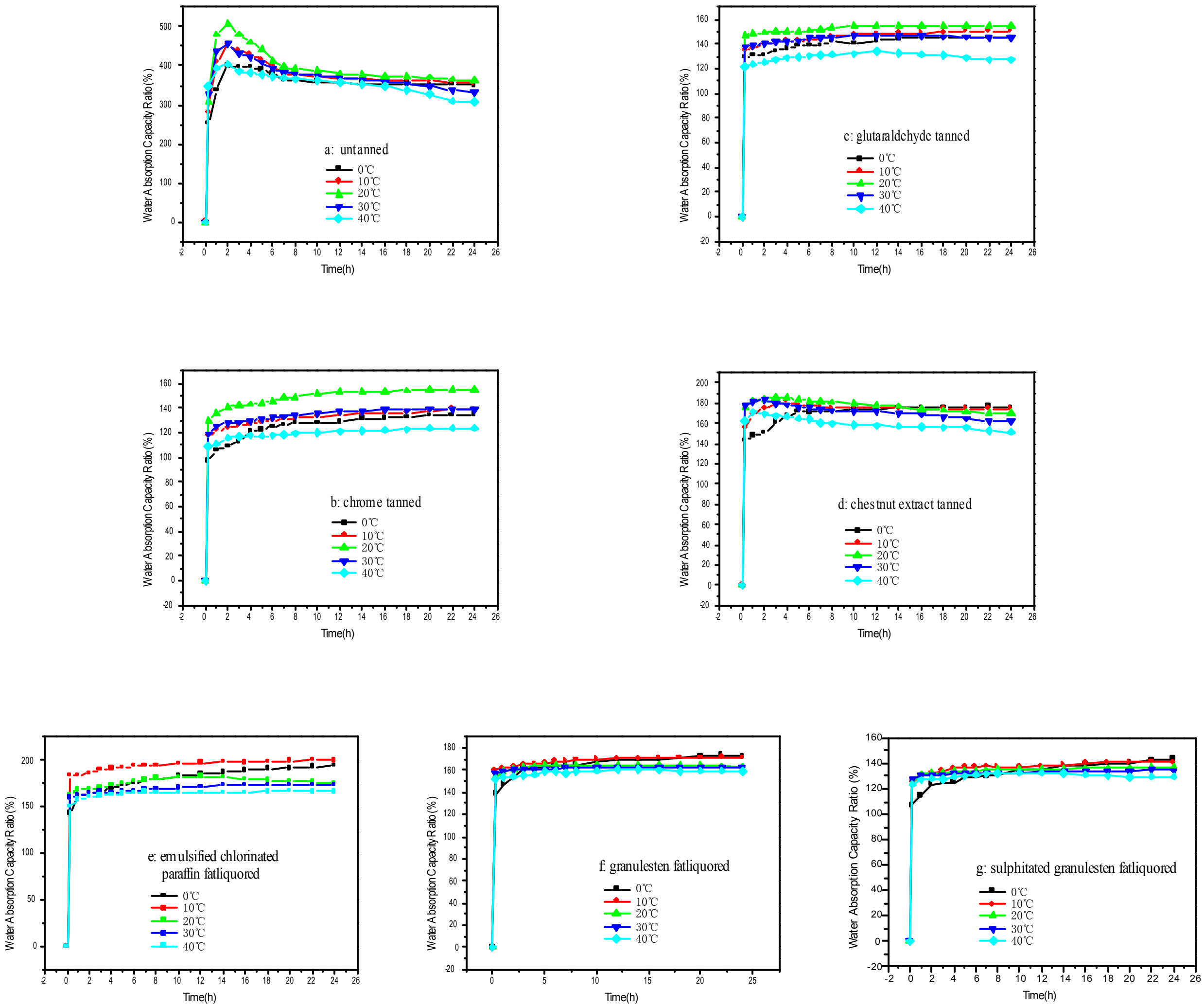

Fig. 3 Water adsorption capacity of goatskin collagen matrices at different temperatures

The water adsorption curves of goatskin collagen matrices at different temperatures are shown in Fig. 3. For un-tanned and tanned samples, the largest absorption capacity appeared at 20 ºC and the smallest one appeared at 40 ºC. For fatliquored samples, the largest absorption capacity appeared at 10 ℃ and the smallest one appeared at 40 ℃. The activity of water molecules and collagen fibers increases with the increase of temperature, and the water adsorption rate and capacity of samples increases accordingly. The water adsorption is an exothermic process from the viewpoint of thermodynamics. The lower the temperature is, the more the capacity of water adsorption is. The water adsorption capacity does not strictly increase with increasing the temperature because water adsorption is essentially a process of adsorption. Furthermore, the change in temperature affects the structure of collagen fibers, which may change the water adsorption capacity. The water adsorption mechanism of goatskin collagen matrices is very complex, and the subsequent research is still being done.

4 Conclusions

The water adsorption behaviors of goatskin collagen matrices are very complex. Tanning reduces the water adsorption capacity of goatskin leathers. In all the tanned samples investigated, chestnut extract tanned sample has the largest water absorption capacity, whereas chrome tanned one has the smallest. Emulsified chlorinated paraffin fatliquored sample possesses the largest capacity in all the fatliquored samples. The water adsorption capacity of goatskin leathers strongly depend on the capillary in them. In the second stage, the water adsorption capacity of un-tanned sample and chestnut extract tanned sample shows a downtrend phenomenon.

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