Modification of the materials based on protein fibers in a low-pressure high-frequency plasma flow

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Abstract. The effect of low-pressure high-frequency (HF) plasma treatment on the structure of the materials formed by bundles of natural protein (collagen) fibers is considered. The outer surface of the material is being affected by a constant flow of ions and a pulse-periodic flow of electrons. During this procedure the electrons flow at opposite sides of the sample in antiphase. This leads to that an alternating electric field is created, which intensity is estimated approximately at 105 V/m, inside the material. As a result, in the capillaries and pores, a breakdown occurs and charged particles are forming during this process. The recombination of these particles releases an energy of 15.76 eV on the surface of pores and capillaries, which is transferring to the surface molecules of the protein, which leads to the bulk modification of the material based on protein fibers. Such volumetric processing provides an effective modification of structural elements, allowing you to significantly improve the quality of liquid treatments in the production of collagen-containing materials and their properties in general.

1. Introduction

Modification of materials of various nature with the help of low-pressure RF plasma is a current area of research. Materials based on natural protein fibers, which have a complex structural organization, so as the dermis (the main layer of the animal skin) has a multi-level system formed as a result of interweaving bundles of collagen fibers, the fibers themselves and the fibrils and subfibrils that form them [2].

The most complete picture of the changes taking place as a result of plasma treatment can be obtained on the basis of studies of the structure of the leather material.

Materials and methods

As objects of our research, samples of the dermis of sheepskin skins were considered in the work. An experimental high-frequency low-pressure capacitive discharge plasma unit was used to modify materials based on protein fibers. The evaluation of the results of modification of materials based on protein fibers by high-frequency low-pressure plasma was carried out in terms of the welding temperature and the degree of change in the dimensions of the structural elements of the dermis.

2. Results

Traditionally, technological processes, during the obtaining semi-finished leather products from animal skins, can be divided into two categories. The first category includes processes aimed at separating the collagen structure (soaking, ashing, pickling, etc.). The second category is aimed at fixing the resulting structural organization (tanning, retanning, etc.). It should be noted that the first group of processes is characterized by a decrease in the welding temperature, and the second, on the contrary, by an increase in this indicator. (figure 1)
It was found that HF plasma treatment of a material based on natural protein fibers (collagen) occurs due to the following factors. Ions with the energy of 70-100 eV are bombarding the outer surface of a material. And a burning non-self-sustaining discharge in the supramolecular interstructural space causes recombination of ions on the surface of capillaries and pores which leads to volumetric processing of materials. The transfer of energy to the atoms of the near-surface layer of the material leads to the removal of contaminants, the rupture of some of the non-valent bonds, which makes it possible to change the conformation of protein molecules and leads to the separation of the supramolecular structure of collagen [1].

With the help of electronic microscopy, a comparative assessment of the structural elements of the dermis of control (untreated with plasma) and experimental (treated with plasma) samples was carried out. It was found that the fibers of unmodified samples are characterized by a denser arrangement of fibrils, with an average fibril diameter of 103 nm and an interfibrillar distance of 5.5 nm. In the case of HF plasma modification of the samples, the average fibril diameter is 124 nm, and the interfibrillar distance is 39.1 nm, which indicates an increase in the fibril diameter by 20%, and the interfibrillar distance - by 7 times. These changes provide a deeper diffusion of working solutions, which improves the efficiency of technological processes.

To confirm this assumption, measurements were made of the temperature of dermal welding, which is a characteristic of the degree of structuring of the material. A sample of material based on protein fibers treated with HF plasma was characterized by a lower welding temperature compared to the control sample from the soaking to the pickling included (figure 2), which indicates a better flow of these processes as a result of deep and uniform diffusion of working solutions deep into the dermis. As a result, the welding temperature rises after the tanning process, which is a prerequisite for obtaining a semi-finished product with higher strength properties.

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**Figure 1** – The change in the temperature of derma welding during the technological cycle of semi-finished leather production.
Figure 2 – Changes in the derma welding temperature during the technological cycle of semi-finished leather production (blue color - without plasma processing of raw materials, red color - with plasma processing of raw materials).

3. Conclusion.
Thus, the modification of materials based on natural protein fibers with the use of low-pressure RF plasma allows for a better separation of the supramolecular structure of the material. Such changes in the structure increase the efficiency of subsequent treatments and, as a result, obtain a semi-finished leather product with higher mechanical properties.

References
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