Nonequilibrium low temperature plasma in process of collagen containing polymer materials electrical properties modification

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Abstract. The process of treatment with nonequilibrium low temperature plasma allows to reduce collagen materials electric potential due to charges dissipating along leather surface. Under certain conditions the main reason for the generation and accumulation of static electricity is the high hydrophilicity of the material. Leather surface hydrophobization is achieved through water repellent application and bulk nonequilibrium low temperature plasma treatment. Despite material surface hydrophobization nonequilibrium low temperature plasma processing parameters for genuine collagen containing polymer materials hygroscopicity increase are determined. Collagen containing polymer materials plasma treatment also increases its biological compatibility and antimicrobial properties, improves mechanical characteristics by changing the internal structure of the material.

1. Introduction
High molecular weight leather materials are capillary porous polymers. Genuine collagen containing polymer materials are in stable high demand for the production of goods and products of textile industry [1,2]. One of the main consumer properties of textile industry goods determining its value and competitiveness in the international market is reliability and safety in consumption [3-6]. Currently, Russian textile industry attracts an increasing number of experts from various fields of production. There is an active discussion of ways to solve growing problems in the industry, which include the lack of competitiveness of domestic goods, the active growth of dependence on imports of raw materials and finished products. The same problems were encountered with goods related to special products, which include footwear. Reliability and safety of leather footwear are the first level comprehensive indicators. Reliability is determined by properties such as reliability, durability and maintainability. Indicators of the second level of consumption safety are mechanical, electrical, chemical and biological safety.

The electrical safety of footwear is associated with the use of artificial materials for its manufacture. The large electric charge accumulated by such materials negatively affects the human body. Genuine leather, unlike artificial materials, has significant advantages [7]. The electrification of genuine leathers is much lower, but the package of materials is also able to accumulate an electric charge. Nonequilibrium reduced pressure low temperature plasma processing (LTP) of collagen materials allows to reduce the electric potential by dissipating charges on material surface [8,9]. These properties make footwear possible and safe for application as special goods in industries with increased risk.
2. Research methods
The studies were carried out with experimental high-molecular-weight leather materials made by two technologies: nanostructured samples (genuine materials that were processed by low pressure nonequilibrium LTP at the final stage of finishing production), nanomodified samples (genuine materials that at the stage of fat liquoring, during coating dyeing and applying the coating film fixer a biocidal agent, a solution of silver nanoparticles 0.2% was introduced twice, and at the stage of finishing production materials were processed by LTP).

The plasma torch with flat electrodes for receiving a flow of a nonequilibrium low temperature capacitive type plasma is two water-cooled copper plates 20x30 cm in size or 40 cm in diameter [10,11].

The platform chamber construction with an equipment for studying its processing and exposed material properties unlike inductive coupled makes treatment to disseminate in bulk throughout all porous surface [12].

A capacitively coupled plasma system is driven by radio-frequency (RF) power supply at 13.56 MHz [13-17].

The SurPASSTM 3 analyzer, Anton Paar GmbH, measurements were made to find out the zeta potential of control leather samples of cattle hides processed by LTP, as well as modified by LTP with silver to evaluate the electrical properties of the material.

IR spectroscopy studies of collagen containing polymer materials control samples and samples processed by LTP were carried out to evaluate effect on leather chemical composition after plasma treatment [18].

3. Results and discussion
The results of measuring the relative permittivity using a SurPASS™ 3 analyzer, Anton Paar GmbH of collagen containing polymer materials control samples are shown in Fig. 1. Genuine leather of cattle hides processed by nonequilibrium LTP and modified by LTP with silver were studied along with control untreated sample.

![Figure 1. Relative permittivity of control collagen containing polymer material samples processed by LTP and modified by LTP with silver.](image)

Fig. 1 shows that relative dielectric permeability of the samples processed by LTP is below the control and decreases over time. Under certain conditions the main reason for the generation and accumulation of static electricity is the high hygrophilicity of the material. Hydrophobization of collagen containing polymer materials surface, i.e. giving water-repellent properties is achieved through the use of a water repellent and bulk processing by LTP [19]. Despite the material surface hydrophobization LTP parameters for collagen containing polymer materials hygroscopicity increase are determined.

Hygroscopicity depends on the porosity of the structure and the hydrophilicity of its protein fibers. The hygroscopicity was determined as a percentage by the increase in the mass of samples aged at 100% air humidity for 16 hours. The measurement results are presented in Figure 2.
Figure 2. Change in the hygroscopicity index collagen containing polymer material samples as a function of discharge power ($G_{Ar} = 0.04$ g/s, $t = 3$ min).

The results presented in Figure 2 show that the best mode for collagen containing polymer materials hygroscopicity increase is $W_p = 1.6$ kW, $P = 26.6$ Pa, $G_{Ar} = 0.04$ g/s, $t = 3$ min. It is associated with the dispersion and splitting of fiber bundles (the value of the control is 18%). High-energy and thermal effects increase with an increase in the discharge power. This leads to a densification of leather structure and hygroscopicity decreases.

RF LTP plasma treatment contributes to a change in the hydrophilicity of the material, which is associated with a change in the spatial conformation of the macromolecule in the bulk of the material. It was found that plasma treatment does not lead to a change in the chemical composition of the material, as evidenced by the identical spectral patterns for the control and experimental samples, shown in Figure 3.

Figure 3. IR spectroscopy of control collagen containing polymer material samples before and after processing by LTP.

The results of IR spectroscopy studies (fig. 3) show that genuine leather materials of cattle hides processing by reduced pressure LTP makes it possible to control the hydrophilic properties of the material without changing its chemical composition.

In turn, genuine leather plasma treatment also increases its biological compatibility and antimicrobial properties [20], improves mechanical properties without changing chemical composition of the material. Collagen containing polymer materials processing by nonequilibrium LTP allows to increase their operational performance and extend final product life.

4. Conclusions
Based on the experiments it can be concluded that collagen containing polymer materials made of cattle leather hides treatment by nonequilibrium low temperature reduced pressure plasma leads to electric potential decrease by dissipating charges through the surface. The magnitude of zeta potential determines the degree and nature of the interaction between the particles of the system. Despite the material surface hydrophobization the parameters

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![Graph showing hygroscopicity change](image)
of nonequilibrium LTP for genuine collagen containing polymer materials hygroscopicity increasement without changing the chemical composition of the materials are determined. Thus, the potential of the sample subjected to plasma modification by nonequilibrium reduced pressure LTP is significantly lower than the sample from the control batch. It determines safety and reliability of the final products during operation.

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