Modification of semi-finished rabbit pelts by low-temperature plasma

A R Garifullina¹, V A Sysoev¹, G G Lutfullina¹, V P Tihonova¹, O P Kuznetsova², R A Nasirova¹ and A E Astafeva³

¹ Department of Plasma Technology and Nanotechnology of High Molecular Weight Materials, Kazan National Research Technological University, Kazan, 420015, Russia
² Department of technology of paints and coatings, Kazan National Research Technological University, Kazan, 420015, Russia
³ Department of Foreign Languages in Professional Communication, Kazan National Research Technological University, Kazan, 420015, Russia

E-mail: garalf@inbox.ru

Abstract. The influence of the effect of plasma processing and non-isocyanate urethanes on the skin of rabbit pelt has been investigated. Synergistic effect of modification resulting in the change of microstructure of high-molecular material and increasing chemical activity of collagen is established. In order to study the regularities of plasma effect on the skin of rabbit pelt the following indicators were determined: heat resistance temperature, relative moisture content (in mass), strength characteristics.

1. Introduction

Technological improvement that takes into consideration advanced achievements of Russian and foreign science is the most important requirement for the work of a successful company.

Among the different methods of modifying natural high molecular weight fibrous materials, chemical modification is of particular importance and it makes it possible to carry out targeted changes in structure and properties at the nanoscale level. Much attention is paid to plasma processing methods, which, in turn, allow to intensify liquid processes of leather and fur manufacture. Chemical modification in combination with plasma processing of material in high-frequency capacitive discharge can solve problems associated with operational characteristics, as well as a number of technological problems (reducing the time of liquid processing, reducing the concentration of chemicals used, reducing the wastewater) [1-3].

2. Materials and methods

Semi-finished rabbit chrome tanning was used as an object for research. Semi-finished rabbit is used in dyed, sheared, natural form, both for outerwear and as a lining material. This type of semi-finished material has a significant defect – its skin is penetrated by a large number of bursa pili and has low physical and mechanical characteristics. An analysis of various methods of capillary-porous materials processing suggests the usefulness of technologies using electrophysical and chemical modification methods. The synergistic effect obtained with this modification can be very significant. The use of chemically active, completely water-soluble non-isocyanates (urethane glycol (UG), ethylenediamine-based urethane glycol (ED-based UG) and urethane-formaldehyde oligomer (UFO)) will improve not...
only the strength properties of skin of rabbit pelt, but due to their structural ability will eliminate chrome tanning agent while retanning [4, 5].

The plasma processing of the semi-finished rabbit under optimal conditions for this type of semi-product was carried out. The processing was performed using a pilot plant of high-frequency capacitive discharge under reduced pressure (see Table 1).

### Table 1. Modes of plasma processing of the semi-finished rabbit pelts.

| Characteristics | Pressure, Pa | Argon flow rate $G_{ar}$, g/s | Processing time, min | Electric current $I_a$, A | Voltage U, kV |
|-----------------|-------------|-------------------------------|----------------------|--------------------------|--------------|
| Mode 1          | 30          | 0,04                          | 3                    | 0,39                     | 3,5          |
| Mode 2          | 30          | 0,04                          | 3                    | 0,4                      | 4,0          |
| Mode 3          | 30          | 0,04                          | 3                    | 0,55                     | 5,0          |
| Mode 4          | 30          | 0,04                          | 3                    | 0,68                     | 5,5          |

### 3. Results and discussion

To determine the effect of plasma processing on the penetrating ability of non-isocyanate urethanes, the samples after the tanning process were treated in UG, UGD, UFO solutions $5g/dm^3$ for 2 hours at the temperature of 25 °C [6, 7]. The process was controlled according to the cure temperature of the skin of rabbit pelts. After plasma modification the maximum increase in the cure heat resistance of samples up to 85 °C is achieved compared with the control samples, the heat resistance temperature of which is 75 °C (Figure 1).

![Figure 1. – Heat resistance temperature of the skin of rabbit pelts samples after plasma processing](image)

The obtained experimental data confirm the hypothesis about an increase of non-isocyanate urethanes diffusion into the dermis thickness of the samples after plasma modification. The decrease in water absorption time in modes 3 and 4 is associated with conformational changes in the fibrous structure of the porous material while high-frequency capacitive processing. It has been established that the changes in the ability of capillary-porous materials to absorb solutions result from exposure to a low-temperature plasma. The ability to absorb solutions changes both by diffusion of solution molecules and by mechanical capture of liquid particles by pores of high molecular weight material. Plasma modification results in the separation of dense sections of the dermis of the capillary-porous
material forming microcapillaries while the hydrophilicity increases (Figure 2). In turn, this results in increasing of water absorption as well as the number of reagents dissolved in the liquid, non-isocyanated urethanes in particular. This explains the increase in the heat resistance temperature for samples subjected to the processing by UG, ED-based UG and UFO.

An increase in hydrophilicity (Figure 1) can occur due to several reasons. During plasma modification, contaminants are removed from the surface. Macropores are cleaned by removing fatty substances, as well as by breaking transverse hydrogen bonds between hydroxyl and peptide groups, since the energy of plasma ions of 20-90 eV is sufficient for this.

![Figure 2](image1.png)

**Figure 2** – Microphotographs of rabbit skin slice after plasma processing: a) of control sample; b) of sample processed by ED-based UG; c) of sample processed by UFO.

![Figure 3](image2.png)

**Figure 3** – Indicator of porosity of rabbit skin after plasma modification and processing by non-isocyanate urethanes.

The formation of microcapillaries in the rabbit skin is confirmed by the values of porosity indicators (Figure 3). They were determined after drying under natural conditions up to a final value of moisture content in the samples not more than 14%. The obtained data correspond to GOST 2974-75 (Russian National Standard). Skin properties such as air permeability, heat conductivity, vapour permeability, water absorption and water permeability are closely connected with porosity. These properties are very important for the hygienic characteristics. Porosity measurement of the control and
Experimental samples showed larger degree of fixation of the dermis porosity after it is processed by plasma and products of UG, ED-based UG, UFO.

Due to the macromolecules collagen cross-linking by non-isocyanate urethanes, the physical and mechanical properties of the semi-product significantly change.

It has been established that plasma pre-processing and retanning of rabbit pelts by non-isocyanate urethanes improves the mechanical characteristics of the semi-product (Table 2).

| Table 2. Results of physical and mechanical characteristics of rabbit samples. |
|---------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Samples                          | Stress, N  | Ultimate tensile strength, MPa | Elongation, mm | Percentage elongation, % |
|                                | Corresponding to admissible strain 4.9 MPa | | at strain 4.9 MPa | at break | at admissible strain 4.9 MPa | at break |
| Control                         | 20 | 40 | 10.1 | 5.0 | 6.0 | 20 | 25 |
| Experimental UG 1 mode          | 20 | 51 | 13.4 | 7.0 | 18 | 28 | 72 |
| Experimental ED-based UG 1 mode | 17 | 46 | 13.5 | 8.0 | 20 | 32 | 80 |
| Experimental UFO 1 mode         | 21 | 48 | 15.5 | 9.0 | 21 | 36 | 84 |
| Experimental UG 2 mode          | 23 | 34 | 9.7 | 8.0 | 18 | 32 | 72 |
| Experimental ED-based UG 2 mode | 18 | 41 | 12.8 | 9.0 | 16 | 36 | 64 |
| Experimental UFO 2 mode         | 19 | 43 | 17.2 | 12.0 | 15 | 48 | 60 |
| Experimental UG 3 mode          | 27 | 73 | 20.3 | 6.0 | 15.0 | 24 | 60 |
| Experimental ED-based U 3 mode  | 36 | 81 | 21.3 | 8.0 | 12.0 | 32 | 48 |
| Experimental UFO 3 mode         | 32 | 65 | 20.9 | 9.0 | 11.0 | 36 | 44 |
| Experimental UG 4 mode          | 25 | 87 | 17.4 | 6.0 | 10.0 | 24 | 40 |
| Experimental ED-based UG 4 mode | 23 | 63 | 12.9 | 8.0 | 15.0 | 32 | 60 |
| Experimental UFO 4 mode         | 30 | 70 | 20 | 6.0 | 10.0 | 23 | 40 |

4. Conclusions

The effect of high-frequency capacitive plasma on the rabbit skin of the capillary-porous material results in the separation of the fibrous structure of the dermis and the increase of interfibrillar distance. This, in turn, increases the diffusion of structuring agents to the areas which are difficult to reach and their more uniform fixation. Separating the fibrous structure and fixing it by non-isocyanate products reduces the friction between structural elements and increases their ability to reorient under tension.

Thus, the research carried out allowed to make a conclusion that it is advisable to use a joint plasma modification by nonisocyanate urethanes. So, in the case of processing rabbit skins by plasma and non-isocyanate urethanes in modes 3 and 4, the heat resistance temperature increases by 10 °C. Moisture content satisfies the requirements of GOST (Russian National Standard) and is 12%. The tensile strength of rabbit skin increases by 1.5 times, the elongation increases by half.

References:

[1] Abdullin I et al 2012 Study of the effect of plasma treatment on the dyeing processes of beaver skins (Kazan: KSTU) pp.57-58.
[2] Berseleva M et al 2014 Assessment of structural changes in the fur coat after plasma treatment (Kazan: KSTU) pp.14-20.
[3] Antonova M. et al 2018 J. Phys.: Conf. Ser. 1058 012003
[4] Sysoev V. et al 2009 *Improving the efficiency of chrome tanning when using cyclocarbonate modification products* (Russian) pp.16-17.

[5] Garifullina A. et al 2014 *The use of propylene carbonate modification products in the manufacture of rabbit skins* (Kazan: KSTU) pp. 88-90.

[6] Garifullina A. et al 2015 *Modified propylene carbonate as retanning agents in the manufacture of beaver skins* (Kazan: KSTU) pp. 146-147.

[7] Garifullina A. et al 2014 *The use of non-isocyanate urethanes when dressing black-brown fox skins* (Kazan: KSTU) pp. 154-156.