

Studies of the influence of nonequilibrium plasma thermal exposure on the characteristics of the capillary-porous polymer material

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Abstract. Capillary-porous materials, which include natural macromolecular tanning material, are exposed to a number of factors during the treatment by a nonequilibrium plasma. Plasma particles exchange the charge and energy with the atoms of the material during the interaction of the plasma with the surface. The results of treatment are desorption of atoms and molecules from the body surface, sputtering and evaporation of material's particles, changes of the structure and phase state. In real terms during the modification of solids by nonequilibrium low-temperature plasma thermal effect influences the process. The energy supplied from the discharge during the process with low pressure, which is converted into heat, is significantly less than during the atmospheric pressure, but the thermal stability of high-molecular compounds used in the manufacture of materials and products of the tanning industry, is very limited and depends on the duration of the effect of temperature. Even short heating of hydrophilic polymers (proteins) (100-180 °C) causes a change in their properties. It decreases the collagen ability to absorb water vapor, to swell in water, acids, alkalis, and thus decreases their durability. Prolonged heating leads to a deterioration of the physical and mechanical properties. Higher heating temperatures it leads to the polymer degradation. The natural leather temperature during plasma exposure does not rise to a temperature of collagen degradation and does not result in changes of physical phase of the dermis. However, the thermal plasma exposure must be considered, since the high temperatures influence on physical and mechanical properties.

1. Introduction

Plasma consists of active and inactive particles with high kinetic and potential energy, that determine the physical and chemical nature of their interaction with the surface. Furthermore, physical and chemical transformations on the treated surface depend not only on the characteristics of the plasma stream but also on the charging state of surface [1-3].

Capillary-porous materials, which include natural macromolecular tanning material, are exposed to a number of factors during the treatment by a nonequilibrium plasma. Plasma particles exchange the charge and energy with the atoms of the material during the interaction of the plasma with the surface.



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In real terms during the modification of solids by nonequilibrium low-temperature plasma thermal effect influences the process. The phenomena of physical and chemical nature can take place at the same time. Physical processes include transfer of thermal energy between the plasma gas and the processed natural capillary-porous material, resulting in a substantial increase in temperature and, as a result, physical transformations. The chemical process is accompanied by the occurrence of one or more chemical reactions in the gas phase and on the polymer surface.

Due to the structure of the polymers and the macromolecules flexibility capillary-porous materials do not require a big amount of energy to carry out structural changes of macromolecules, their geometric shape changing, changing of the polymer physical state.

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Analysis of elementary processes of low pressure RF plasma discharges interaction with a capillary-porous materials shows that the largest contribution to the modification of the surface layer in the non-equilibrium low-temperature plasma processing is made, first of all, by ion bombardment, the kinetic energy of which ranges from 10 to 100 eV, the second, is the recombination of ions (argon - 15.76 eV, oxygen - 15.6 eV, the nitrogen - 14.8 eV), the third, the deactivation of excited atoms at the surface, the energy is transferred to 3-5 eV, the fourth, thermal effect.

Changing of the parameters of the plasma torch (discharge power, pressure in the discharge chamber, the gas flow rate) allows to obtain the concentration of particles with a certain energy. The nature of the particles is determined by the effects of interaction with the polymer molecules of atoms. Time of macromolecule excitation depends on the molecular weight, structure of polymer, the packing density of the atoms. Due to the special properties of polymers related to their conformational mobility as a result of interaction with ions, there is a high probability of realization of the process of structural transformations in the polymer without changing the chemical composition [7].

2. Results and discussion

An important mechanism of the the physical exposure of plasma is ion sputtering. Despite the fact that the energy of the sputtering threshold of 10-40 eV, and the energy of the atoms on the surface of various materials is in the range of 2-8 eV, an unambiguous answer to the question whether there is sputtering in the interaction of the low-temperature RF plasma with high-molecular materials in the investigated range of characteristics of the plasma torch is impossible, as polymer systems have strong forces within - and intermolecular interaction energy and cohesion in polymers are often much more than energy of chemical bonds of individual atoms.

Thermal resistance of capillary-porous hydrophilic polymers depends on their moisture content. Momentary heating of collagen at temperatures near the welding point or prolonged heating at temperatures well below the sealing temperature causes a change in a number of properties. When heated in the dehydrated state and under certain conditions in the presence of water collagen can sequentially move to the highly elastic, and then in a plastic state.

The electron temperature in the jet was evaluated by measuring the value of the current density in a nonequilibrium plasma $j_{\phi} = (0,4 - 1,4) \cdot 10^6 \text{ A/m}^2$. Since the electron mobility is several orders higher ion mobility conduction current in the plasma is determined by the movement of electrons by the formula:

$$j_e = n_e \bar{V}_e e ;$$

where \bar{V}_e - the average velocity of ordered motion of electrons. The kinetic energy of the ordered motion of electrons:

$$K_e = \frac{m_e \bar{V}_e^2}{2} = \frac{m_e j_e^2}{2n_e e^2} ;$$

At the $n_e = 10^{15} - 10^{16} \text{ m}^{-3}$, the kinetic energy of the electrons $K_e = 63 - 0.63 \text{ eV}$.

For the jet the thickness of the double layer is $n_e = 10^{16} \text{ m}^{-3}$, $T_e = 10000 \text{ K}$, $r_{de} = 7,64 \text{ mkm}$, at $n_e = 10^{15} \text{ m}^{-3}$, $T_e = 10000 \text{ K}$, $r_{de} = 8,23 \text{ mkm}$.

Thermal processes do not make a significant contribution to energy processes of modification.

Theoretical calculations confirmed by experimental data.

To determine the influence of thermal plasma on investigated high-molecular compounds temperature measurement of the sample was performed during plasma processing. The objects of study were natural tanning materials at various stages of their production.

Processing was carried out in air, argon. The discharge current density (j_ϕ) and plasma exposure time (τ) were ranged. The samples were dried before treatment to constant weight in an oven at 107°C (method1), by evacuation (method 2), by extracting the water by the alcohol (method 3). The temperature change of leather material are shown in Fig. 1-2.

The temperature of leather samples increases during the plasma treatment, but does not rise more than 90°C , thus it remains below the welding temperature.

Skin temperature depends on the degree of processing and the amount of water contained in it: so pelts is heated up to 70°C (welding temperature 90°C); colored semi-finished up to 95°C (welding temperature 120°C). Increasing of the current density in the discharge above $1,6 \cdot 10^5 \text{ A/m}^2$ in the plasma flow results in degradation of the samples.

The higher the moisture content of the sample, the lower the temperature rises, since the water filling the capillary and pore volume reduces the effectiveness of the plasma exposure. A sample with an initial moisture of 60-80% is heated up to $50-60^\circ\text{C}$, the skin, dehydrated beforehand, is heated up to $70-100^\circ\text{C}$ [3]. This is happened due to the fact that for the ionization of water molecules the energy 12.60 eV is necessary, and while for air - 13.62 eV . Consequently, part of the energy that was input to the discharge is spent on the ionization of water molecules and the heat capacity (enthalpy) of water is much greater than air or argon. Consequently, for the heating of one water molecule to the same temperature as air or argon molecules is necessary to spend more energy.

The temperature depends on the pre-dewatering methods of samples ($T_g < T_c < T_k$). The difference between TV and TCS is 8 to 13°C and depends on the degree of processing of the dermis.

The presence of dyes in samples promotes greater heating of tanning samples if thermal conductivity and heat capacity of the samples is higher than the gas phase and substances in the pores. Leather-painted semi-finished product is heated more than unpainted 8-10 % and much greater than raw pelts and 20-40 % [8]. The presence of metal ions in the samples and other chemicals (dyes) results to the temperature increase.

Analysis of the results leads to the conclusion that the temperature of the wet sample is increased less than dehydrated because water, filling the pore volume reduces the effectiveness of the nonequilibrium low temperature plasma impact by reducing the recombination energy of ion flux to the inner surface of the material. Increasing of the samples temperature due to the higher thermal conductivity of water than air is insignificant, as in the range of investigated plasma parameters deposited energy to the discharge used to increase the energy of the ions, and the proportion of the heat flow is negligible. Desorption of water in the plasma jet is not more than 1.5 – 3 % of the initial weight of the dehydrated sample.

Table 1 Maximum temperature of materials heating

(air, $G = 0,04$ g/s, $\tau = 300$ s, $j_\phi = 1,2 \cdot 10^5$ A/m², $P = 53.3$ Pa)

Dehydration process	Temperature, °C			
	Leather materials			
	raw	pelts	tanned unpainted semi-finished	tanned painted semi-finished
1	56	70	83	93
2	48	61	73	80
3	53	67	79	88
Without dehydration	22	52	62	71

The change in dermis samples welding temperature and its processed products after plasma exposure in the test range of the technological parameters of the plasma torch is investigated. Raw materials, pelts, tanned unpainted and painted semi-finished leather products in watered and in the dehydrated state are taken as samples. Samples were dried by vacuum, hot air and alcohol.

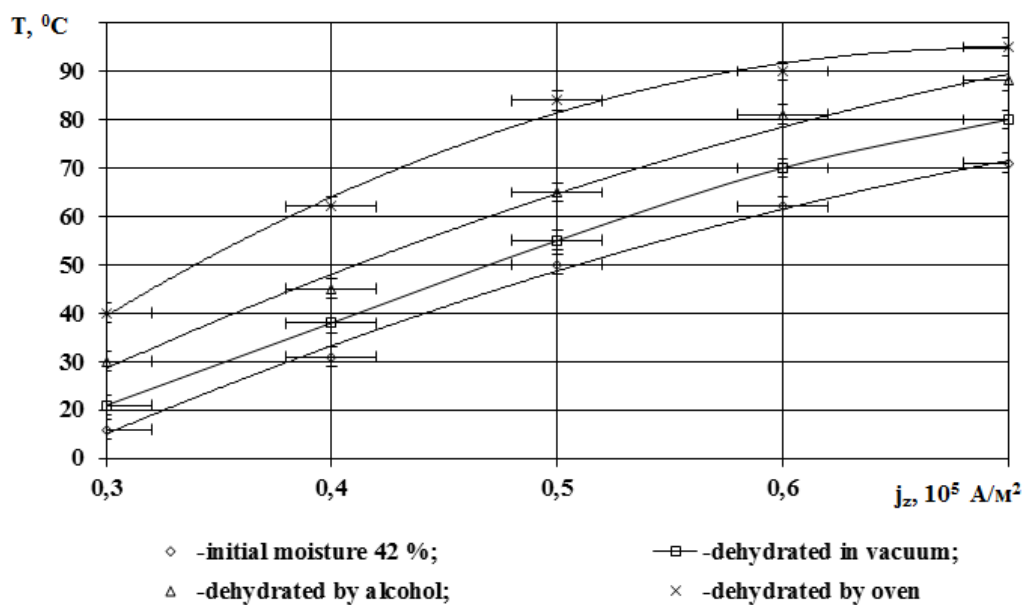


Fig. 1. Changing of the raw material temperature on the current density in the discharge

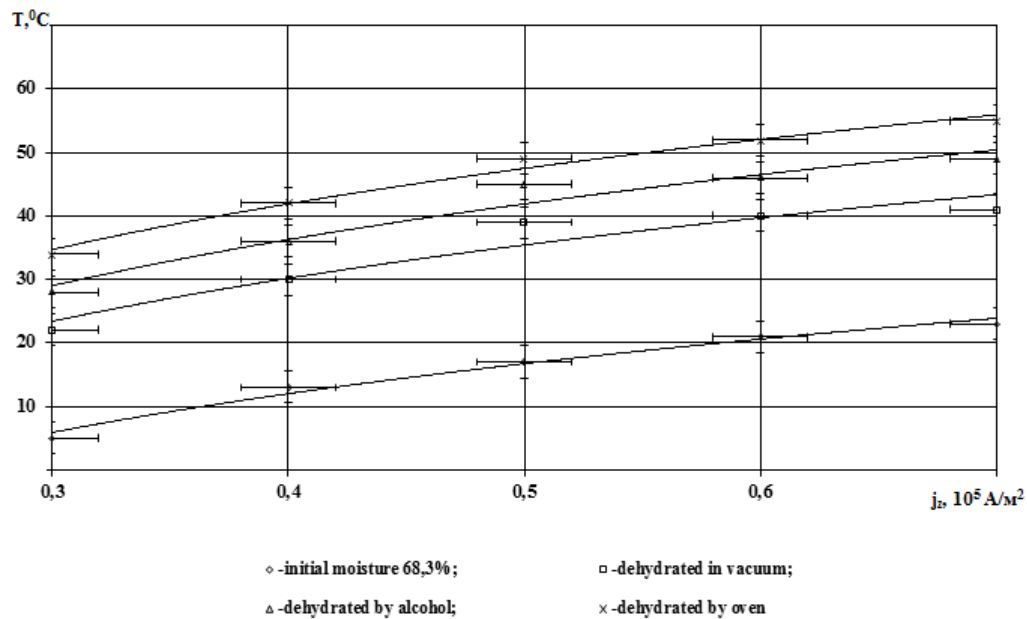


Fig. 2. Changing of the painted semi-finished temperature on the current density in the discharge

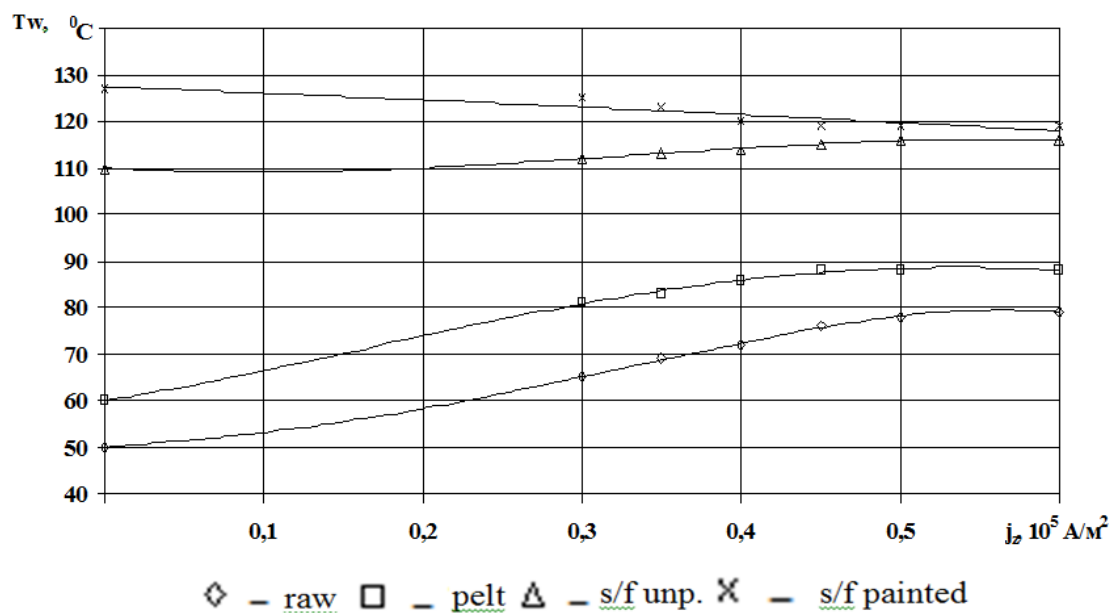


Fig. 3. Changing of dermis welding temperature on the current density in the discharge

Figure 3 shows the curves of the welding temperature of the dermis and processed products on the current density in the plasma. According to information received, the nature of the gas has little effect on T_w . T_w in the argon plasma is only 2-3 $^\circ\text{C}$ higher than in the air. A marked increase in the welding temperature is observed for samples of raw materials and pelt with increasing of current density in the discharge of about 30 $^\circ\text{C}$. Welding temperature of tanned unpainted semi-finished product is increased by 5-10 $^\circ\text{C}$ and painted is decreased by 3-5 $^\circ\text{C}$. Welding temperature change of all samples is registered in the range of discharge current density from 0 to $1.0 \cdot 10^5 \text{ A/m}^2$. With further j_d increase the temperature does not vary.

3. Conclusions

On the basis of the experiments it can be concluded that the nonequilibrium plasma flow has no thermal effect on the material being processed in these modes of the installation ($P = 53.3$ Pa, $\tau = 300$ s, $G = 0.04$ g/s, the gas - air) and at the same time it increases the welding temperature - the temperature of leather phase changes.

Thus, the natural leather temperature during plasma exposure does not rise to a temperature of collagen degradation and does not result in changes of physical phase of the dermis. However, the thermal plasma exposure must be considered, since the high temperatures influence on physical and mechanical properties. Exposure to low pressure RF plasma in studied range does not lead to polymer etching. Therefore, the non-equilibrium low-pressure plasma can be used in modifying of the collagen materials properties.

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