Electrolyte-plasma product treatment

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Abstract. The low-temperature plasma of direct current electric discharges in the process of surface treatment of a product investigated. The types and forms of discharge burning investigated. The electric parameters of the discharge, oscillations of the current and voltage of the discharge, the power invested in the discharge investigated. The temperature distributions of the electrodes in the combustion zone of the discharge investigated. The composition of the discharge plasma, the electron concentration, and the rotational and vibrational temperatures of the heavy components are studied. The micro relief of the surface of the product studied before and after electrolyte-plasma treatment.

1. Introduction
Discharge plasma with conventional solid electrodes dedicated s generalizing e are scientific e work s [1 - 3]. Modification characteristics of polymeric materials under the influence of electrolytic plasma-exposure is new m promising m technologically m advance processor m in industrial manufacturing. Electrolyte-plasma exposure includes both plasma-chemical processes in electrolyte solutions and the direct effect of non-equilibrium plasma of electrical discharges. Promising for use in various industries are electrical discharges with electrolytic cathode during use and DC sources as well as sources of power frequency current with a voltage of several kilovolts. The most productive is the use of gas-discharge plasma, ignited directly in the volume of electrolyte around the workpiece. In this case, as the workpiece is subjected to a plasma discharge intended a, and interacts with the active species in the electrolyte. It is known that under the action of electrolyte-plasma treatment on cellulose products, its properties change depending on the degree of its destruction and oxidation. In addition, their degree of polymerization decreases. A qualitative and quantitative change in its properties depends on the shape and parameters of the discharge, the time of exposure to the discharge plasma, the composition and concentration of the electrolyte solution. In the case of a “diaphragm” discharge, the degree of polymerization decreases to a higher degree, since the product is also affected by acoustic waves propagating at the interface between the media in the combustion zone of the discharge. Exposure
discharge type supramolecular structure of cellulose is not affected. However, the use of an “end” discharge for electrolyte-plasma treatment to initiate oxidation processes is higher. This is due to the fact that in the case of the use of an “end” discharge, the surface area of the workpiece to a greater extent interacts with the discharge plasma and active particles in the electrolyte solution. Based on this, the search for optimal modes and parameters of electrolyte-plasma processing of cellulose products is an urgent task. From the analysis of published works it follows that electrolyte-plasma systems have been studied for a long time [4-8]. Since the physics of the processes of these systems is quite difficult and, once produced, attempts to compare them with bits of conventional electrodes. In some studies, atmospheric-pressure electrolyte-plasma systems are classified as a normal glow discharge, the physicochemical characteristics of which are closely related to the processes of transfer of the liquid cathode components to the gas phase, and the non-equilibrium plasma character of these discharges is noted. Additional studies were carried out research on the effects of electrolytic-plasma systems made of polymers, where it was found that on the surfaces Rep polymers formed oxygen-containing group. On the basis of these studies provides new technological approaches to treating of e polypropylene products. Another promising area is the diffuse (bulk) processing of external and internal structures of porous-capillary materials. Here, the key influence factor is the chemical transformation of the microstructure of the surface of capillaries and pores. At the same time, the use of this technology in the production of leather and furs may cause local fixing and deposition of structural D and Gent, which in turn can cause structural deformation. The technology necessitates the production of large-volume electrolytic baths and does not take into account the dry processing of products. The aim is comprehensive experimental investigation of low temperature plasma discharges in the processes of electrolytic plasma-treating the surface of the polymer porous body under atmospheric pressure. The results of experimental studies can be used to construct various mathematical models for the qualitative or quantitative interpretation of the data and calculation for engineering s pilot plants for electrolytic-plasma treatment.

2. Experiment

Experimental studies of electric discharges in the processes of electrolyte-plasma treatment of porous-capillary products made of polymers were carried out in an experimental setup (Fig. 1), where an electrolyte stream 4 from a dielectric tube with a faucet 5 is supplied from the upper electrolytic cell 2 to the lower electrolytic cell 2. In the lower electrolytic cell 2 is placed a porous-capillary product 6 on a metal substrate with a positive potential brought to it. Experimental studies of the object were carried out at set voltage parameters \( U = 100-1000 \) V, jet length \( l = 3-10 \) mm, jet diameter \( d = 3-5 \) mm, stream velocity \( v = 0.05-0.15 \) m / s, electrolyte composition and concentration. A polypropylene household sponge was used as a porous-capillary product. A 7% solution of NaCl in tap water was used as an electrolyte. The process of electrolyte-plasma surface treatment of a porous-capillary product was carried out for a time \( t = 30 - 180 \) s.
Figure 1 - Functional diagram of the installation for ignition and discharge research in the processes of electrolyte-plasma treatment of porous and capillary products, where 1 is an electrolytic cell; 2 - electrolyte; 3 - plate for supplying a negative potential to the electrolyte; 4 - a stream of electrolyte; 5 - a dielectric tube with a regulating tap; 6 - porous-capillary product on a metal substrate with a positive potential brought to it.

To solve this problem, the following methods and diagnostic equipment were used:
1. The discharge burning in the process of electrolyte-plasma processing was recorded using high-speed video recording on the Casio EX-F1 aperture, with a video recording speed of 600 and 1200 frames per second. To suppress the intrinsic luminescence of the plasma, a DKSSh-250 arc xenon lamp with a power of 250 W was used.
2. The emission spectrum of the discharge plasma during the electrolyte-plasma treatment was determined by a PLASUS EC 150201 MC optical fiber spectrometer with a collimator for fixing light rays in the wavelength range from 195 to 1105 nm. To evaluate the hardware function, the calibration lamp “SIRSH 6 - 100” was used. The minimum width of single optically thin lines was $\Delta \lambda g = 1$ nm, which is taken as the hardware width. Investigation of the discharge at atmospheric pressure was carried out by bringing the collimator to a minimum distance from the generated discharge, taking into account the distance to protect the collimator from breakage. The radiation under investigation was collected from the discharge volume; the composition and components of the plasma were estimated without reference to a specific area. The spectrum was decoded by identifying the lines by comparing the experimental spectrum with the international database of the National Institute of Standards and Technology.
3. The vibrational and rotational temperatures of the molecules were estimated by comparing the experimentally recorded spectrum with the calculation model in the LIFBASE and Specair 2.2.0.0 software packages.
4. Infrared thermography of the electrode surface in the discharge burning zone during electrolyte-plasma processing was carried out using a FLIRA 6500 SC thermal imager, and ALTAIR v.5.91.010 software was used to process the obtained data.
5. Studies of fluctuations in the current and voltage of an electric discharge during electrolyte-plasma processing were carried out by a digital oscilloscope of the GDS-806S and GOS-6030 brands.
6. The roughness parameters of the samples before and after electrolyte-plasma treatment were carried out using confocal laser scanning microscopy using Olympus LEXT OLS 4100 brand equipment. Evaluation of the surface microrelief of the products before and after processing was carried out using a Carl Zeiss AURIGA microscope with an INCA X-MAX energy-dispersive spectrometer. An increase of 100-5000 times was used.

When a jet is supplied to the surface of a porous-capillary product, the jet collides with the surface of the material, disintegrates and penetrates into the pores of the processed product. The pores are filled with electrolyte, and their outer and inner surfaces are wetted. After the potential is applied to the
electrodes, a physicochemical electrolysis process takes place in the system with the release of substances dissolved in it from the electrolyte. This process is accompanied by evaporation of the electrolyte, boiling at the electrode space and the release of convective flows. Gas bubbles appear on the outer and inner surfaces. Penetrating along the porous-capillary product, the electrolyte reaches the metal substrate and the electrical circuit is closed. When the applied voltage reaches the ionization potential of atoms and molecules in the vapor-gas shell, a breakdown is generated in the system with the formation of a vapor-plasma shell. After the breakdown, the support of the charge can be affected by direct electron impact ionization, photoionization, stepwise ionization, dissociative ionization in the volume, as well as plasma-chemical reactions at the interface between the liquid volume and the discharge plasma. At large values of the applied voltage, the intensity of the combustion of the discharge plasma increases (Fig. 2a).

The discharge pulsates along the porous structure in the direction of the metal substrate, to which a positive potential is drawn, penetrating into the deep layers of the polymer product. From an analysis of the structure of the discharge it follows that it can occur in several areas of the system under consideration. The first zone of discharge formation is in the region of local decay (thinning) of the jet, which is due to an increase in the current density in this section and the appearance of an electromagnetic field pulse. The second zone is at the interface between the jet and the surface of the workpiece. And the third - inside the porous-capillary product with the development in the direction of the metal substrate.

The internal structure of the sample was studied using a microscope at the time of discharge formation (Fig. 2b).

Figure 2 - Electrolytic-plasma treatment of a porous-capillary product, where U = 1000 V, I = 2 A, l = 10 mm, d = 4 mm and v = 0.15 m/s (a) and the development of a discharge inside a porous-capillary product at p = 10^5 Pa, U = 700 V, l = 30 mm, d = 4 mm and v = 0.15 m/s (b).

From an analysis of the internal structures of a porous-capillary product during an electrolyte-plasma treatment using a microscope, it follows that an electric discharge is formed in the form of microchannels that drift and pulsate on a wetted surface of a dielectric or in the form of a continuous plasma channel that “spread” along the surface of pores (Fig. 2b).

We studied the temperature distribution on the inner and outer surfaces of a porous-capillary product, a jet electrode. From the analysis of the thermogram of the inner surface of the sample along its cross section, it follows that the temperature increases exponentially, reaching T = 48 °C, which corresponds to the interaction region of the wet polymer surface with the vapor-plasma shell. Since the discharge is formed in the form of microchannels, and is very uneven along the surface of the workpiece, therefore, the graph has peaks of temperature increase (Fig. 3).
Figure 3 - Distribution of the temperature of the medium on the inner surface of the porous-capillary product in the process of electrolyte-plasma treatment.

Based on the analysis of the temperature distribution along the jet electrode, it follows that the temperature increases linearly to the interaction region of the jet-discharge plasma to $T = 105 \, ^\circ$C. It was also found that the temperature in the region of thinning (decay) of the jet increases to $T = 58 \, ^\circ$C. Then, the heated liquid flows along the metal plate into the lower electrolytic cell 2.

The oscillations of current and discharge voltage in the process of electrolyte-plasma processing of the product are investigated. From waveform analysis (Fig. 4) it follows that the electric discharge is formed in the form of current pulses with the corresponding sections of the voltage drop of $\sim 150$ V in the range from 0.3 to 2.1 A. The frequency of the formation of the current pulse varies in the range of $\sim 100$ Hz. The current pulse width is $\sim 15$ ms. The power invested in an electric discharge in a specified range ranges from 0.3 to 2.1 kW. The discharge pulse is caused by the periodicity of the electrolyte closure on the metal substrate, the complexity of the porous-capillary structure of the product, and the features of the formation of the vapor-gas shell.
Figure 4 - Oscillogram of fluctuations in current and discharge voltage during electrolyte-plasma processing of a polypropylene product, where $\Delta I = 2$ A, $\Delta U = 500$ V, $\Delta t = 50$ ms.

The radiation spectrum of an electric discharge was studied during the electrolyte-plasma treatment of a porous-capillary product. From the analysis of the emission spectrum it follows that the plasma discharge consists of various molecules and atoms, including the hydroxyl group OH ($A - X$), the lines of the Balmer hydrogen series (H$\alpha$, H$\beta$ and H$\gamma$), sodium atoms Na I, oxygen OI and potassium K I. The presence of potassium in the electrolyte is due to the composition of the Volga water, which was used to prepare the electrolyte solution.

The concentration of electrons in the plasma of the electric discharge was estimated by comparing the half-width at half maximum of the hydrogen lines of the Balmer series with reference values. As a result of the calculations, the electron concentration turned out to be $n = 2.5 \times 10^{16}$ cm$^{-3}$.

The vibrational and rotational temperatures of the hydroxyl group OH ($A - X$) were studied by comparing the experimental spectrum with the model one. As a result, the vibrational and rotational temperatures of the discharge plasma turned out to be equal to 3500 K.

The microrelief of the surface of the product was studied before and after electrolyte-plasma treatment. It is established that the surface after treatment is cleaned of organic and inorganic contaminants, becoming more smoothed. From the analysis of the roughness parameters of the sample, it follows that the roughness class increases by 1 class.

3. Conclusion
The formation of an electric discharge in the form of microchannels that drift and pulsate along a porous-capillary polypropylene product has been established. It was found that the temperature of the inner surface of the sample along its cross section increases exponentially, reaching $T = 48$ °C, which corresponds to the interaction region of the wet polymer surface with the vapor-plasma shell. It was found that an electric discharge is formed in the form of current pulses with corresponding sections of a voltage drop of $\sim 150$ V in the range from 0.3 to 2.1 A. The frequency of the formation of a current pulse varies in the range of $\sim 100$ Hz. The current pulse width is $\sim 15$ ms. The power invested in the electric discharge in the specified range is calculated; it ranges from 0.3 to 2.1 kW. The composition of the plasma discharge is established. It consists of molecules, atoms of various names, including the hydroxyl group OH ($A - X$), the lines of the Balmer hydrogen series (H$\alpha$, H$\beta$ and H$\gamma$), sodium atoms...
Na I, oxygen O I and potassium K I. The electron concentration turned out to be equal $n_e = 2.5 \times 10^{16}$ cm$^{-3}$. The vibrational and rotational temperatures of the discharge plasma were equal to 3500 K. It is established that the surface after treatment is cleaned of organic and inorganic contaminants, becoming more smoothed. From the analysis of the roughness parameters of the sample, it follows that the roughness class increases by 1 class.

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