Improvement of Technological Properties of a Vegetal Tanning Agent in Gas Discharge Plasma

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Abstract. The article considers the possibility of modification of the vegetal tanning agent quebracho in the plasma of a radio-frequency induction discharge at low pressure. It is established that plasma treatment leads to a decrease in the size of colloid fractions and a decrease in the molecular weight, while the functionality of the vegetal tanning agent is preserved. Application of the obtained product in the process of leather retanning allows improving its physical, mechanical and consumer properties.

1. Introduction
Natural tannin-containing vegetal extracts, such as oak, mimosa, quebracho, have a good binding ability, therefore they are used to structure collagen fibers in the production of the leather. However, vegetal tanning agents are significantly inferior to toxic chromium as to their ability to penetrate in the dermis, because of the large molecular weight and the formation of large aggregates in solution.

It is proposed to activate the dry tanning vegetal extract of quebracho in the conditions of a radio-frequency induction (RFI) discharge at low pressure in order to improve its technological properties. The treatment of the plant extract was carried out on the equipment described in the source [1], the following parameters of plasma treatment were used: plasma-forming gas – argon, pressure in the working chamber 30 Pa; consumption of argon 0.04 g/s; energy of plasma ions 10–15 eV; the ion current density 20 A/m²; the dry material was injected into the discharge with a stream of plasma-forming gas and trapped after processing.

2. Experimental studies
Technological properties of vegetal tanning agent mainly depend upon the ability of molecules to diffuse in the dermis structure, which is determined by the molecular weight and the size of colloid fractions in solution.

A comparison of the infrared spectra of the control and experimental samples does not reveal any significant differences, there are small fluctuations in the intensity of absorption bands. On this basis, one can conclude that treatment does not significantly affect on the content of active groups of the sample and does not cause its complete destruction.

It was experimentally established that the plasma modification leads to a decrease in the moisture content of the sample from 5.85 % to 0.45 %.
When the control and experimental samples are dissolved in the water, a certain deterioration of the solubility is observed in the experimental sample, probably due to dehydration in conditions of radio-frequency plasma. The solution of the experimental sample has a visually more intense colour. The initial sample forms a less coloured turbid solution.

The values of the intrinsic viscosity of solutions of the experimental sample are 2.7 times lower than those of the control sample. This may indicate a decrease in the molecular weight due to partial destruction in conditions of radio-frequency plasma.

The size distribution of colloid fractions was determined using the ZetaPALS 90Plus Nanoparticle Size Analyzer (Brookhaven, USA) (Fig. 1).

![Fig. 1. Histograms of the particle size distribution in the solution of quebracho samples: a – control, b – experimental](image)

The results show that the size of tanning agent colloid fractions decreases from 68.94–98.13 nm and 367.33–502.88 nm in the control sample to 48.37–68.94 nm and 260.28–405.29 nm in the experimental sample.

The molecular weight distribution was determined using a MALDI UltraFlex III TOF/TOF mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany).

MALDI mass spectra are obtained in a linear mode. The Nd: YAG laser (\( \lambda = 266 \text{ nm} \)) was used. Data was processed using FlexAnalysis 3.0 (Bruker Daltonik GmbH, Bremen, Germany). Positively charged ions were fixed. A metal target was used. 2,5-Dihydroxybenzoic acid (DHB) or para-nitroaniline (p-NA) was used as a matrix. 0.5 \( \mu l \) of a 0.1 % solution of the matrix in \( \text{CH}_3\text{CN} \) and 0.5 \( \mu l \) of the sample were successively applied to the target and evaporated (Fig. 2, 3).

The molecular weight range using the DHB matrix is 200–1000 for the control and experimental samples. However, in the samples, two predominant fractions can be identified (I > 400 arb. units): 311.16; 545.13 in the control and 255.23; 375.20 in the experimental.

The range of molecular weights using the p-NA matrix is 300–1000 in the control, 400–1000 in the experimental sample. In the samples, it is also possible to identify the predominant fractions: 685.78 (I > 1250 arb. units); 686.74 (I > 500 arb. units) in the control and 360.41 (I > 400 arb. units) in the experimental. So, the MALDI mass spectra show a change in the dispersity of molecules, a decrease in the molecular weight of the predominant fraction of the vegetal tanning agent in the conditions of RFI treatment.

To study the diffusion of vegetal extract molecules, the retanning process is performed with control and experimental samples in laboratory conditions. The retanning process of the semi-finished sheepskin using the modified tanning agent should be carried out at \( \text{pH} = 4 \); in this case the heat resistance of the leather increases by 9 °C; the strength limit – by 15 %; the relative elongation – by 50 %. The obtained leather also has improved properties: softness and uniform colour of the surface.
Fig. 2. MALDI mass spectra of quebracho samples using the matrix DHB:

a – control, b – experimental
Fig. 3. MALDI mass spectra of quebracho samples using the matrix p-NA:

a – control, b – experimental

3. Conclusion

Thus, the results indicate the production of light fraction of the vegetal tanning agent with improved technological properties from the plant extract in conditions of low-pressure RFI-plasma.

Acknowledgments

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References

[1] Abdullin ISh, Zheltukhin VS, Kashapov NF. Radio-frequency plasma-jet treatment of materials at low pressures. Theory and practice of application. Publishing house of Kazan State University, 2000.