Structural and chemical changes of aramid fibers modified by low temperature plasma

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Abstract. The article considers changes in the properties of Rusar-S brand aramid fiber due to the treatment of low-pressure plasma of radiofrequency capacitive discharge. After modification, there was recorded the growth of hydrophilicity in the environment of inert and oxidizing gases. The paper discusses the results of IR spectroscopy of Rusar-S aramid fiber before and after plasma modification. An obtained data of research can explain the influencing mechanisms of RFC discharge plasma of a low-pressure on the properties of aramid fiber.

1. Introduction
Aramid fiber is characterized by the high elastic modulus, strength and heat resistance, has a low density. Due to the high physical and mechanical characteristics, textile materials made of aramid fibers are widely used in the production of overalls, fire hoses, in the reinforcement of automobile tires, as well as for the production of body armor. The complex properties of aramid fiber make it possible to use it as a reinforcing filler of durable, lightweight and thermally stable composites that can replace concrete, aluminum, steel, and other structural materials. Composites based on aramid fiber materials are used to strengthen various sports equipment, aerospace constructions, transport parts, and other products.

The modern scientific community recognizes the necessity to modify existing polymer fibers to give them extra operational and technological properties. Modification of fibers is carried out at...
different stages of production: during the synthesis of fiber-forming polymer; in the process of converting the polymer into a fiber or thread; at the stage of final finishing of the molded fiber or directly before using the completed fiber [1-3]. It is known that the treatment in the low-pressure RFC discharge does not cause bulk destruction of the fiber and allows improving the surface and physicomechanical properties of polymeric fibrous materials. Thus, the use of plasma modification in the RFC discharge appears to be the most appropriate method for regulating the properties of aramid fibers. This work aims to study the degree of influence of plasma in the RFC discharge on the chemical and structural changes of aramid fiber.

2. Materials and methods
Modification of aramid fibers was carried out on an experimental plasma adjustment of the RFC discharge. During modifying the fibers, the following parameters were set: processing time $\tau=180$ s; pressure in the chamber $P=26$ Pa; volumetric flow rate of plasma-forming gas $G=0.04$ g/s.; discharge capacity $W_p$ (kW) was varying; plasma-forming gas was selected depending on the purpose of modification (argon, argon–propane-butane 70/30, argon–air 70/30, argon–nitrogen 70/30).

For describing the capillary properties, it is necessary to measure the height of the liquid rise for a certain period. The capillarity of aramid fibers was determined by the level of altitude of the aqueous solution according to GOST 29104.11-91.

The contact angle was determined by the method of a sitting drop on the device Kruss Easy Drop DSA 20E. Drops, of a diameter of not more than 2-3 mm, were applied on an aramid fibrous material that was obtained by unidirectional winding. The software of the device has the means to analyze the image of the drop and calculate the contact angle.

After recording the changes in the physical and mechanical properties of fiber, researches of conformational and chemical conversions were carried out due to the possibility of changes in the supramolecular structure and surface transformations of chemical type.

Methods of infrared spectroscopy, x-ray diffraction analysis, different methods of thermal analysis were used to assess the impact of plasma treatment. A Fourier-transform spectrometer FSM-1202 was used for obtaining IR-spectra, the shooting mode: wavenumber range 400-4000 cm$^{-1}$, resolution 0.5 cm$^{-1}$, scanning speed 10 KHz.

A synchronous thermal analyzer STA 409 PC Luxx of Netzsch company (Germany) was used for evaluating the thermal characteristics. It represents a measuring complex that combines the functions of differential scanning calorimetry (DSC) and analytical scales of high accuracy.

3. Results and discussion
The studies on the hydrophilic properties of the fiber, namely capillarity and contact angle, were carried before and after the modification.

Table 1 shows the changes in the hydrophilic properties of the fiber before and after its modification in various gaseous environments.

| The regime of plasma treatment | Type of plasma-forming gas | Capillarity, mm | Contact angle, degrees |
|-------------------------------|---------------------------|----------------|----------------------|
| Without treatment             | –                         | 5              | 112                  |
| $W_p=2.0$ kW                  | argon                     | 103            | 0                    |
| $W_p=1.2$ kW                  | argon–propane-butane 70/30| 3              | 110                  |
| $W_p=1.4$ kW                  | argon–air 70/30           | 140            | 0                    |
As can be seen from table 1, after the plasma treatment of fibers in the environment of argon and its mixtures with oxidizing gases, the hydrophobic fiber acquires hydrophilic properties. In using of a plasma-forming gas mixture of argon-propane-butane fibers show a slight decrease in capillarity.

Figures 1-3 show the IR spectra of the aramid fiber Rusar-S before and after plasma modification in a different environment.

According to IR spectroscopy data presented in Figure 1, no significant chemical changes occur in the sample material during the processing of the aramid fiber Rusar-S in low-pressure plasma of an RFC discharge in the argon environment.

**Figure 1.** IR spectra of samples of aramid fiber Rusar-S: curve 1-without plasma exposure; curve 2 - after plasma treatment in an argon environment.

According to the results of IR spectroscopy of aramid fiber Rusar-S treated in argon–propane-butane (figure 2), it can be told about more significant changes in the composition and structure, compared with the fiber treated in pure argon. A decrease in the intensity of the absorption bands characterizing the oscillations of the groups N-H, C=N, C=O, C-N is observed, which explains an even greater decrease in the hydrophilic properties of the fiber compared to the control sample.

**Figure 2.** IR spectra of samples of aramid fiber Rusar-S: curve 1-without plasma exposure; curve 2 - after plasma treatment in a mixture of gases argon-propane-butane.
Although the hydrophilic properties of the original fiber are minimal, the capillarity of the fiber is reduced by 1.7 times. It is also possible to talk about the grafting of propane or butane ions to free radicals with the formation of a surface grid on a fiber-forming polymer. Free radicals are formed on the fiber as a result of ion bombardment in the surface layer. Such hardening of the surface layer of the fiber by cross-linked and mesh structures during processing in the plasma-forming gas argon-propane-butane leads to an increase in the strength of the fibers, which is established experimentally. Brief information on the strength of aramid fiber Rusar-S before and after plasma modification is given in table 2.

![IR spectra of samples of aramid fiber Rusar-S](image)

**Figure 3.** IR spectra of samples of aramid fiber Rusar-S: curve 1 - without plasma exposure; curve 2 - after plasma treatment in a mixture of gases argon-air.

| №  | Modification environment     | Relative strength index, % |
|----|------------------------------|---------------------------|
| 1  | initial sample               | 100                       |
| 2  | argon                        | 100                       |
| 3  | argon-butane-propane         | 110                       |
| 4  | argon-air                    | 85                        |

Table 2. Comparison of the strength of Rusar-S fiber modified in different plasma-forming gases.

After treatment of the Rusar-S fiber in a mixture of argon-air gases (figure 3), the absorption bands characterizing the oscillations of the C=N, C=O and NH groups are completely disappeared, which indicates a strong weakening of hydrogen bonds as a result of plasma etching. This causes an increase in hydrophilicity (capillarity increases to 140 mm, i.e. increases by 28 times) and a decrease of a fiber strength (table 2).

According to the thermogravimetric analysis of unmodified fiber Rusar-S, there can be observed 3 mass loss effects: at 111°C - 2.1%, at 317°C - 5.7%, with 410°C begins the process of intense mass loss. The first mass loss effect is associated with the removal of the hydrophobizer (the boiling point of aramid fiber hydrophobizers varies between 40-170°C), and the second effect is related to the removal of the oiler components from the fiber surface. It corresponds to the DSC data, which shows no exothermic effects up to the degradation temperature, hence no changes in the polymer chain occur. According to the thermal analysis of the aramid fiber Rusar-S, it can be concluded that the samples of aramid fibers treated in an RFC discharge plasma of a low-pressure have no internal structural changes since the DSC curves of the original and plasma-modified sample demonstrate the same maximum exothermic effects. Consequently, the degree of crystallinity, determined through the energy expended
in the process of thermal destruction, practically does not change (the areas of the peaks of thermal destruction are approximately equal) [4].

An important component of the modification in the processing of aramid fiber Rusar-S with RFC discharge plasma of low-pressure is the directional effect of active plasma particles with an energy of 30-100 eV on the surface of the fiber. Charged particles in the process of impact lose their energy, causing the process of physical dispersion of the components of the oiler. Thus, it becomes possible to realize the hydrophilic properties of the fiber due to the presence in the fiber-forming polymer of polar groups N-H, C=O, N=C. Also, due to the rupture of low-energy NH bonds and the separation of the hydrogen atom from the benzene ring, free radicals R1N• and R2C6H5 * appear on the surface of the fiber, which, reacting with each other, can form additional unsaturated bonds C=N. The formation of such bonds leads to the production of more thermostable structures in the surface layer, which is confirmed by the data of thermal analyses.

In a using of polymerizing plasma (plasma-forming gas argon-propane-butane) free radicals, appearing in the process of ion bombardment, interact with a monomeric unit of plasma-forming gas to form a surface grid and growth centers of the polymer membrane. At the same time, conformational changes occur, leading to the ordering of macromolecules of the amorphous phase of the fiber-forming polymer and an increase in the degree of crystallinity of the fiber, which also contributes to the strengthening of aramid fibers.

When processing fibers in a mixture of argon with active gases, the predominant process is plasma etching, confirmed by IR spectroscopy. In this case, after purification of the fiber from mechanical impurities and the oiler, there is a violation of the integrity of the surface layer and the formation of a more developed relief of the fiber surface, which causes a sharp deterioration in strength characteristics and a significant increase in the hydrophilic properties of the fibers compared to samples treated in an inert gas.

4. Conclusion
After experimental studies of the impact of plasma modification on the properties of aramid fibrous materials, the influences of RFC discharge plasma on the surface and conformational transformations of aramid fibers were studied.

In the course of experimental research, it was determined that in some regimes, plasma modification allows increasing the hydrophilicity, strength characteristics and other properties of aramid fibers. Based on the obtained results, it is confirmed that the effect of plasma treatment depends on the technological parameters of the plasma and the composition of the plasma-forming gas.

Thus, as a result of ion bombardment after modification of aramid fibrous materials by low-pressure plasma of RFC discharge, when processed in an inert gas, conformational transformations, physical spraying, as well as changes in the chemical composition of the surface layer of the fiber occur, which happen more intensively in chemically active plasma-forming gases.

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