Interaction of low-temperature plasma with knitted fabric based on natural cellulose fibers

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Abstract. The influence of low-temperature plasma on a knitted fabric of natural cellulose fibers is considered. It is shown that the plasma ion energy is sufficient for the waxy layer destruction. It was determined that the ion bombardment and the paraffin vaporization lead to disintegration of the natural waxy fiber layer and cause the defects in paraffin layer. The local ruptures of carbon chains of alkane molecules of the paraffin layer are caused by the low-energy plasma ions bombardment and the ions recombination. The alkyl radicals which react with the plasma gas particles and with each other were identified. As a result of reactions of radicals, the hydrophilic functional groups was evaluated by IR spectroscopy and secondary ion mass spectrometry. All these changes facilitate the penetration of the working solutions in the fiber. Plasma effect leads to an increase in the hydrophilic properties of the material and can replace the liquid processes of preparing knitted fabrics for dyeing.

1. Introduction
Plasma technologies are widely used for the processing of textile materials of different nature. The advantage of plasma treatment is the versatility. Plasma allows changing the properties of the textile material in the desired direction. These changes depend on the type of plasma-supporting gas and processing parameters, such as discharge wattage – W, processing time – t, etc. Plasma processing can be used at any stage of fiber finishing. The main advantages of plasma treatment are the use of the gas medium and the minimum expenses for recycling. The economic efficiency of plasma and plasma chemical technologies mostly depends on the level of the equipment use and the duration of the production cycle [1]. Reduction of the latter can be achieved by the intensification of traditional processes or by the exclusion of some liquid-phase stages from the technological chain.

All types of plasma used for the modification of textile materials can be divided into two main groups - atmospheric pressure plasma and low pressure (vacuum) plasma [2]. The main advantages of the atmospheric pressure plasma (APP) are higher processing speed and lower cost of the equipment. On the other hand, the low-pressure plasma (LPP) provides the flexibility and easiness of process control and the reproducibility of effects. The LPP facility can be simply adapted to various materials treatment [2]. So, it is possible to regulate the obtained effects widely, using different plasma-supporting gases [3]. There are many other factors that prove the advantages of LPP: utilization of ozone and nitrogen oxides is not necessary; lower applied voltages can be used; plasma effects over time are more stable.

According to some researchers [4, 5] it is shown, that the intensity of textile materials processing is higher in the LPP than in the APP, on equal watts input. It is obvious that the lifetime of active particles is higher in the LPP than in the APP. In vacuum, active particles (e.g. atomic oxygen) can
diffuse inside the structure of the textile material deeper. Conversely in the APP a very thin surface layer is mainly processed.

Among other things, the APP processing effects are sensitive to atmospheric humidity and moreover to the material moisture content. The latest can vary (sometimes quite significantly) from the edge to the center, across the fabric. Alternately, the material processed in the LPP is degassed, what results in the higher treatment uniformity.

The influence of the LPP produced by a radio-frequency capacitive coupled discharge (RFCCD) on knitted materials of cellulose fibers is under consideration in the given article.

2. Materials and methods

Knitted materials are obtained by knitting of yarns from cellulose fibers. The paraffin is applied to the yarns to facilitate knitting and reduce yarn breakage, but it should be removed before dyeing. Traditionally, the paraffin and other non-cellulosic contaminants are removed by boiling in an alkaline medium at high temperatures (95-105 °C). As a result, the cotton fiber loses its strength and the fabric hand properties become worse. Plasma processing is offered by the authors to prepare knitted fabrics for dyeing, as an alternative to the traditional liquid processes.

The object of the research is unbleached cotton knitted fabric with a surface weight - 165 g/m². Refined oil paraffin was used as a model of traditional wax coating. The paraffin was applied on a glass substrate and then was treated with plasma. The paraffin layer thickness was from 0.005 mm to 0.01 mm.

The plasma processing was carried out on the facility with the following characteristics of RFCCD: the charged particle density - \( n = 10^{16} \text{-} 10^{19} \text{ m}^3 \), the ions energy in the ionic layer of positive charge - \( W_i = 70\text{-}100 \text{ eV} \) and the ion current density on the sample surface - \( j_i = 0.3\text{-}1.0 \text{ A/m}^2 \) [6].

3. Results and discussion

The original unbleached knitted fabric is hydrophobic and is not wetted by water. So, there is no capillary rise of water through the fabric. But, the fabric becomes hydrophilic and gets perfect wetting ability after plasma exposure. The height of the capillary rise of water is 180-220 mm depending on the processing conditions. It was also determined, that the hydrophobic surface of model paraffin becomes hydrophilic after plasma treatment (Figure 1). Consequently, the hydrophilization of the unbleached cotton knitted fabric depends on the hydrophilization of paraffin, covering the fibers and filaments.

The content of paraffin on the fabric decreases on average by 18-25% in air plasma and by 5-8% in argon plasma after plasma treatment during 300-500 sec (Figure 2).

Plasma treatment changes the surface structure of the cotton fibers (Figure 3). The surface becomes bulkier after treatment in the argon plasma, but no noticeable damage is observed. The discharges on
fibers and an increase in the fiber roughness are fixed after its’ processing in air plasma. The size of etched areas is 10-20 nm [7].

![Graph](image1)

**Figure 2.** The removal rate of paraffin (determined by extraction with CCl4) from the unbleached cotton fabric as a function of the processing time in air plasma.

![Microphotographs](image2)

**Figure 3.** Microphotographs of cotton fibers (× 20000): a - check sample, b – the sample treated in argon plasma, c - the sample treated in air plasma.

Thus, according to the results of experimental studies, the unbleached fabric properties are similar either after processing in air plasma or after alkaline boiling. So, the paraffin is partially removed, the knitted fabric is hydrophilic and the wholeness of the outer layer of cotton fiber is damaged in places.

It is necessary to evaluate the plasma effect on cotton fiber and mostly on the upper paraffin layer. For this reason, the modeling by the Monte Carlo method was performed and the changes in the paraffin surface during the bombardment by low-energy plasma ions were studied.

The initial data for the model were the following: the expected composition of argon and air plasma [8] and the molecular weight distribution of the paraffin [9]. The breaking process of carbon chains of paraffin molecules was simulated because of impact of plasma-supporting gas ion. Since the body placed in the plasma is charged negatively [10], then positively charged ions were considered. Only the singly charged ions were included in the simulation. So, the wattage W of all ions was chosen equal. The model of the paraffin layer was simplified and was based on a set of molecules of alkane hydrocarbons of different lengths. It was supposed that molecules are arranged relative to each other in a random manner.
The unit cell area of 100 nm$^2$ was studied within the simulation. The plasma processing of paraffin layer for 420 secs with the gas ions energy $W_i = 50-100$ eV was simulated. Such ions energy corresponds to the discharge wattage – $W_d = 0.8-2.0$ kW. The processing of the fibers surface in the interfibre space was simulated in breakdown conditions (assisted discharges). Those discharges are formed due to the energy - $W_i = 18$ eV, which released by the ions recombination [6]. The processing intensity was set equal to 7 ions / (nm$^2 \cdot$sec).

The Figures 4-6 depict the results of numerical simulation of argon and air plasma processing with the ions energy $W_i = 70$ eV. The fractional composition of paraffin and generated alkyl radicals are shown in the given figures.

According to the calculation results, the impact of plasma ions with the energy $W_i = 50-100$ eV causes some changes in the fraction composition of the paraffin. These changes are more obvious after air than after argon plasma processing. Paraffin is also processed due ions recombination in the interfibre space, with the low energy - 18 eV [6], so the changes in the molecular weight distribution are not so significant in this case.

Among the alkyl radicals that are formed during the plasma treatment over than 70% correspond to the gaseous fraction (Figure 6). Since, with a decrease in pressure, the boiling point of paraffin is reduced under vacuum and gas purge, fractions with a carbon number of 16 and less will be removed. The removal of the gaseous fraction results in a change in the molecular weight distribution of paraffin. In this case, according to calculations, the average molecular weight $M_{av}$ of paraffin increases from 331.4 to 334.8 in air plasma and to 334.7 in argon plasma.

Therewith the calculated weight loss of paraffin $\Delta m$ (when $W_i = 50-100$ eV) is $(0.69 - 1.09) \times 10^{-8}$ mg/m$^2$ in argon plasma, and $(0.96-1.72) \times 10^{-8}$ mg/m$^2$ in the air plasma (Figure 7). The calculated minimum depth of penetration of the plasma-supporting gas ions is 1.5-8 nm.

![Fractional composition of paraffin wax](image)

**Figure 4.** Fractional composition of paraffin before and after the treatment in air plasma, $W_i = 70$ eV.
Figure 5. Fractional composition of paraffin before and after the treatment in argon plasma, $W_i = 70$ eV.

Figure 6. Distribution of fractional composition of paraffin alkyl radicals after the treatment in air plasma, $W_i = 70$ eV.

$m, 10^8 \text{mg/mkm}$

Figure 7. Mass $m$ of removed paraffin fractions, as a function of the ion energy $W_i$: 1 - air, 2 – argon.
According to the results of simulation and experimental studies it is shown that the physical effect of plasma is insignificant. Such effect doesn’t lead to increase of the parameters of hygroscopic properties (wetting ability, capillarity) of unbleached knitted fabrics. Quite the opposite, the chemical effect of the plasma has the greatest contribution, while the fabric is processing in air plasma.

The developed model is approximate, because it doesn’t consider the chemical interaction between the radical residues and their reactions with the particles of the plasma-supporting gas. However, the obtained simulation results are sufficient to explain and evaluate the achieved effects. To determine the adequacy of the proposed model, additional experimental studies were carried out.

The average molecular weight of the paraffin $M_{av}$ correlates with the self-diffusion coefficient $D$, which was determined by NMR method. It is known that an increase of polymers’ $M_{av}$ complicates the molecules diffusion within the system. According to NMR results, plasma treatment leads to a change in the diffusion attenuation of the sample signal. Along with this, the number of the components with the lower self-diffusion coefficient is directly proportional to the plasma treatment time. According to calculations, there is a reduction of the average self-diffusion coefficient of paraffin in 1.7 times: $D_{\text{check}} = 4 \times 10^{-9}$ m$^2$/sec, $D_{\text{treated}} = 2.3 \times 10^{-9}$ m$^2$/sec. The given results indicate an increase in the paraffin $M_{av}$ after plasma treatment.

According to the proposed model, ion bombardment of the paraffin surface leads to the formation of alkyl radicals. These short-lived radicals can react with plasma particles; thus the products of such reactions were found. The oxygen-containing functional groups in the treated paraffin were registered by different methods. So, acid groups are determined in the amount of 0.95 mg KOH/g after treatment in argon plasma. There are no acid groups in the check and in the argon treated samples and acid number is 0.00. In addition to it, the IR spectrums in ATR mode were studied. The occurrence of signal at 1720 cm$^{-1}$ is recorded, which is relevant to the asymmetric stretching vibrations of the C=O groups. IR spectrums of the initial paraffin sample and after the treatment in argon plasma are identical.

It is known [11] that for paraffin oxidation reactions rather rigid conditions are required: elevated temperature, the action of ultraviolet or radioactive radiation and/or the presence of initiators as sources of active free radicals. In our case plasma is the source of active free radicals and ultraviolet radiation. Except but, the oxidation reactions occur locally and only at the interface, causing changes in the thin surface layer of the paraffin.

The oxygen is in the active form in the gas medium of air plasma. It can be in the form of ions, excited molecules, atoms, ozone, etc. So, all these oxygen forms can cause the complete oxidation of paraffin and organic substances in the contact layer. It is known that such reactions proceed by the release of carbon dioxide CO$_2$. When the amount of oxygen is insufficient for complete paraffin oxidation, then partial oxidation products are formed: carbon monoxide CO and carbon. Mass-spectrometry was used to reveal these oxidation products in a plasma medium.

There are the changes in the gases ratio within the processing medium during the plasma treatment. A noticeable increase in N$_2$, CO$_2$, and CO and reduction of O$_2$ and N$_2$ are determined in the air plasma treatment process. There are no significant changes in the gases ratio after the paraffin processing in argon plasma. Only the increase of H$_2$ quantity is recorded. It is known [12] that the release of hydrogen into the gas phase is usual for the plasma treatment of polymeric materials. It occurs due to radical reactions because of transfer of excitation energy from plasma particles to macromolecules [5]. The expenditure of oxygen in oxidation reactions can be indicated by the increased CO and CO$_2$ and reduced O$_2$ quantity. The alkyl radicals are also involved in oxidation reactions. Radicals appear in gaseous medium due to local rupture of paraffin carbon chains and have the C$_{16}$ or less carbon number in the chain.

The balance of atomic molecular composition of the gaseous medium before and after plasma treatment was determined. It was found that the O$_2$ consumption is higher than it is required for reactions of CO and CO$_2$ formation. On the contrary, the number of carbon and hydrogen atoms increases. These changes indicate the oxygen consumption in the reactions with non-volatile components formation.
The cellulose fiber surface was studied by secondary ion mass spectrometry (SIMS). The appearance of the products of the cellulose interaction with air plasma was detected. SIMS method provides the surface composition analysis to a depth of 0.3-10 nm. There is a sharp increase of ions corresponding to oxidized hydrocarbons (up to 20-50 times): $\text{C}_{17}\text{H}_{34}\text{O}_2^+$, $\text{C}_{18}\text{H}_{38}\text{O}_2^+$, $\text{C}_{19}\text{H}_{38}\text{O}_2^+$, after RFCCD air plasma treatment. Along with this, the quantity of nitrogen-containing ions increases. The SIMS results indicate reactions of oxygen and nitrogen of the plasma-supporting medium with some substances located on the fiber surface.

According to the above-mentioned simulation results, the alkyl radicals are formed in the process of paraffin plasma treatment, where the largest proportion (40-50%) take the radicals with the $\text{C}_{16.19}$ amount of carbon atoms in the chain (Figure 6). They react with each other and with plasma particles including oxygen and nitrogen, what results in their contents increase as recorded by SIMS. This position is approved by the increase of oxygenates ions content with the number of $\text{C}_{17.19}$ carbon atoms on the fiber surface.

As the waxy substances on cellulose fibers contain saturated hydrocarbons, so such processes are likely to occur in the fibers wax layer.

4. Conclusion

LPP changes on the thin surface layer of cotton fiber including the paraffin layer, which is used to cover yarns for facilitating the knitting process during knitted fabrics manufacture. The local ruptures of carbon chains of alkane molecules of the paraffin layer are caused by the low-energy plasma ions bombardment and the ions recombination. Further, the alkyl radicals emerge and react with the plasma gas particles and with each other. As a result, the volatiles form and then they are removed by the gas purge under reduced pressure. This procedure helps to clean knitted fabric. The radicals react with oxygen on the paraffin layer surface and then the hydrophilic functional groups appear. These changes lead to the increase of wetting ability and capillarity characteristics.

The paraffin heats and spreads over the fibers and filaments surface during the plasma treatment. At low pressure, the boiling point of the paraffin is reduced and the evaporation of its low molecular weight fractions starts. The defects of paraffin layer are formed in the evaporation field. Since paraffin composition on the fibers and filaments surface is uneven, so in the areas with the smallest paraffin layer thickness and with the absence of paraffin the ion bombardment affects waxy substance. The ion energy is sufficient for the waxy layer destruction. Therefore, the areas with “naked” cellulose appear.

The ion bombardment and the paraffin vaporization lead to disintegration of the natural waxy fiber layer and cause the defects in paraffin layer. All these changes facilitate the penetration of the working solutions in the fiber and increase cellulose accessibility for dyes.

By this means, the plasma processing is more gentle method as compared with traditional boiling processes, because the plasma treatment does not lead to degradation of the cellulose fibers and has an influence only on a thin surface layer.

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