Influence of plasma and radio wave treatment on paper structure

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Abstract. A paper for offset printing was exposed to radio frequency discharge plasma and radio frequency electromagnetic field. Optical response and structural features of paper before and after the treatment have been investigated by several techniques: digital laser speckle photography, laser Stokes polarimetry and attenuated total reflectance (ATR). The changes of statistical distributions of speckle patterns has been observed for plasma treated paper as a result of increase of correlative dimensions of structural heterogeneity of modified paper. It is shown also that the radio wave treatment leads to anisotropy reduction in the paper structure that is more apparent if the magnetic field lines are oriented transversely to the plane of a paper sheet.

1. Introduction

Last years low-temperature plasma and radio wave treatment has been confirmed to be effective techniques for modification of natural polymers like cellulose based materials because of the possibility of a predictable change in their physical and chemical properties for various practical application [1-9]. In particular, plasma processing of cellulose based paper changes its layer properties [7-9]. It is reported that in a magnetic field changes occur in light transmission and the efficiency of small-angle scattering of polarized radiation by polymers belonging to the class of cellulose derivatives [6]. According to idea about the mechanisms of action of an external magnetic field on diamagnetic materials, the appearance of some orientational effects in extended polymer macromolecules (reorientation or a change in their conformational structure) is connected with anisotropy in the diamagnetic susceptibility of polymer fibers [10-12].

In this paper we study an influence of low-temperature radio frequency (rf) plasma as well as rf electromagnetic field on a paper for offset printing that is a complex material consisted of sulphite bleached wood cellulose with other substances including alum, rosin, glue, kaolin and fillers. Interest to such problem is connected with the purposeful change of a paper structure with the aim of paper samples identification and their operating characteristics improvement for different application.
2. Experimental conditions

2.1. Experimental set-up
Paper sheets (thickness about 70 μm, size (10 x 10) mm²) were processed with rf helium plasma at pressure 0.5–5 Torr and exposed to rf electromagnetic field at atmospheric pressure under conditions of the prebreakdown mode operation of a capacity coupled rf discharge.

The experimental set-up is schematically depicted in figure 1. The discharge was operated on frequency 5.28 MHz between two parallel rectangular copper electrodes with dimension of 40 x 5 mm². The distance between electrodes was 3 mm. The samples were placed on the grounded electrode. Duration of the process was 1 – 5 min.

![Figure 1. The experimental set-up.](image)

The experimental conditions for magnetic field treatment were as follows: the alternator frequency was 5.28 MHz, the root-mean-square value of magnetic field strength was \( H = 590 \) A/m. The paper sheets were oriented transversely or parallel to the force lines of the magnetic component \( H \) (figure 2). Duration of the exposure to electromagnetic field was 15 min.

![Figure 2. A scheme of the magnetic inductor.](image)

Structural features of paper before and after the treatment were studied by digital laser speckle photography, laser goniophotometric Stokes polarimeter and attenuated total reflectance (ATR).

2.2. Digital laser speckle photography
The microstructure changes in plasma treated paper were tested by the methods of digital laser speckle photography [13]. The speckle-field recorded from the paper was formed as a result of 3D-interference of repeatedly scattered coherent radiation. The speckle images were recorded with a high resolution CCD camera Nikon D70S (the resolution of the matrix is 3008 x 2000 pixels). The statistical functions
of the first order have been analyzed for speckle images recorded before and after the treatment of paper. The details of the data processing have described in [14].

2.3. A laser goniophotometric Stokes polarimeter
A block diagram of the measurement set-up using a laser goniophotometric Stokes polarimeter is shown in figure 3. He-Ne laser was the source of probing radiation with wavelength 632.8 nm. The diameter of the laser beam was ~5 mm and the power of the generated radiation was 12 mW. Using polarimetric plates, the electric vector of the linearly polarized laser radiation was oriented parallel (||) or perpendicular (⊥) to the plane of incidence. The intensity \( I \) and the Stokes parameters \( P_1, P_2, P_3 \) of the studied radiation were recorded using a one-channel setup with rotating quarter-wave (\( \lambda/4 \)) phase plate and a fixed analyzer [15]. The distribution of the intensity of the probing laser radiation, directed at an angle \( \varphi = 5^\circ \) relative to the normal to the surface of the material, that was reflected by the specimen \( (I') \) and transmitted through it \( (I'') \) was measured in the plane of incidence in the angular range \( \Theta'(\Theta'') = 5-85^\circ \). The solid angle of the detection system \( (\Delta\Theta) \) within which the scattered radiation was picked up was \( 7.2 \cdot 10^{-3} \) sr, which corresponded to an angular resolution in the plane of observation \( \Delta\Theta = 5^\circ \). The field of view of the photodetector was greater than the size of the irradiated spot on the specimen, but was smaller than the area of the specimen itself for all measurement angles. This made the dependence of the radiation power reflected by a Lambert surface on the observation angle \( \Theta \) take the form of a function proportional to \( \cos \Theta \) [16]. The relative error in measurement on the intensity of the reflected (transmitted) laser radiation was -5%, while the absolute error in determination of the degree of polarization was no greater than 0.06. As the photometric parameters characterizing the studied material, we used distribution functions over the detection angles for the bidirectional reflection coefficients \( F'(\Theta') \) and the bidirectional transmission coefficients \( F''(\Theta'') \) [17, 18]:

\[
F'(\Theta') = \Delta I_r(\Theta')/I_{0\delta} \cos \Theta' (\Delta\Theta),
\]

\[
F''(\Theta'') = \Delta I_t(\Theta'')/I_{0\delta} \cos \Theta'' (\Delta\Theta),
\]

where \( \Delta I_r \) and \( \Delta I_t \) are the intensities of laser radiation reflected in the \( \Theta' \) direction and transmitted in the \( \Theta'' \) direction, detected within solid angle \( \Delta\Theta \) of the detection system; \( I_{0\delta} \) is the intensity of the laser radiation incident on the specimen, polarized in the plane of incidence or orthogonal to it. We also determined the indicatrices \( f(\Theta) = \Delta I_r/\Delta\Theta \) of the reflected laser radiation power, normalized to the...
values $f(\Theta' = 5^\circ)$, and also the degree of polarization of the reflected and transmitted laser radiation [19]:

$$P = (P_1^2 + P_2^2 + P_3^2)^{1/2}/I.$$

In order to estimate the effect of structural inhomogeneities on the surface and within the volume of the sheet of paper on formation of reflected radiation field the values of $f'(\Theta')$ of the indicatrices of the reflected laser radiation power were multiplied by the degree of its polarization $P(\Theta')$ or by the quantity $(1 - P(\Theta'))$. In the first case, we obtained the indicatrices of the radiation power for the polarized component of the radiation reflected by the surface of the paper when it is probed by radiation polarized in the plane of incidence $f_{(S)}^r = P(\Theta') f'(\Theta')$ or orthogonal to it $f_{(N)}^r = P. (\Theta') f . (\Theta')$; in the second case, we obtained the corresponding indicatrices of the radiation power for the unpolarized component of the reflected radiation, formed by scattering within the volume of the paper: $f_{(S)}^r = (1 - P(\Theta'))/ f'(\Theta')$ and $f_{(N)}^r = (1 - P(\Theta'))/ f(\Theta')$.

3. Results and discussion

3.1. Plasma treatment

The histograms of intensity in the speckle-fields of paper before ($G(I_{pq})$), after ($G^{*}(I_{pq})$) the plasma treatment and the difference between them ($\Delta = G^{*}(I_{pq}) - G(I_{pq})$) are shown in figure 4. The shape of histogram changes after the treatment. It is obvious that the correlative volumetric dimensions of paper micro heterogeneity increase for plasma modified paper. The main reason for the paper microstructure changes is the porosity increase of the paper because of the micro discharges occurred in micro pores between the cellulose fibrils in plasma.

![Figure 4](image)

**Figure 4.** Histograms of intensity in speckle-field of untreated (a), plasma treated (b) paper and the difference between them (c).

3.2. Radiowave treatment

The surface and volumetric components of indicatrices of light power reflected by paper is shown in figure 5.

We should note the differences in the shape of the indicatrices of the reflected radiation power $f_{(S)}^r$ (especially for parallel orientation of the magnetic component of the field to the plane of the specimens and before exposure to the electromagnetic field) and the scattered laser radiation power as a function of the azimuth of its polarization and the orientation of the specimen relative to the force lines of the magnetic component of the field (Figure 5). However, for $f_{(N)}^r$ these differences appear to a lesser degree due to multiple scattering of light within the volume of the paper, which leads to depolarization and broadening of the indicatrices of the radiation power transmitted through the volume of the paper.
As a result of exposure to a high-frequency electromagnetic field with parallel orientation of the magnetic component force lines $\mathbf{H}$ to the surface of the specimen, the anisotropy of the surface layer of the paper decreases (Figure 5b). Exposure to a field with the perpendicular orientation of magnetic component force lines to the surface of the specimen, completely removes the anisotropy, and the surface layer of the paper becomes practically isotropic (Figure 4c). Similar trends also appear in the shape of the indicatrices $J_r^{(s)}$ (Figure 4e, f). Thus exposure to a high-frequency electromagnetic field, the force lines of which are perpendicular to the surface of the studied paper specimens, removes the anisotropy not only in the surface layer of the paper but also within its volume. So exposure to a high-frequency electromagnetic field leads to disorientation of the cellulose fibers making up the matrix of the paper, and causes a decrease in their degree of crystallization.

It is shown also that the effect of the magnetic component of an rf electromagnetic field on the paper appeared in the frequency shift in the ATR spectra (in the range of $1300 - 1500 \text{ cm}^{-1}$) (figure 6). It may be connected with orientation effects of cellulose macromolecules and change their conformation structure.

![Figure 5. The surface (a-c) and volumetric (d-f) components of indicatrix of the radiation power: reflected by the untreated specimen (a, d) and after its exposure to an electromagnetic field with parallel (b, e) and transversal (c, f) orientation of paper sheet to the magnetic lines; probing laser radiation polarized in the plane of incidence (1) and orthogonal to it (2).]
Figure 6. ATR spectra of paper in the range of 1200-1500 cm⁻¹: 1- untreated sample; 2- after exposure to rf electromagnetic field; 3- after treatment and artificial ageing by thermal processing at 120° C.

4. Conclusions
The effect of radio frequency plasma and radio frequency electromagnetic field treatment on some physical and chemical properties of a paper for offset printing is studied. Plasma treatment changes the microstructure of paper. The exposure of paper to the rf magnetic field decreases the structural order in the material, causes a decrease in their degree of crystallization, changes the shape of surface component of indicatrices of the reflected laser radiation power with the wavelength of 632.8 nm, induces a frequency shift in the ATR IR spectra (in the range of 1300 – 1500 cm⁻¹).

The anisotropy of the diamagnetic susceptibility of the cellulose molecule leads to the fact that when the force lines of the magnetic component of the electromagnetic field are oriented perpendicular to the surface of the paper, the decrease in structural ordering of the material is more substantial than for the parallel orientation.

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