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Ar-O_2 plasma of resonant UHF discharge for chitosan's films processed

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Abstract. This article explores the modification of chitosan films by treating Ar-O_2 with microwave plasma. The main idea is to use resonant plasma generation methods to treat chitosan films. Spectral and energy characteristics of microwave plasma are obtained. The mechanical properties, swelling, and solubility of chitosan films exposed to microwave plasma are studied. The dependence of film properties on the duration of treatment with resonant microwave plasma is demonstrated.

Key words and phrases: plasma, resonance, UHF discharge, microwave plasma, chitosan, film modification, swelling, solubility, experimental studies

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1. Introduction

Nowadays, promising applications have emerged in the field of plasma modification of surfaces, such as cleaning, sterilization, modification and coatings for biomedical applications. For these purposes, the functions of biomaterial surfaces are frequently controlled by their contact to biological materials. These functionalities are often used to improve the polymer biocompatibility to obtain a selective control of the biological response. Thus, the development of techniques for rapid and convenient directed modification of physicochemical properties of chitosan film materials is an important task for the field of polymer science focusing on direct interaction with regenerative medicine. It is known that low temperature plasma exposure of film materials currently represents one of the most effective and most environmentally friendly approaches aimed at modifying the surface properties of polymeric materials [1–3]. It has been repeatedly demonstrated in several works that high-energy low-temperature plasma exposure holds great promise in molding various materials from chitosan and/or its derivatives and modulating their properties for subsequent potential biomedical applications [4, 5]. In the presented study, we evaluated the effect of exposure to microwave plasma discharges of an argon-oxygen mixture on the mechanical properties, swelling, and solubility of chitosan films. The main difference between this study and early-published works is that the research installation with a resonant microwave discharge as a source of plasma flow provides a wide variation of the generated plasma parameters.

2. Set Up and Diagnostics

The linear magnetized plasma multistage device RAPIRA (Resonant Accelerated Plasma Installation Research & Application) was used as a test bed to address anticipated research and development issues associated with RF(Helicon) and UHF (ECR)-discharges and establish the physics basis for investigation of Plasma Material Interactions (PMI). The ECR and Helicon setups is parts of the RAPIRA device, which is a cylindrical, linearly magnetized plasma experiment. Fig. 1 shows a schematic drawing of RAPIRA indicating the position of the Helicon and the ECR parts. Installation is a 4 m long hybrid stainless steel - quartz vacuum volume. The diameter of the quartz tube is 65 mm, while stainless-steel receiving chamber is of the 0.82 m inner diameter, 2.0 m long.

Vacuum volume including stainless-steel receiving chamber 7, quartz tube 2 and system of gas feeder 1 (Fig. 1) was evacuated down to a base pressure of 10^{-6} Torr by tandem of turbomolecular pump and a rotary pump connected to receiving chamber. Plasma-forming gases (Ar; H_2; N_2; He; Kr; O_2) and their mixtures were fed into the chamber using a mass-flow controller, typical values of pressure during operation lay in the 0.5 mTorr range. Pressure was monitored using Pirani and ionization gauges. This paper presents the results of processing chitosan films with a mixture Argon (80%) and O_2 (20%) plasma flow generated only by a UHF source. ECR plasma sources are known to provide very high ionization efficiencies due to the resonant transfer of microwave energy to the electrons [6, 7]. The experiments with UHF-discharge have been carried out on the part of RAPIRA, which is sketched in Fig. 1. The UHF-cavity 4 excited by a microwave source in pulsed or continuous operation mode immersed in static magnetic field produced by coils 5 which allows to keep induction within cavity's volume up to 1500 Gs and variable longitudinal gradients of magnetic field no less 25 Gs/cm. A 2.45 GHz magnetron (Muegge MX3000D-160KL) delivers up to 3 kW of microwave power, which is coupled via a rectangular-to-coaxial waveguide transition into the cavity. The coaxial adapter, waveguide and the cavity were matched. When the cavity is in resonance UHF-power reflection is very small. But if the cavity is loaded by plasma, power reflected from the cavity comes back to the circulator where it can be measured correctly. The use of a circulator with a cooled load virtually removes restrictions on the level of reflected power. The pulse durations of the microwave source can vary widely from 1 s to continuous operation. The cavity is excited by the TE_{111} oscillation mode, which is optimal for generating electron cyclotron resonance plasma under typical conditions.

The main parameters of the installation are presented in Table 1. The use of these parameters allows to obtain plasma formations with temperature in the range from 5 to 50 eV, concentrations of charged particles in the range from 10^9–10^{11} cm^{-3} and plasma flow, with ionic current density on sample processing up to 200 μA/cm^2.

For spectrometric studies, we used an MS3504i monochromator-spectrograph with astigmatism compensation. The spectrum was recorded in the monochromator mode. The spectrometer was

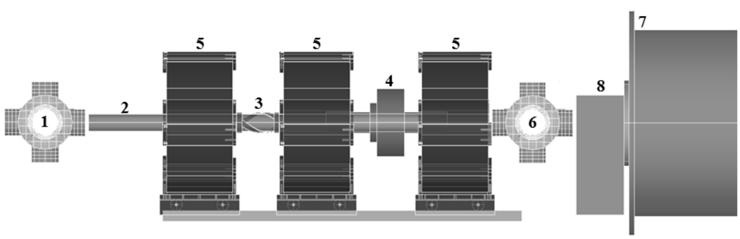

Figure 1. Multistage device RAPIRA

Table 1

Installation parameters

Working gas	Working pressure, Torr	RF-discharge		UHF-discharge		Magnetic system		Film mounting system for processing
		Frequency, MHz	Power, W	Frequency, GHz	Power, W	Field amplitude, G	Field gradient, G/cm	
H_2, N_2, O_2, Ar, gas mixtures	10^{-4} through 10^{-2}	13.56	to 750	2.45	to 3000	to 2800	to 100	From 1 to 12 films are simultaneously placed in the vacuum volume

calibrated over the wavelength by using a DRS 50-1 mercury lamp with allowance for the parameters of the recording system and over the absolute intensity by using an SIRSh 6-40 lamp (certified at the All-Russia Research Institute of Optical and Physical Measurements). The plasma flow generated was diagnosed using multigrid energy analyzer inserted receiving chamber (7, Fig. 1).

For plasma flow treatment, polymer biocompatible biodegradable films based on natural (chitosan, pullulan, gelatin) and synthetic (polylactide) polysaccharides are produced with the possibility of adding inorganic fillers (0.1–5% of layered double hydroxide Mg2+/Fe3+ or commercially available montmorillonite) [8, 9]. Polymer and composite films are produced by pouring molding solutions into Petri dishes, followed by drying at room temperature at either 60°C, or 90°C in a dry oven. Purified water (GF XV) is used as a solvent, and if chitosan is present in the molding solution, a 1% aqueous solution of acetic acid is used.

To accumulate statistical data on the results of plasma treatment, a lot of six film samples was simultaneously loaded into the receiving chamber. The samples were mounted on a mechanical carousel system that ensured precise positioning of the sample under the plasma flow. The remaining films are not exposed and are processed in experiments with changed parameters.

The RAPIRA-Experiments is equipped with a large diagnostic suite. Table 2 gives an overview of the diagnostics used.

The process of film modification needs to be monitored. Mechanical properties of the obtained films were studied in uniaxial tensile mode on a tensile machine (REM, Russia, the size of the samples was 6×2 cm, the speed of uniaxial tension was 50 mm/min). The solubility and swelling of the obtained films in purified water were evaluated gravimetrically [10, 11]. Infrared spectroscopy allows detection of the mentioned processes but has not yet become widespread as a monitoring of surface chemical modification of films [12]. In this work, the aim was to record the presence or absence of changes of plasma-treated chitosan films under UHF-discharge.

Table 2

Summary of RAPIRA-Experiments Plasma and Physicochemical Diagnostics

Plasma diagnostics	Physicochemical diagnostics
Falling and reflected power measurements UHF, RF	Swelling (%)
Distributer pressure measurements	Solubility (%)
Langmuir probes (T_e, n_e)	Tensile strength (MPA)
Retarding field analyzer probe (ion, electron EDF)	Elongation at break (%)
Optical emission spectroscopy (T_e, n_e)	IR-spectroscopy (cm^{-1})

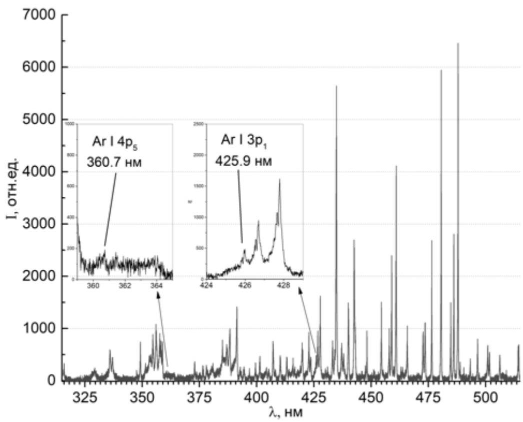

Figure 2. Typical EOS spectrum with marked lines for density analysis

3. Results and discussion

In the main operating modes of the installation, measurements of the plasma flow parameters were carried out in the area of its transportation and in the area of landing on the substrate. Typical results are shown in Fig. 2. The optical emission spectrometry (OES) gives an estimate (Fig. 2) of the electron concentration, relative to the line intensities of 360.7nm and 425.9nm [13–15]. The average concentration of plasma at 1200W of incident microwave power is $\approx 5 \cdot 10^{10} cm^{-3}$.

Based on the results of measurements with a retarding field analyzer probe (Fig. 3).

An estimate of the ion concentration density in the flow in the area of the sample location was obtained $\approx 2 \cdot 10^9 cm^{-3}$ [16–19].

The treatment was carried out in one of the discharge modes (working gas mixture Ar–O_2, gas pressure $\approx 5 \cdot 10^{-4}$ Torr, input microwave power 1200 W, electron temperature 5 eV, electron concentration $\approx 5 \cdot 10^{10}$ cm^{-3}, current density of the ionic component of the plasma flux in the irradiation region of chitosan samples ≈ 70 $\mu A/cm^2$). Constancy of the treatment mode is maintained by registration of the discharge emission spectrum and stability of operating parameters. Film 6 acted as a control sample, was placed in a vacuum chamber but not treated with plasma, films 1,

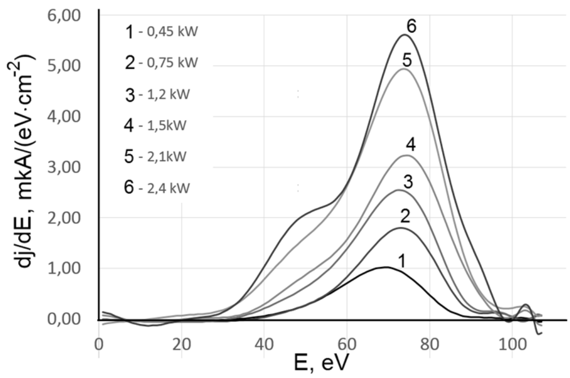

Figure 3. Energy distribution of ion current density in the sample location region with variations in microwave power

Table 3

Qualitative functional analysis of IR spectra of the films

Functional group	$\omega_{C\text{-}H}$	cycl. C-O-C cycl. -OH	$\nu_{C\text{-}O}$	ω_{CH2}	$\delta_{O\text{-}H}$	$\delta_{C\text{-}H}$	$\delta_{N\text{-}H}$	$\nu_{C=O}$	ν_{CH}	ν_{OH} and ν_{NH}
Characteristic frequency, cm^{-1}	893	985, 1024, 1059	1150	1320	1375	1419, 1454	1542, 1589	1649	2868, 2914	3291, 3352

2, 3, 4 and 5 were placed in a vacuum chamber and treated with plasma for 10, 35, 70, 105, 140 s, respectively.

The IR spectra of films treated with plasma for different periods of time (1–5) and the film that was in the RAPIRA apparatus but not exposed to plasma (control film 6) are shown in Fig. 4. Table 3 demonstrates a detailed qualitative functional analysis of the observed signals in the spectra, i. e., the correspondence of characteristic frequencies to certain functional groups.

The IR spectra of the obtained films (Fig. 4) are almost identical, indicating the presence of identical functional groups on the surface of the prepared chitosan-based films. However, the IR spectra of the films show some differences in the wavenumber range of 1300–625 cm^{-1}, that is, in the so-called fingerprint region, which is a strictly individual characteristic of the compound.

Thus, the differences in the fingerprint area do not indicate that all the films are slightly different in their surface characteristics [20, 21]. This is not surprising, as the films were exposed to plasma for different durations. This superficial modification is certainly minor, but nevertheless such changes can result in a pronounced change in the physicochemical characteristics of the film surface, hydrophilic-hydrophobic properties, swelling, adhesion capacity and, consequently, biological properties.

The most important mechanical properties of films — strength and ductility — are quantitatively described by tensile strength and elongation at break, respectively. In this study, we evaluated the

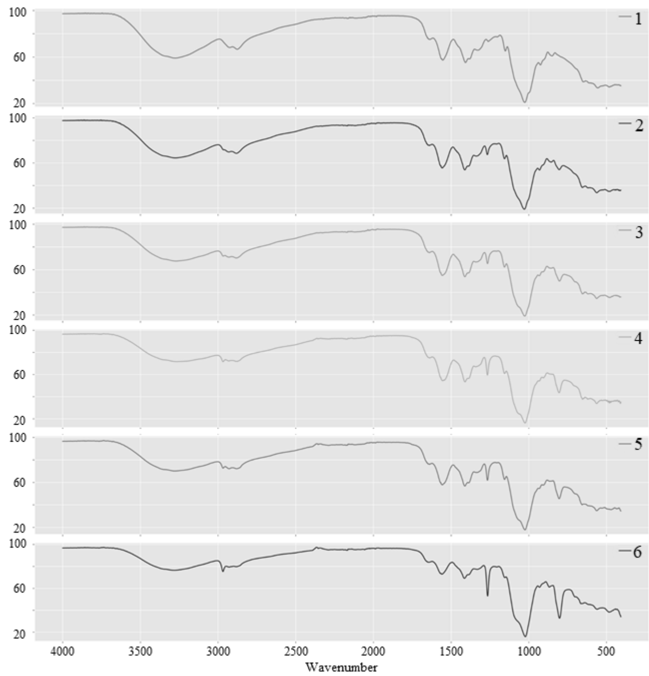

Figure 4. IR spectra of the prepared chitosan-based films

Table 4

Effect of argon-oxygen plasma treatment on the mechanical characteristics of chitosan films

Film	Tensile strength, N/mm^2	Elongation at break, %
1	24.3	36.0
2	26.1	37.4
3	27.2	37.3
4	26.3	38.5
5	24.0	37.1
6	19.9	33.1

effect of argon-oxygen plasma treatment on the mechanical characteristics of chitosan films (Table 4). Plasma treatment affects film strength. All treated films (1–5) were slightly stronger than the film that did not receive direct plasma exposure (6). The maximum increase in strength, 35%, was observed for film 3. Plasma treatment also increased film ductility, but this effect was significantly less pronounced. The maximum increase in ductility was characteristic of film 4 and amounted to only 15%.

The results of the solubility study of the processed films are presented in Fig. 5. All films are characterized by the tendency to dissolve partially in distilled water within 60 min. The solubility

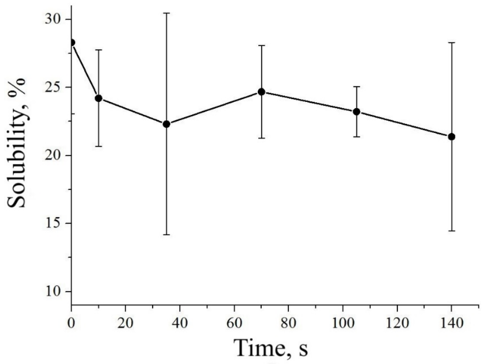

Figure 5. Solubility of films in distilled water at 25°C

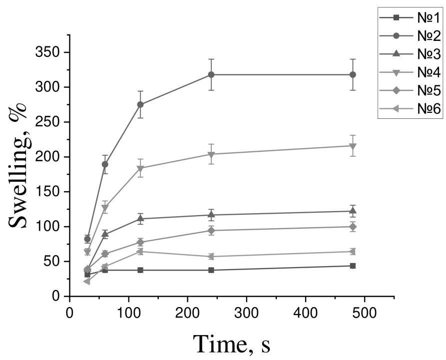

Figure 6. Swelling of the films

of all films 1–5 for the specified time interval practically does not differ from the solubility of the control film 6 and it is in the range of 23–31%.

Fig. 6 exhibits the results of swelling studies of the prepared films. All films exhibit limited swelling. Film 2 swells the most (more than 3 times), while films 1 and 6 swell the least (approximately 50%). The presented film swelling results are consistent with those obtained in their solubility studies (partial solubility is typical of films with limited swelling).

It should be noted that this behavior of films treated with a microwave discharge of the specified mixture differs from their properties when processed in pure argon, where there is an increase in swelling in the specified range of treatment exposures up to 2500%.

This fact indicates a limitation of the hydrophilicity of the resulting film, on the one hand, and the ability to retain large amounts of water, on the other.

4. Conclusion

The influence of Ar/O_2-plasma of resonant UHF discharge parameters on the change of physicochemical properties of thin chitosan films is determined. Plasma treatment leads to some chemical changes on the surface of the films, which is expressed in differences in the IR spectra in the "fingerprint region". Initial experiments have shown the presence of deviations in the IR properties of the model films. Moreover, plasma discharges of an argon-oxygen mixture processing significantly change the hydrophilicity of chitosan films; improve their solubility and mechanical properties. Further spectroscopic and structural-chemical studies are needed to identify these changes. Further research is aimed at finding plasma generation modes under both microwave and HF discharge conditions and creating a plasma flow with optimal parameters that ensures a given variability in the physico-chemical properties of films.

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Ar-O_2 плазма резонансного СВЧ-разряда для обработки хитозановых плёнок

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Аннотация. Статья посвящена исследованию модификации хитозановых пленок при обработке Ar-O_2 плазмой СВЧ-разряда. Основная идея заключается в использовании резонансных методов создания плазмы для обработки хитозановых плёнок. Получены спектральные и энергетические характеристики плазмы СВЧ-разряда. Исследованы механические свойства, набухание и растворимость хитозановых плёнок под воздействием плазмы СВЧ-разряда. Показана зависимость свойств плёнок от времени обработки плазмой резонансного СВЧ-разряда.

Ключевые слова: плазма, резонанс, СВЧ-разряд, микроволновая плазма, хитозан, модификация плёнок, растворимость, набухание, экспериментальные исследования