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Effect of low-pressure radio-frequency air plasma on chitosan films

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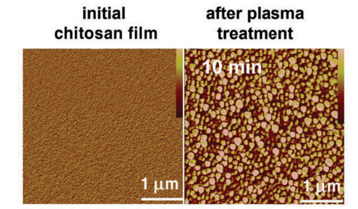
The effect of low-frequency (15 kHz), low-pressure (10 Pa) air plasma treatment on freshly prepared chitosan films at processing times from 3 to 10 min has been explored. The films were prepared using chitosan solutions in dilute acetic acid. The influence of the plasma exposure time on the composition, morphology, and hydrophilic properties of the film surfaces is discussed.



Pronounced changes in surface morphology

Keywords: chitosan films, plasma treatment, AFM, roughness, wettability.

Chitosan (a deacetylated chitin derivative) is in demand as a starting substance for the design of new multifunctional catalytic,[1–3] adsorption,[4–6] and antibacterial[7–9] materials due to its biocompatibility, biodegradability, and low toxicity. Chitosan-based films are useful in medical practice for treatment of wounds and burns. Since chitosan is a glycosaminoglycan, it can participate in all stages of wound healing.[10,11] The films are commonly prepared by dissolution of the polymer in low-percentage acetic acid followed by solvent removal (air drying at atmospheric pressure, freeze drying, *etc*.).[12] The uniform low-energy surface with insufficient number of polar groups on the top is reflected on the biological activity of the films.[13] Cold plasma treatment[14] is used to increase the biocompatibility and antimicrobial action of biomaterials used in medicine, including chitosan films, membranes, and bandages. Plasma treatment allows one to modify the surface of biomaterials without changing the bulk properties.[15]

The surface topography, surface energy, and composition of chitosan films can be controlled by varying the gas composition, the processing time, and other plasma treatment parameters to change the functional properties of films, such as permeability, hemostatic activity, and ability to support cell adhesion, proliferation, and growth.[16–20] Plasma pretreatment can be applied to create a suitable surface for the deposition of metal nanoparticles or other antimicrobial agents in order to impart bactericidal properties.[21] At short plasma treatment times with atmospheric gas composition, O- and N-containing groups can be incorporated onto the film surface. This procedure can be used to increase the biocompatibility of films and to modify the surface for further grafting with antibiotics, hormones, *etc*.[22–24]

In this work, we investigated the effect of air plasma generated by a radio frequency generator at low pressure on the surface composition, morphology, and wettability of spin-coated chitosan films. First, chitosan films were prepared by casting a solution of chitosan in acetic acid on freshly cleaved mica substrates using a spin coating procedure, which was described previously,[25] followed by exposure in alkali and rinsing with water. The plasma treatment of chitosan films mounted on a grounded electrode was carried out in a gas-discharge glass chamber for 3, 5, or 10 min. The plasma source gas corresponded to atmospheric air. After the plasma treatment, the films were placed in sealed containers. The films were characterized using X-ray photoelectron spectroscopy (XPS), FT-IR spectroscopy, and atomic force microscopy (AFM). The experimental details can be found in the Online Supplementary Materials.

Table 1 gives the surface chemical composition of the chitosan films before and after treatment at different times. A nonlinear effect of plasma exposure time on the elemental composition is observed.

After treatment for 3 min, the C/N atomic ratio decreased and the C/O atomic ratio increased likely due to the deacetylation of chitosan and the formation of a new layer rich in polar functional groups. With the increase of the processing time, the discussed ratios approach the initial values. This can indicate the physical destruction of the pre-formed layer rich in polar groups on the chitosan film surface under prolonged exposure time. Note that the XPS quantitative elemental analysis is applicable only to the near-surface region of the film at 5–8 nm. A similar effect is known for cellulose films,[26] where pure oxygen burns out the polymer surface to increase the roughness, but it does not increase the number of oxidized groups with the processing time.

Figure 1 shows the FT-IR spectra of chitosan films before and after plasma treatment. The spectra were recorded two days after the plasma treatment. The positions of absorption peaks remained

Table 1 Results of the quantitative XPS analysis of the chitosan films before and after treatment with air plasma.

Treatment time/min	Concentration (at%)				
	C	N	O	C/N	C/O
0	66.9	4.3	28.8	15.6	2.3
3	70.4	6.1	23.5	11.6	3.0
5	68.9	4.7	26.4	14.6	2.6
10	65.5	4.0	30.4	16.2	2.2

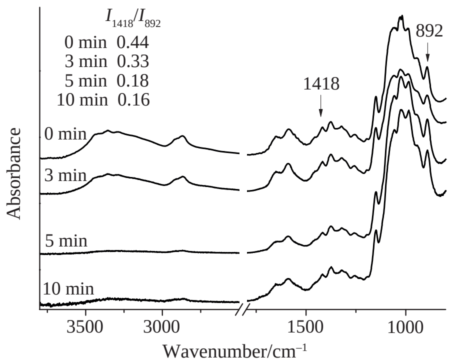


Figure 1 ATR FT-IR spectra of plasma treated chitosan films.

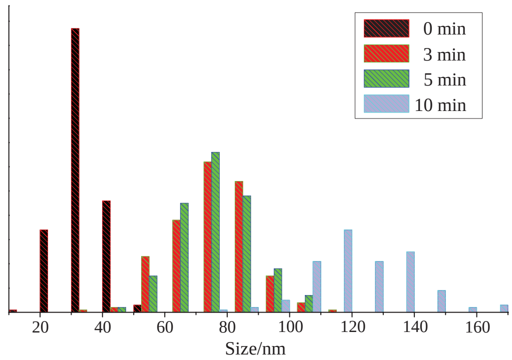


Figure 3 Lateral dimensions of globular-like structures for chitosan films obtained at different plasma treatment times.

unchanged after the plasma treatment of the chitosan films, but absorption band intensities significantly changed.

The intensity of a wide band in the region of 3500–3200 cm^{-1} associated with intra- and intermolecular stretching vibrations of N–H bonds and O–H bonds in amino groups and weakly bound water decreased with the plasma processing time, which is in good agreement with XPS analysis data. This can be caused by both the oxidation of surface amino and hydroxyl groups with active plasma-generated oxygen species[27] and a decrease in the water content of the films.[28] In addition, the bands at 2872 and 2917 cm^{-1} corresponding to C–H stretching vibrations in methyl and methylene groups became weaker upon plasma treatment. FT-IR spectroscopy proved to be a simple and fast method to examine crystallinity of polysaccharides.[29] The ratio between band heights at 1418 and 892 cm^{-1} (I_{1418}/I_{892}), which correspond to CH_2 scissoring and ring valence vibrations, can be used for tracking changes in the crystallinity of chitosan. A gradual decrease in the I_{1418}/I_{892} ratio (see Figure 1) with plasma treatment time indicates an increase in the crystallinity of the films. This tendency to an increase in crystallinity with plasma treatment time was observed earlier in chitosan films.[27] Note that considerable spectral changes, given the informational depth of the method, indicate the effect of plasma in the deep layers of the film (several micrometers).

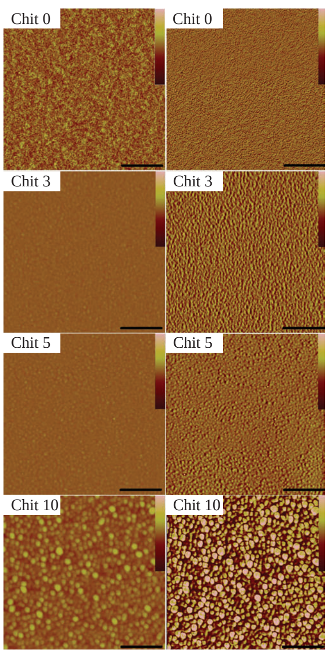


Figure 2 AFM images of chitosan films on mica surfaces: left column, height images; right column, phase images; scale bar, 1 µm; height scale, 30 nm; and phase scale, 50 deg.

The effect of plasma treatment on the morphology of chitosan films was studied by AFM (Figure 2). The morphology of the pristine chitosan film, which consisted of globule-like structural units, was similar to the morphology of chitosan films reported previously.[25,30,31] Globule-like structures were also observed in the plasma-treated chitosan films. Figure 3 shows the lateral dimensions of structural units observed in pristine and plasma-treated chitosan films.

It can be seen that the increase in the sizes of the globules is proportional to the plasma treatment time. In the pristine film, the sizes were in a range of 10–50 nm, and globule size distributions in plasma-treated chitosan films slightly shifted towards higher values. It is most likely that the size of the film units is increased both due to globule aggregation initiated by an increase in the mobility of chitosan chains and due to the removal of low-molecular-weight polymer fragments when exposed to plasma.[32]

Roughness analysis of the film surfaces, which was performed using the NanoScope software, revealed a decrease in the roughness values from 1.8 nm (for the initial film) to 1.0 nm (after 10-min plasma treatment).

We evaluated the wetting properties of the films treated with plasma. Table 2 summarizes the contact angles measured using water and diiodomethane as test liquids. Silva *et al.*[19] obtained similar angles upon treating chitosan membranes with plasma, where argon and nitrogen were used as working gases.

According to Table 2, the treatment led to a slight increase in water contact angles due to deterioration in the hydrophilic properties of the films. The data are consistent with the fact that the plasma treatment makes a smoother surface compared to that in the initial film.

The processing time is a key factor affecting wettability properties. Previously, Augustine *et al.*[11] found that plasma treatment in an argon atmosphere for more than 120 s impaired the hydrophilic properties due to the initiation of polymer degradation. This effect was also observed in ion bombardment with an increase in the energy of argon and nitrogen ions.[33]

Thus, the processing of chitosan film coatings deposited on the mica surface with radio frequency plasma leads to surface

Table 2 Effect of air plasma treatment on the wettability properties of chitosan films.

Plasma treatment time/min	Contact angle/deg	
	Water	Diiodomethane
0	77 ± 1	39 ± 2
3	84 ± 1	44 ± 2
5	82 ± 2	39 ± 2
10	84 ± 2	42 ± 1

etching, which significantly changes the surface morphology and crystallinity of the films without significant changes in the surface energy of the chitosan films. This result can be beneficial for the development of chitosan films with controlled surface parameters.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.044.

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