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CHANGES IN HYDROPHILIC CHARACTER OF CHITOSAN THIN-FILM BY HMDS COLD PLASMA TREATMENT.

Odilio B. G. Assis*, Douglas de Britto

Embrapa Instrumentação Agropecuária - CNPDIA – odilio@cnpdia.embrapa.br; britto@cnpdia.embrapa.br
Caixa Postal 741, 13560-905 São Carlos/SP

This study evaluated the effects of the deposition of a hydrophobic silicon structure onto polysaccharide surface. The goal was to improve the water vapor barrier of a hydrophilic film for potential application as packaging. Cold-plasma technique was used for creation of a thin hexamethyldisilazane (HMDS) deposit at chitosan film surface. The resultant film was colorless and transparent. The effect on wettability was characterized through contact angle measurements and by swelling degree. A significant reduction in hydrophilicity was observed.

Introduction

Chitosan is a polycationic polysaccharide that occurs naturally or can be derived from chitin, via deacetylation in the presence of alkali. Their importance resides in a broad antimicrobial activity (1) in conjunction with an excellent film forming ability (2). Moreover the biocompatibility and the biodegradability of chitosans make them a very interesting polymer for applications such as agriculture, medicine, environment, food, etc.

Chitosan has, however, the disadvantage of having a high affinity for water. Its structure contains a high number of amine (N-H) and hydroxyl groups, which favors the migration of water molecules. The water uptake induces swelling and consequently increases permeation rate and reduces mechanical properties and long-term stability.

A possible technique to eliminate such disadvantage is by implanting organosilicon monomers by glow-discharge plasma. This is an environmentally friendly process and has the ability to initiate a surface reaction while keeping bulk characteristics unchanged (3).

In this work, we use hexamethyldisilazane ($C_6H_{19}Si_2N$), commonly referred to as HMDS, as a precursor gas for cold plasma deposition on chitosan thin-film's surface.

Experimental

Chitosan film preparation

1.0 wt% chitosan (medium molecular weight, Sigma-Aldrich), was dissolved in 1% acetic acid in deionized water with constant stirring for 2 hours and heated to 30-40 °C to facilitate dispersion.. Films were then prepared by solution casting onto an acrylic plate. Solvents were allowed to spontaneous evaporation at room temperature. After drying the films were peeled from the plate.

Hydrophobic treatment

The films of chitosan underwent cold-plasma discharge of HMDS + O_2 (industrial grade, Sigma-Aldrich) in a conventional rf-powered two parallel plate Oxford reactor 80Plus. The plasma power supplied was set at 60W at a frequency of 13.56 MHz at 180mTorr for 2 minutes operation. The HMDS was fed in to the chamber and allowed to stabilize before glow-discharge.

Contact Angle and Measurement of degree of swelling in water

Contact angle were measured in air at room temperature using the sessile deionized water drop. The droplets images on the film surface were recorded using a Tantec CAM-PLUS device. The recorded angle is the average of six measurements on each sample.

The degree of swelling was measured from immersion assay, following Möller, et al. (4) procedures. Pieces of film in dried state were weighed and immersed in deionized water for 24 hours at room temperature. Then the samples were taken out of the solvent, wiped quickly with filter paper, and weighed. The degree of swelling was expressed as a percentage of water after immersion compared to initial dry weight from:

$$DS = \frac{W_s - W_d}{W_d}(100\%) \qquad (1)$$

where DS is the degree of swelling of the film, Ws the weight of swollen sample and Wd is the dried sample. All experiments were conducted in triplicate .

Results and Discussion

HMDS deposition

During plasma treatment the surface of the sample is continuously bombarded with ions, electrons, radicals, neutrals and UV radiation from the plasma phase. The polymerization takes place by components being incorporated and crosslinked on the surface. For HDMS plasma environment, very thin films are obtained. Typical deposition rates are stated in the range of 60–100 nm/min (5). The resultant polymerized structure is amorphous and highly hydrophobic (3).

Contact angle

For noncrosslinked chitosan films, the literature reports a range of water contact angles values, from 60° (6) to angles >83° (7). For the materials studied in this work, the measured contact angles are shown in Table 1.

Table 1 - Surface water contact angle on the tested chitosan films (n = 6).

Sample	Contact angle (°)
Chitosan (control)	64 ± 2
Plasma-modified chitosan	88 ± 3

The increase of the angle of 24° is a clearly indication of the effect of a superficial hydrophobization due to plasma deposition. These values are similar to those found by Hayakawa et al. (8), for organosilicon plasma layers deposited on metals (around 83°).

Swelling

The degree of swelling is one of the important factors in determining the usefulness of a biomaterial, mainly considering the potential applications as food coatings or as packing materials. The swelling is a complex mechanism in polymers, dependent on the relative contribution of penetrant diffusion and polymer chains relaxation (8).

Figure 1 compares our sample's degree of swelling after 24 hours. It is possible to conclude that the plasma organosilicon deposition, provides a relatively good water inhibitor generating, in the experimental conditions used in this work, a reduction of around 30% on the medium degree of swelling. The swelling value for non-treated chitosan is in good agreement with those found in the literature (9).

Since the swelling process starts from interaction through polar functional groups on the surface, the results show that the plasma deposition was successful in a formation of a less polarized surface, i.e., in the growth of hydrophobic layer on the chitosan film.

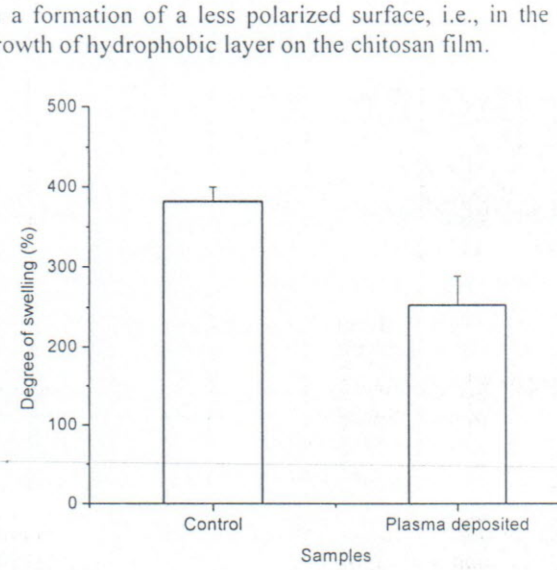

Figure 3 - Swelling degree of chitosan films for non-treated and treated samples. After 24 hours, pH 7.0 at room temperature.

Conclusions

Cold-plasma polymerization of HMDS on organic substrates is a highly complex process and there are a number of parameters that affect the permeability properties of the combined layers. In particular, the polymerization of hexamethyldisilazane hydrophobic layer on chitosan thin film have good influence in reducing the swelling degree and on the increasing of the water contact angle.

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