



Non-monotonic wetting behavior of chitosan films induced by silver nanoparticles



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ABSTRACT

The present work is devoted to the study of structural and wetting properties of chitosan-based films containing silver nanoparticles. In particular, the effects of silver concentration on the morphology of chitosan films are characterized by different techniques, such as atomic force microscopy (AFM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). By means of dynamic contact angle measurements, we study the modification on surface properties of chitosan-based films due to the addition of silver nanoparticles. The results are analyzed in the light of molecular-kinetic theory which describes the wetting phenomena in terms of statistical dynamics for the displacement of liquid molecules in a solid substrate. Our results show that the wetting properties of chitosan-based films are high sensitive to the fraction of silver nanoparticles, with the equilibrium contact angle exhibiting a non-monotonic behavior.

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1. Introduction

Natural polymers have attracted a remarkable interest over the past decade due to their abundance, low cost, biodegradability and biocompatibility, as well as their ability to form flexible and free-standing films for a large variety of applications [1]. In particular, it has been demonstrated that biopolymers derived from polysaccharides are suitable host materials for metal nanoparticles, providing them chemical stability and a suitable environment for use in biological systems [2,3]. In this context, chitosan has played an important role due to its excellent capability of being structurally modified, leading to the adjustment of their properties for specific purposes [4]. Chitosan is a pseudo-natural polymer obtained from the deacetylation of chitin (poly-N-acetyl-D-glucosamine) which is a polysaccharide present in the exoskeleton of crustaceans and insects, fungal biomass and mollusk shells [4,5]. The process of deacetylation of chitin takes place from the partial or full replacement of a N-acetyl group in the chitin by an amine group [5]. The presence of the amine group in the chitosan molecular structure has opened the possibility of using such system in several practical problems, such as enzyme immobilization [6], controlled drug releasing [7,8], sorption phenomena [9,10] and metal

complexation [4,11]. Further, chitosan exhibits a high surface energy and excellent adhesive properties on solid substrates, making it an ideal setup to produce functional films [12,13].

It is well established that the introduction of metallic nanoparticles is a successful procedure to induce profound physical and chemical modifications in polymeric hosts for specific purposes [14–16]. The main reason is that metallic nanoparticles exhibit interesting optical and electrical properties associated with the surface plasmon resonance, which can be tuned by adjusting the size, shape and concentration of nanoparticles [17–19]. In particular, mechanical, electric and optical properties of nanocomposites can be reasonably modified by controlling the nanoparticles morphology added in the polymeric host. A prominent example is the improvement in the performance of photovoltaic devices due to the interplay between surface plasmons of nanoparticles and exciton generation which enhances the mechanism of charge transfer [20]. Further, nanocomposites have been used in sensor devices for biorecognition due to the high sensitivity of the surface plasmon resonance to the external conditions [21,22]. Concerning thermal and mechanical properties, it has been demonstrated that the addition of nanoparticles may affect the elasticity, thermal conductivity, and stability of polymeric systems, depending on the concentration and size of the guest particles [23,24]. As a consequence, the comprehension of processes behind the surface and structural modifications of such systems has become an important step in the development of new technological devices.

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Recently, special attention has been devoted to the modification of chitosan films from the addition of silver nanoparticles, due to the large potential of resultant materials for different applications [25–28]. Several studies have demonstrated that chitosan–silver nanocomposites exhibit a high antimicrobial activity, which can be used in wound dressing [25,26] and water purification [27]. Because its cytotoxic efficacy and selectivity, such a system also presents an antiproliferative activity against a series of cancer cell lines [29]. Further, it has been shown that chitosan–silver nanocomposites can be employed as a low cost substrate for ultrasensitive detection of molecules by using surface-enhanced Raman spectroscopy [28,30]. Regarding electro-optical properties, it has been reported that linear and nonlinear refractive indices of chitosan-based nanocomposites are highly sensitive to the concentration of silver nanoparticles [31], opening the possibility of using such soft materials in planar waveguide and optical signal processing.

Although biomedical applications of chitosan–silver nanocomposites have been widely investigated, the influence of the nanoparticles concentration in the interfacial properties of chitosan films has not been explored so far. In this work, we study the concentration effects on the wetting and structural properties of chitosan–silver composite films. By using the molecular-kinetic theory to describe the time evolution of the contact angle, we estimate how the surface contribution to the wetting free energy and the surface density of adsorption sites are affected by the nanoparticles concentration. Structural properties of nanocomposite films are also investigated from atomic force microscopy (AFM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques. Our results show that the addition of silver nanoparticles plays an important role in the wetting and structural properties of chitosan films.

2. Materials and methods

2.1. Sample preparation

Chitosan (85% DA, $M_w \approx 3 \times 10^5$) was obtained from Acros and it was used as received. Silver nanoparticles with polyvinylpyrrolidone (PVP) as dispersant were purchased from Sigma–Aldrich, being used as received. The average diameter of nanoparticles was 100 nm. Chitosan solutions were prepared by dissolving chitosan 1.0% (w/v) in 0.25 molL⁻¹ acetic acid at room temperature and contentiously stirred for 48 h. After the preparation of the chitosan solution, we have computed the required amount of silver nanoparticles to obtain a final solution containing a specific wt.% of nanoparticles. Silver nanoparticles powder was added in chitosan solutions at room temperature, with the final solution being stirred until the contents have been fully blended. The concentration of silver nanoparticles was varied in the range of 0–1.0 wt.%. Composite films were obtained by casting chitosan–silver nanoparticles solution onto soda lime glass plates that were previously cleaned. After solvent evaporation, the samples were dried under air at room temperature. Resultant composite films exhibit a mechanical aspect similar to the cellophane, with the film opacity increasing as the concentration of silver nanoparticles is enhanced. Using a digital micrometer, the average thickness of composite films was estimated to be around 10 μm .

2.2. UV–vis spectroscopy

The extinction spectra of chitosan films were recorded using a spectrophotometer Perkin Elmer Lambda 1050. All measurements were carried out in chitosan–silver composite films deposited on soda lime glass plates.

2.3. FTIR spectroscopy

In order to study the chemical and structural changes in chitosan-based films associated with the addition of silver nanoparticles, FTIR spectra were recorded using a Shimadzu IR Prestige-21 spectrophotometer at the wavenumber range region between 4000 and 400 cm⁻¹. Free-standing chitosan-based films were prepared and all infrared spectra were recorded in the transmission mode at 4 cm⁻¹ intervals and 20 scans.

2.4. Contact angle measurements

The wetting phenomena on the surface of chitosan films were investigated by using the sessile drop method. Castor oil was used as the probe liquid in order to minimize the effects associated with the liquid absorption by the solid substrate [32]. Castor oil drops were deposited on chitosan–silver composite films and the dynamic contact angles were automatically acquired by means of an optical goniometer Tetha (Attension Instruments). The time evolution of the contact angle was determined from the digital analysis of castor oil drop images which were captured in intervals of 4 ms. All measurements were performed at a constant temperature (22 °C) and the procedure was repeated at least 10 times for each concentration of silver nanoparticles.

2.5. X-ray spectroscopy

X-ray diffraction studies were carried out using a Shimadzu XRD-6000 diffractometer, with Cu K α radiation source ($\lambda = 1.54056 \text{ \AA}$), with power of 40 kV and 30 mA. The diffraction angle, 2θ , was varied from 5° to 70°, with the diffraction measurements performed at constant temperature (22 °C). The measurements were performed in free-standing chitosan-based films containing distinct concentrations of silver nanoparticles.

2.6. Atomic force microscopy

The morphology of chitosan–silver composite films was characterized by a Multiview 1000™ atomic force microscope from Nanonics (Israel). A Silicon probe (resonant frequency $f = 300 \text{ kHz}$, spring constant $k = 35 \text{ N m}$, AppNano) operating in tapping mode was used. The scanning area was $40 \times 40 \mu\text{m}^2$, with a 512×512 pixels image to determine the roughness on the nanoscale. Surface roughness has been characterized by atomic force microscopy in terms of the average roughness (Ra), root mean squared roughness (Rms), and average height (Ha) using WSxM software [33].

3. Results and discussion

In Fig. 1 is shown the AFM images of chitosan films for different concentrations of silver nanoparticles, c , which was varied in the range of 0–1.0 wt.%. One can notice that the pure chitosan film exhibits a smooth surface, as shown in Fig. 1a. Although composite films seem macroscopically homogeneous, AFM images reveal that the film roughness increases significantly as the concentration of silver nanoparticles is enhanced, as exhibited in Fig. 1b–d. For $c = 0.2 \text{ wt.}\%$, we observe the formation of small clusters of nanoparticles that are uniformly distributed through the film surface, as presented in Fig. 1b. The number and size of silver clusters become larger as the concentration is increased to $c = 0.4 \text{ wt.}\%$, with the presence of some silver grains along the film surface, as shown in Fig. 1c. At this point, we have observed a severe reduction in the mechanical strength and elasticity of composite films, which become brittle and break easily. However, it is important to stress that a systematic analysis is required to determine quantitatively the reduction in the mechanical properties of such composite films

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