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Chitosan-based Films with Silver Nanoparticles incorporated for Food Packaging Applications

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Abstract

Objectives: This work was performed to study aspects such as morphological characteristics, thermal analysis, and antimicrobial activity of chitosan films that incorporate silver nanoparticles. **Methods/Analysis:** The films were analyzed by the followings techniques: a) FT-IR analysis to identify their functional groups, b) Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) to study the morphological structure of the samples. c) UV-spectroscopy to obtain the intensity of the band in the films, d) DSC-TGA measurements to determine the thermal stability of the material, and e) the disk method to examine the antimicrobial activity of the samples. **Findings:** The films showed a good interaction between their components. Also, a good thermal stability, a protective barrier against ultraviolet light, a high rugosity, and high antimicrobial activity were observed in samples that incorporated a higher concentration of silver nanoparticles. **Novelty/ Improvement:** These results suggested that chitosan-based films with silver nanoparticles incorporated are a potential material for food packaging.

Keywords: Antimicrobial Activity, Chitosan, Food Packaging,Nanocomposites, Silver Nanoparticles

1. Introduction

In food packaging industry, the uses of biopolymers become a feasible alternative to mitigate the environmental problems that nowadays the conventional plastics derived from petroleum have generated. Biopolymers are materials derived from plants, animal products, microbial products, and some chemically obtained from naturally derived monomers as an example the polylactic acid.[1]

Chitosan is a linear polysaccharide derived from partial deacetylation of chitin. This polymer presents D-glucosamine and N-acetyl-D-glucosamine units in its structure and is obtained from insects, shell crustaceans, fungi, and algae[2-4]. Chitosan is used in many fields such as agro-industry, medicine, food, textile, environment, agriculture, cosmetic, etc.[2,3] These properties allow to the chitosan to have characteristics as biocompatibility, nontoxicity, biodegradability, chelating capability, and antimicrobial activity.

Deacetylation grade and molecular weight of chitosan affect its solubility and film-forming ability. Similarly, some mechanisms to explain the antimicrobial activity of chitosan have been proposed.[1,3] These mechanisms include the alteration of factors such as the metabolic activity, genetic transcription, and chelating ability. However, in food packaging applications, it has been demonstrated that biopolymers have poor mechanical and barrier properties.[5,6] Therefore, the use of synthetic polymers and nanofillers has become an alternative to overcome these limitations.

Poly (vinyl alcohol) (PVA) is a synthetic polymer which has characteristics such as biodegradability, biocompatible, good chemical stability, non-toxic, water-solubility, chemical stability in blends, etc. For the fabrication of

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polymer films, the combination of this polymer and chitosan has many advantages since the biological activities of both polymers optimize the antimicrobial activity.[7,8]

Nowadays, the incorporation of nanofillers into polymer films becomes an excellent option to improve the physicochemical properties of these materials.[3,5,9,10] This fact has allowed obtaining films with a high strength with antimicrobial capacity.[11-14] Researchers have proposed that the antimicrobial effect of silver nanoparticles is due to their interaction with the cell surface and the capacity to degrade the cell membrane, which allows the interaction with the cell compounds affecting the cell viability.[15,16] In this work, it was studied aspects such as the morphology structure, thermal stability, and antimicrobial activity in chitosan/PVA films that incorporate silver nanoparticles.

2. Materials and Methods

2.1 Materials

Silver nitrate ($AgNO_3$) 99% was purchased from PanReac AppliChem. Acetic acid ACS reagent 99.7%, Chitosan ≥75% (deacetylated), and polyvil alcohol (PVA) were purchased from Sigma Aldrich. Agar solutions were obtained of Mueller-Hinton. Eschericha coli ATCC 25922 and Mangifera indica extract were donated by University of Cartagena.

2.2 Synthesis of Silver Nanoparticles

The synthesis of silver nanoparticles (AgNps) involved the preparation of an initial concentrated solution of 100 mM of $AgNO_3$, by diluting 1.7g of the metallic salt in 100mL of distilled water. Afterward, 10 mM diluted solution was obtained from the original. Green chemistry methodology was implemented for the synthesis of silver nanoparticles by mixing 50mL of $AgNO_3$ solution (10mM) with 5mL of the Mangifera indica extract.[17] The reaction mixture was carried out at room temperature with magnetic agitation for 1 hour. Then, silver nanoparticles were centrifuged at 5500 rpm, washed with distilled water and ethanol, and dried at room temperature.

2.3 Film Preparation with Silver Nanoparticles

In this experiment, the polymer solutions and the nanoparticle solutions were prepared separately. First, polymer solutions were obtained following the methodology used in previous work.[18-20] Chitosan solution was prepared by dissolving 2 g Chitosan in 100 mL acetic acid solution and stirred overnight using a magnetic stirrer until to obtain a homogeneous phase. In the same way, a PVA solution (5 % w/v) was prepared under continuous stirring at 80°C. Then, both solutions were mixed at room temperature under continuous agitation.

On the other hand, solutions from silver nanoparticles (0, 0, 05, and 0, 5% w/v) were prepared in distilled water and ultrasonicated for 30 min. These solutions were added to the polymer solution previously prepared and were subjected to a strong stirring for 2 hours at 70°C. The solutions were casted in glass Petri dishes and dried in a furnace at 45°C for 24 hours.

At last, the dried films with a thickness of ~3 mm were obtained and stored at constant temperature in a desiccator for 48 h to be used later.

3. Characterization

The infrared spectra of Ch-PVA films and Ch-PVA-AgNps were obtained using an FT-IR (Bruker IF 66 V/S). The hydrodynamic diameter of AgNps was measured using a Zeta Sizer NANO ZS. The morphological structure of the films was measured using a Flex AFM Nanosurf and a C3000 controller. JEOL-JSM 6500. UV-visible absorption spectrum was obtained using a Varian Cary-100. DSC-TGA measurements of the films were obtained using a TA instruments-SDT Q600 V20.9.

The antimicrobial activity of chitosan films and chitosan-based nanocomposite films was tested qualitatively by an inhibition zone method.[21,22] Disks with diameters of 6 mm were obtained and subjected to the antimicrobial activity test using a modified agar diffusion assay. The disks were incubated at 37 °C for 24 hours. Then, the indication of inhibition against the microbial species was considered by the presence of any clear zone observed around the disk.

4. Results and Discussion

The infrared (IR) spectra were used for studying the molecular interaction between the materials in the films without nanoparticles and with nanoparticles incorporated (Figure 1). Ch-PVA films and Ch-PVA-AgNps showed a broad absorption peak between 3252 cm^{-1} to 3186 cm^{-1} which corresponding to O-H stretching of

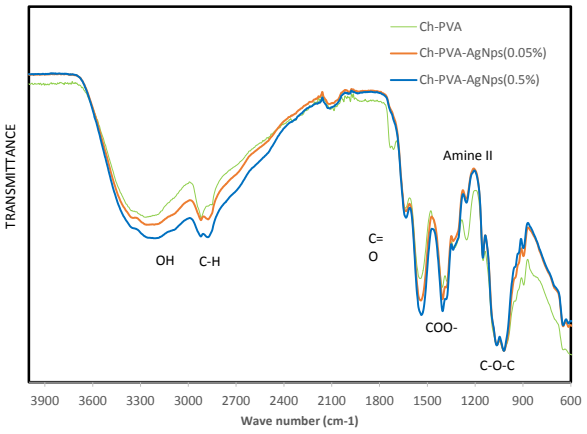

Figure 1. Infrared Spectra of Ch-PVA films without and with AgNps incorporated.

alcohols. The C-H stretching band and C-N stretching band are observed at 2870 cm^{-1}, and 1253 cm^{-1} respectively. These bands are present in secondary amines, and belong to the chitosan polymer chain. The visible peak that appeared at 1634 cm^{-1} was assigned to both the carbonyl stretching of the secondary amide (amide II) bands of chitosan and the interaction between PVA and chitosan.[19,21]

The hydrodynamic diameter of the AgNps nanoparticles in water was found to be 174 ±121 nm. Figures 2-4 show the results obtained by the TGA-DSC analysis. Ch-PVA films and Ch-PVA-AgNps (0.05% and 0.5%) films showed two weight losses. Ch-PVA films exhibited weight loss at 68.67 °C due to moisture vaporization and other rapid weight loss at 252.57 °C due to the degradation of chitosan molecule. The total weight loss was about 70% at 800 °C. The same observation was found in the case of Ch-PVA-AgNps films. The first weight loss at 100 °C is due to moisture vaporization and the other at 291.67 °C is due to degradation of Ch-PVA-AgNps nanocomposite, and the total weight loss of Ch-PVA-AgNps was 82.57% at 800 °C. Therefore, it can be concluded

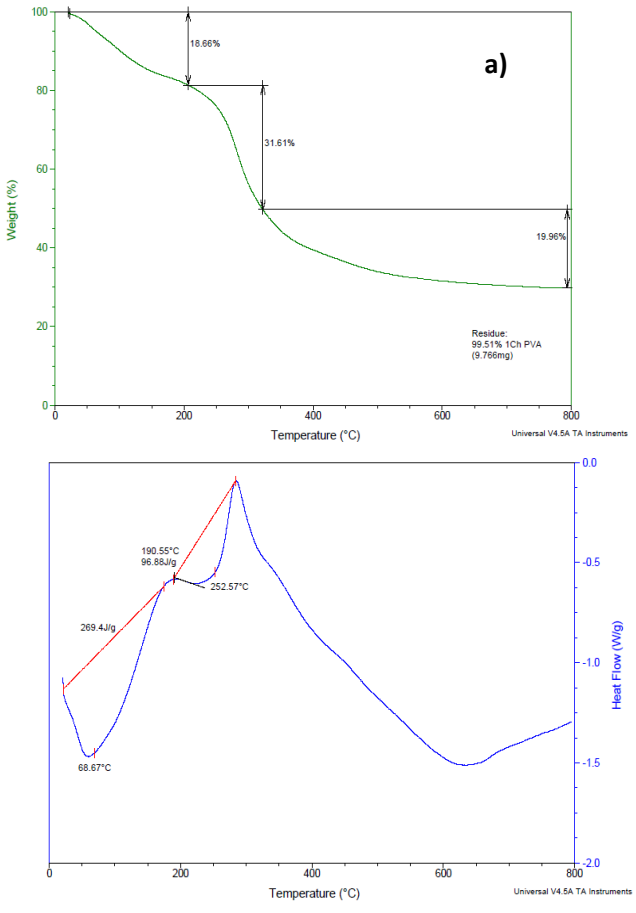

Figure 2. TGA-DSC analysis. a) TGA analysis of Ch-PVA films, b) DSC analysis of Ch-PVA films.

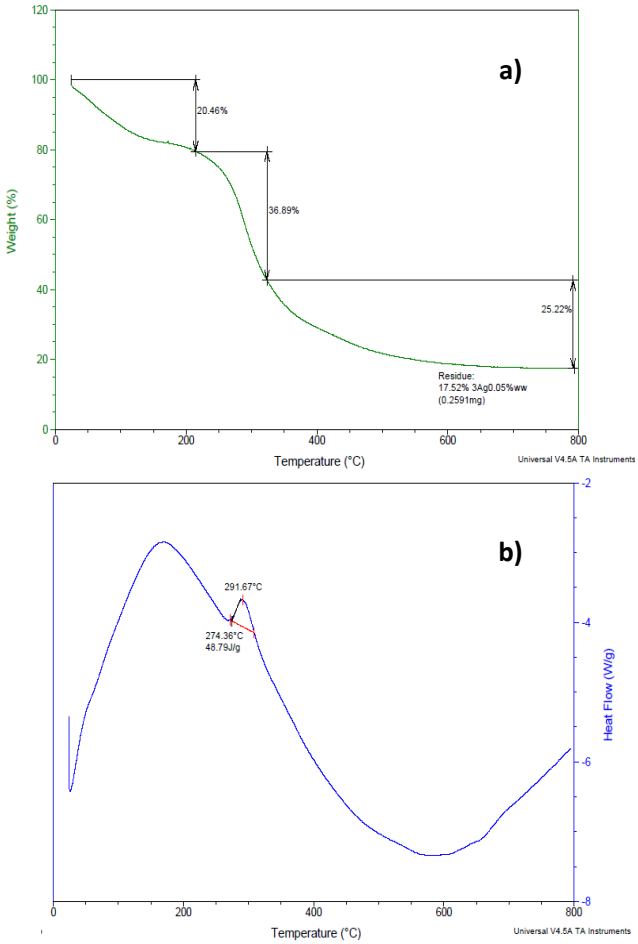

Figure 3. TGA-DSC analysis. a) TGA analysis of Ch-PVA-AgNps (0.05%) films, b) DSC analysis of Ch-PVA-AgNps (0.05%) films.

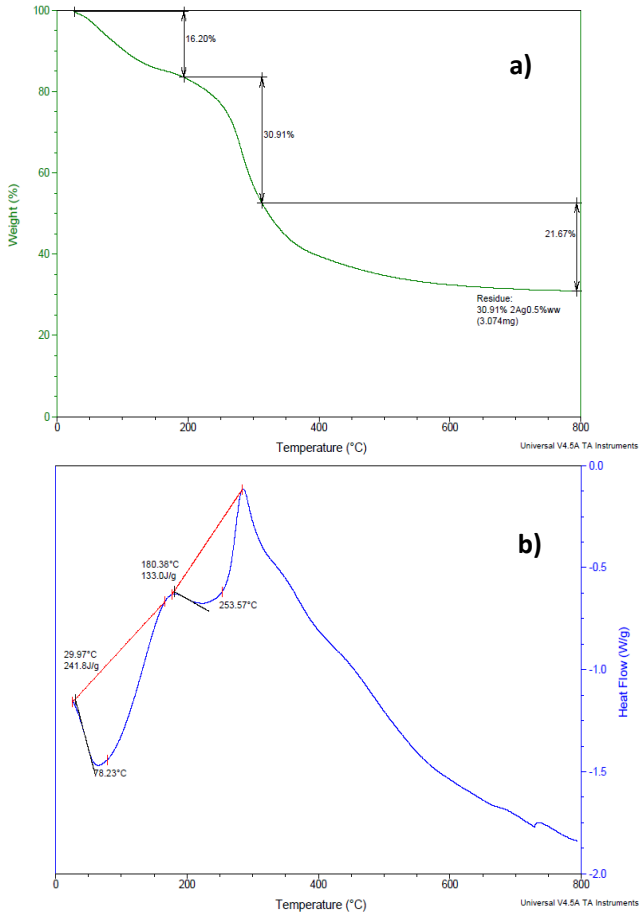

Figure 4. TGA-DSC analysis. a) TGA analysis of Ch-PVA-AgNps (0.5%) films, b) DSC analysis of Ch-PVA-AgNps (0.5%) films.

that Ch-PVA-AgNps films exhibited better thermal stability than Ch-PVA films due to the presence of silver nanoparticles.[13]

Figure 5 displays the result of UV-visible absorption analysis. The UV-visible absorption spectrum of Ch-PVA-AgNps (0.5%) films showed a broad peak between 425 to 470 nm which correspond to the presence of silver nanoparticles in the sample. Conversely, Ch-PVA films and Ch-PVA-AgNps (0.05%) films did not show an appreciable absorption peak in this interval due to the absence and low concentration of silver nanoparticles in the samples respectively. This means that Ch-PVA-AgNps nanocomposite has characteristics as a protector against ultraviolet light.[23-24]

SEM images of Ch-PVA and Ch-PVA-AgNps films showed the morphology of the materials. The Ch-PVA film morphology was rough and non-uniform due to undissolved chitosan present in it, while the Ch-PVA-AgNps

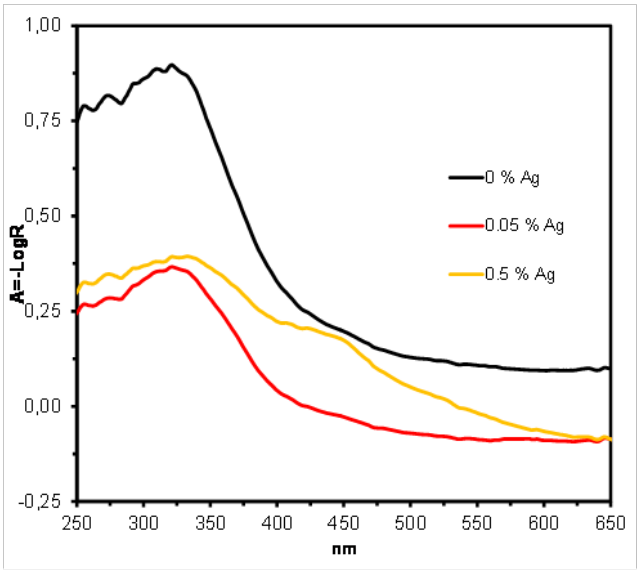

Figure 5. UV-vis analysis of Ch-PVA and Ch-PVA-AgNps (0.05% and 0.5%).

films showed improved homogeneous morphology which is due to the good blending of silver nanoparticles and chitosan materials.[25] Also, Ch-PVA-AgNps films showed island-sea morphology; that is, the nanoparticles were dispersed throughout the Chitosan-PVA matrix.[20] The SEM images are shown in Figure 6. AFM images displays

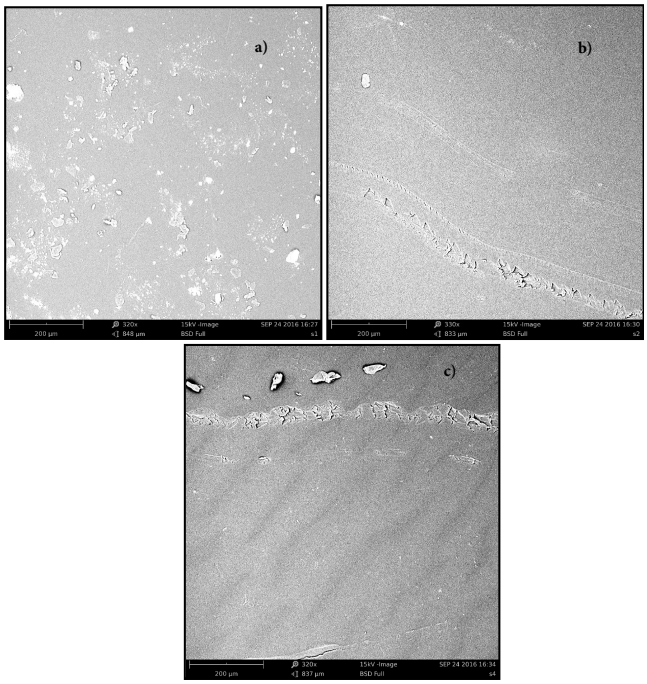

Figure 6. SEM images. a) Ch-PVA films, b) Ch-PVA-AgNps (0.05%) films, and c) Ch-PVA-AgNps (0.5%) films.

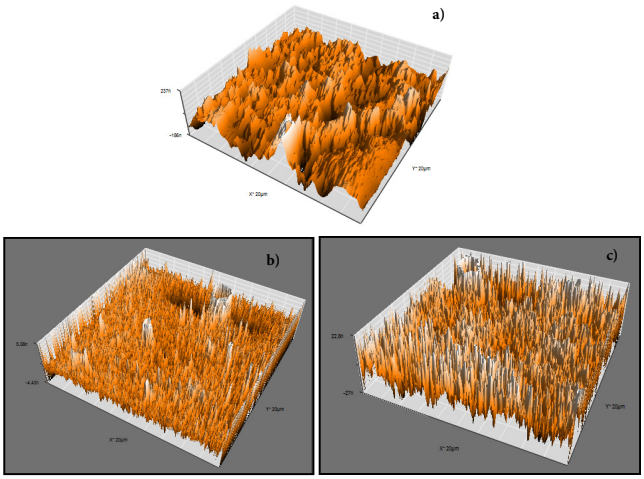

Figure 7. AFM images. a) Ch-PVA films, b) Ch-PVA-AgNps (0.05%) films, and c) Ch-PVA-AgNps (0.5%) films.

the surface morphology of Ch-PVA and Ch-PVA-AgNps films (Figure 7). By comparing the surface of the films, is observed a considerable change in the rugosity produced by the dispersion of silver nanoparticles throughout the Chitosan-PVA matrix. These results are confirmed by the results obtained by SEM.

Antimicrobial evaluation of chitosan-PVA films modified with silver nanoparticles in contact with E-Coli bacteria after 24 h of contact. (a) Ch-PVA film as control sample, (b) Ch-PVA-AgNps (0.05%) films, and (c) Ch-PVA-AgNps (0.5%) films. Figure 8 shows a typical antimicrobial test result of chitosan-based films against E-coli as determined by the disk method. As shown in the picture, for the films with silver nanoparticles incorporated, the higher the antimicrobial activity is obtained with the higher concentration of silver nanoparticles in the films (Ch-PVA-AgNps (0.5% films).[26] This is due to that silver ion impregnated in the nanocomposite have antibacterial and antifungal abilities. The release of silver ions from matrix inhibits the birth and growth of microbes by the interaction and bond to the cellular enzyme.[23]

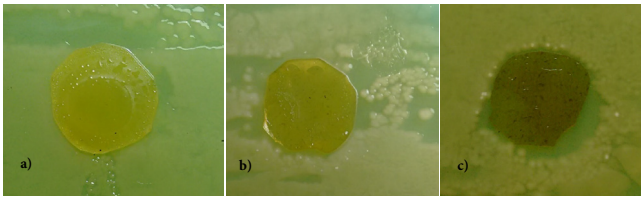

Figure 8. Antimicrobial evaluation of chitosan-PVA films modified with silver nanoparticles in contact with E-Coli bacteria after 24 h of contact. (A) Ch-PVA film as control sample, (b) Ch-PVA-AgNps (0.05%) films, and (c) Ch-PVA-AgNps (0.5%) films.

5. Conclusion

The film synthesized has a high homogeneity due to the application of a good preparation method. The incorporation of nanofillers in the structure enhanced the thermal stability and generated a high rugosity in the material. Besides, a protective barrier against ultraviolet light and high antimicrobial activity were attributed to this fact. The above mentioned predicts that the synthesized nanocomposites in this work can serve as a platform for the fabrication of food packaging.

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