Effect of Carbon Black and Silver Nanoparticle Loading on the Structural and Thermo-Mechanical Properties of Chitosan-Based Films

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ABSTRACT

Chitosan films containing carbon black (carbon black/chitosan ratios of 1, 3, 5% w/w) or silver nanoparticles prepared from starting silver nitrate (1, 3, 5 mM of $AgNO_3$) were synthesized via spin coating. Optical microscopy revealed that the film surface was porous, and AFM confirmed an increase in film roughness in the presence of the dispersoids. XRD spectra indicated that the incorporation of carbon black disrupted the structure of the chitosan films. UV-vis measurements confirmed the presence of Ag nanoparticles in the chitosan films with the plasmon centered at 450 nm. FTIR spectroscopy analyses suggested that the disperse phases did not affect the development of the polymeric matrix. The glass transition temperature and degradation temperatures of the chitosan composite films were determined to be 86±10°C and 256±7°C, respectively. The incorporation of particles increased the glass transition temperature, but did not have a significant effect on the thermal degradation behavior.

Keywords: chitosan film, carbon black, silver nanoparticles, thermomechanical properties

1 INTRODUCTION

Chitosan, a widely available and biodegradable polymer, has gained research attention in applications ranging from water purification to antibacterial coatings on foods or medical devices. Its polycationic nature under acidic conditions allows the polymer to interact electrostatically with heavy metals and bacteria. Furthermore, since it is a biocompatible polymer processed from existing food waste sources (crustacean shells), its production and use will not introduce new problems to the environment. Films made of this polymer may be used as matrices to host bactericidal (e.g. silver) or adsorbent nanomaterials (e.g. carbon black) to enhance the antibacterial and adsorption properties of the resulting nanocomposites.

As a candidate for edible food coverings or for bactericidal applications in sterilized medical environments, these chitosan composite films may be processed at elevated temperatures. To provide additional insight into the material's response under these conditions, this work presents the structural and thermo-mechanical response of nanocomposite chitosan films.

2 EXPERIMENTAL

2.1 Materials

Bare and composites films were synthesized via the spin-coating technique. Medium molecular weight chitosan powder [$(C_6H_{11}O_4N)_n$, degree of deacetylation 82%, Sigma Aldrich], carbon black [C, particle size 30 nm, aggregate size 100 nm, Sid Richardson], and silver acetate powders [$AgNO_3$, purity 99.9%, Alfa Aesar] were used as received. Acetic acid [CH_3CO_2H, purity 99.7%, Alfa Aesar] and sodium hydroxide pellets [NaOH, purity 98%, Alfa Aesar] were also used as received.

2.2 Synthesis

For the synthesis of bare chitosan films, 1.75% w/v chitosan powder was dissolved in 1.75% v/v acetic acid using magnetic agitation for 24 hours. The solution was subsequently vacuum filtered using grade 4 cellulose filter paper (pore size 20-25 μm, Whatman) to remove any remaining undissolved particles. Carbon black was added to the solution after filtering so that the larger carbon black aggregates would be removed. The silver nitrate salt was added to the chitosan solution at different molar concentrations in the 1-5 mM range. The solutions were then ultrasonicated for 30 minutes to ensure that all bubbles were removed from the solution. Resulting solutions were added drop-wise onto a clean glass substrate measuring 47x47 mm and spin-coated at 2000 rpm for 30 seconds. After each coating cycle, the films were dried for 2 minutes at 100ºC to remove any remaining solvent. These spin-coating/drying cycles were repeated 20 times to thicken the films. Produced films were then treated with 0.1 M NaOH for 2 hours to neutralize any remaining solvent, removed from the glass substrate, rinsed in de-ionized water for 5 minutes, then placed between two glass plates and dried at 60°C for 24 hours.

2.3 Characterization

The morphology was determined using a Nikon Epishot 200 optical microscope. AFM images and roughness were obatined using a VEECO CP-II AFM unit. The thickness of the films was determined using a KLA Tencor profilometer and their structure by X-ray diffraction using a SIEMENS D500 unit with a Cu-Kα radiation. The presence of silver nanoparticles was confirmed using a UV-vis DU 800 spectrophotometer. The chemical structure of the

synthesized films was determined by Fourier Transform Infrared spectroscopy using a Shimazdu IRAffinity-1 system. Thermomechanical properties were determined in air using a TMA/SDTA851[e] Mettler Toledo unit to determine the glass transition temperature of the films. Thermo-gravimetric analyses were performed in nitrogen using a TGA/SDTA851[e] Mettler-Toledo unit to determine the degradation temperature of the films.

3 RESULTS

3.1 Optical Microscopy

Optical microscopy images revealed the porous nature of the spin-coated films, which may be attributed to the partial dissolution of the first polymeric layers by the applied precursor solution and the rapid evaporation of solvent during the film thickening stages. The uniform distribution of carbon black clusters are also evident in Fig. 1. The silver induced a brown tone in the corresponding films (Fig. 2), which was visible to the naked eye.

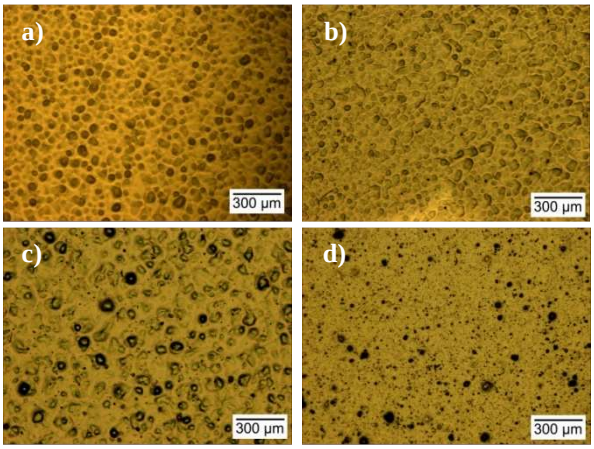

Figure 1: Chitosan films bearing: (a) 0%, (b) 1%, (c) 3%, and (d) 5% w/w of carbon black. Film thickness ranged from 7 to 50 µm.

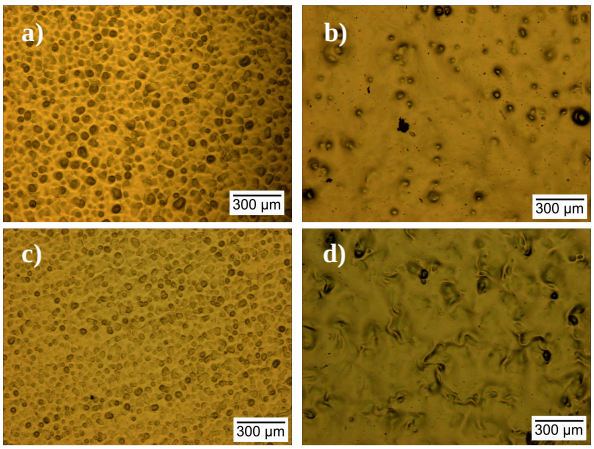

Figure 2: Chitosan films synthesized in presence of: (a) 0, (b) 1, (c) 3, and (d) 5 mM $AgNO_3$. Film thickness ranged from 7 to 50 µm.

3.2 Atomic Force Microscopy Images

Atomic force microscopy images were taken of films spin cast on a 25x25 mm substrate. As seen in Fig. 3, the films bearing silver particles exhibited a smooth surface in comparison to the films with carbon black that exhibited clustered nanoparticles. Roughness values calculated from three 30x30 µm photos are shown in Table 1. As expected, the carbon black bearing films were substantially rougher than both the bare films and the silver bearing films.

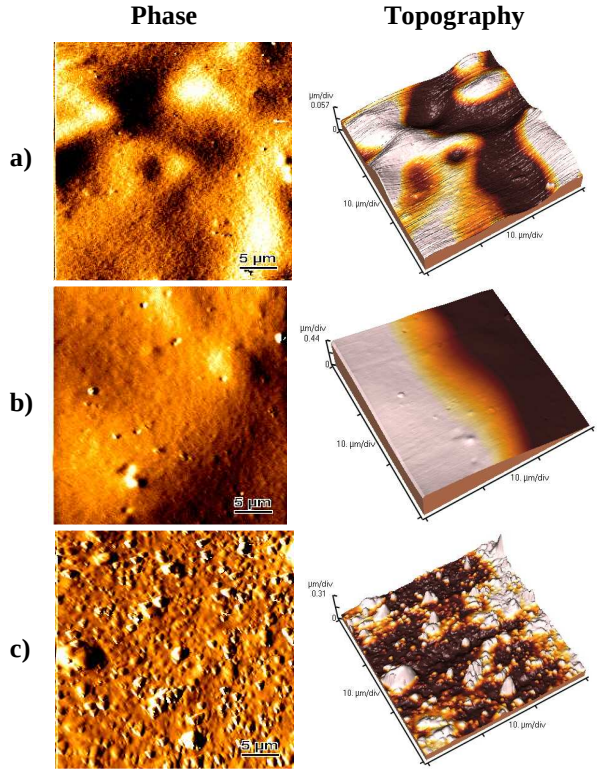

Figure 3: AFM images of (a) bare chitosan film, (b) chitosan film bearing 5 mM $AgNO_3$. and (c) chitosan film bearing 5% carbon black

Chitosan film	Roughness (nm)
Bare	18.1
5 mM $AgNO_3$	25.8
5% Carbon Black	84.7

Table 1: Roughness of chitosan composite films.

3.3 Thickness Measurements

Profilometry measurements indicated that the film thickness fell in the range from 10 to 50 µm (Fig. 4). The films were expected to increase in thickness with an increase in the phase, but the 3 mM $AgNO_3$ and 3 % w/w carbon black composite films were thinner than the other films.

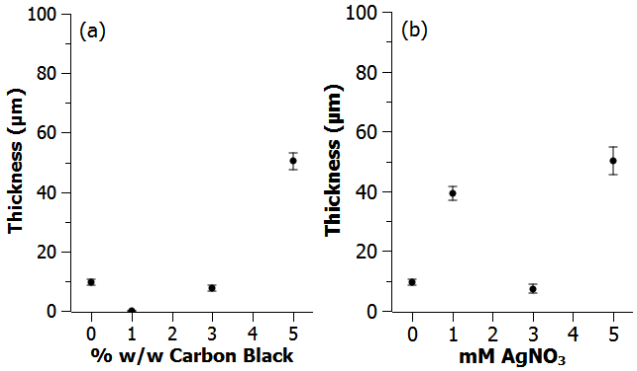

Figure 4: Thickness of chitosan films bearing (a) carbon black and (b) silver. The number of layers was 20 in all cases.

3.4 X Ray Diffraction Analyses

X-ray diffraction evidenced that spin-coated bare and carbon black loaded films exhibit short range crystallinity with broad peaks centered on 10 and 20 degrees (Fig. 5). These peaks correspond to an orthorhombic structure with lattice parameters of a = 0.828 nm, b = 0.862 nm, and c= 1.043 nm [1]. The incorporation of carbon black into the chitosan spin coated films disrupted the arrangement of the chains of chitosan, as suggested by the slight shift to the right in the peak centered at 20° (Fig. 5a). The formation of Ag nanoparticles in the films synthesized in presence of 5 mM $AgNO_3$ is indicated by the weak but noticeable diffraction peak centered at 38° which corresponds to the (111) plane of silver (Fig. 5b). This peak is not noticeable in the other films due to the low concentration of particles which may be attributed to insufficient reaction time and temperature to promote the reduction of silver ions into elemental silver [2].

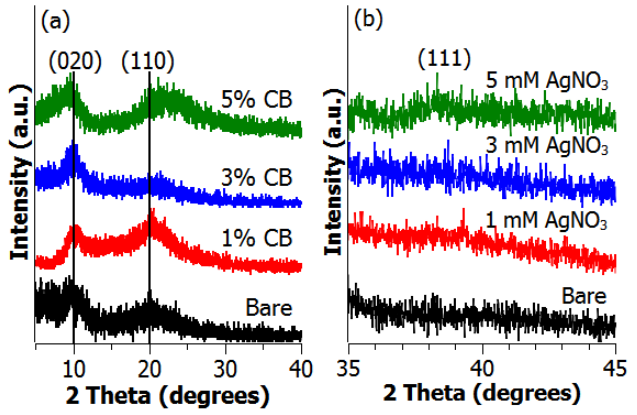

Figure 5: XRD spectra of chitosan films bearing (a) carbon black and (b) silver.

3.5 UV-vis Spectroscopy Analyses

UV-vis confirmed the presence of silver as suggested by the absorption bands near 450 in Fig. 6; the band broadening would indicate polydispersity in the nanoparticles size. While most research groups have reported the plasmon for silver nanoparticles between 400 and 420 nm, it has also been reported at higher wavelengths (440-445 nm) [3,4].

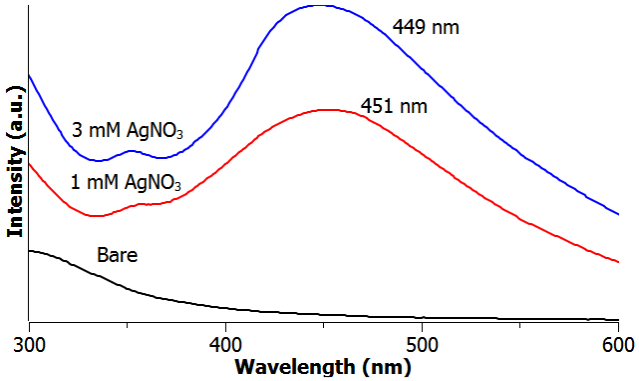

Figure 6: UV-vis spectra of chitosan films bearing silver.

3.6 FT-IR Spectroscopy Analyses

Fourier transform infrared spectroscopy confirmed the chemical structure of chitosan in both the bare and nanocomposite films (Fig. 7). The films were run in ATR mode. The absorption band at 1535 cm^{-1} is related to the stretching of the N-H bond in the amine group; the absorption band at 1450-1465 cm^{-1} is assigned to the asymetrical deformation of the C-H bond in the CH_2 group. [5]. Since both bands are related to chitosan's functional groups, this may indicate that the disperse phases did not affected the development of the polymeric matrix structure.

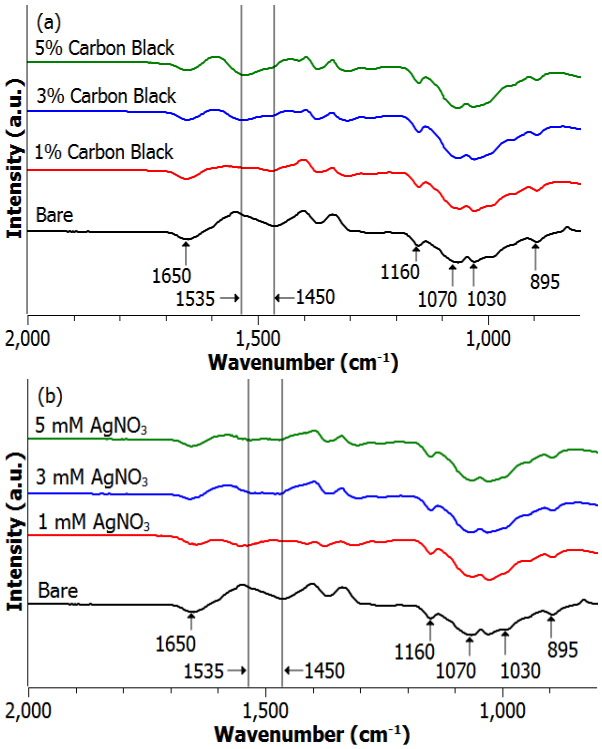

Figure 7: FTIR spectra of chitosan films bearing: (a) carbon black and (b) silver.

3.7 Thermomechanical Analyses

The thermo-mechanical analyses of the composite chitosan films set the glass transition temperature (T_g) at 86±10°C. The T_g was determined by the intersection of tangent lines derived from a fit line as indicated by the arrow in the profile corresponding to the bare chitosan film in Fig. 8a. [6] Three samples were run for each film to determine the reproducibility of the measurements. The corresponding results suggested that the addition of carbon black and silver particles would increase the T_g in spin coated films (Table 2). This may be due to the inhibition of the polymeric chain rotation due to the incorporation of the disperse phases within the chitosan matrix. However, the thickness of the films, which increased at the highest loading of the disperse phases, should have also affected the thermo-mechanical response of the nanocomposite.

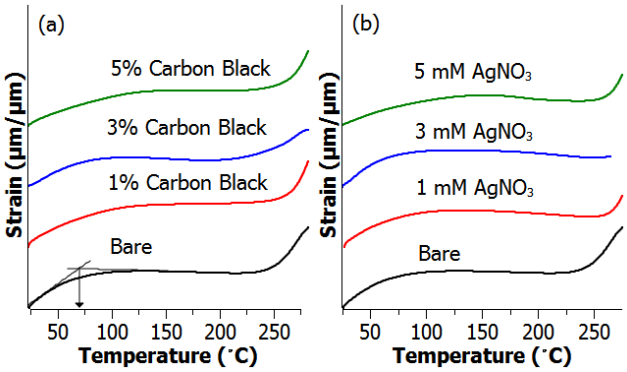

Figure 8: TMA spectra of chitosan films with (a) carbon black, and (b) silver.

w/w % CB	T_g (°C)	mM $AgNO_3$	T_g (°C)
Bare	74 ± 5	Bare	74 ± 5
1	89 ± 3	1	83 ± 1
3	76 ± 5	3	81 ± 8
5	97 ± 4	5	96 ± 4

Table 2: T_g of chitosan composite films.

3.8 Thermogravimetric Analyses (TGA)

TGA analyses revealed that in a nitrogen atmosphere, spin-coated films lost water near 100°C and underwent thermal degradation starting at 256±7°C (Fig. 9). The starting degradation temperature was not significantly altered by the incorporation of carbon black or silver particles (Table 3). This was expected as 40% of the weight loss would be due to the pyrolytic decomposition of the polymer, which would not be siginificantly affected by the inclusion of a disperse phase [7].

w/w% CB	T_{deg} (°C)	mM $AgNO_3$	T_{deg} (°C)
Bare	257	Bare	257
1	266	1	245
3	255	3	263
5	252	5	255

Table 3: T_{deg} of chitosan composite films.

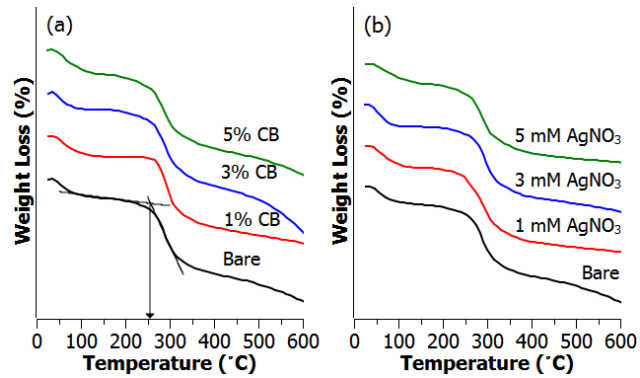

Figure 9: TGA spectra of chitosan films bearing: (a) carbon black, and (b) silver.

4 CONCLUSIONS

Bare and composite chitosan thin films (10-50 µm) were sythesized via spin coating. Optical microscopy indicated that spin coated films were porous and that carbon black was uniformly distributed in the composite films. XRD analyses indicated that the incorporation of carbon black into the chitosan films disrupted the arrangement of the chitosan chains. UV-vis spectra confirmed the presence of silver nanoparticles in the composite films. TMA analysis indicated that the incorporation of a disperse phase increased the glass transition temperature. In turn, TGA measurements evidenced that the onset of the thermal degradation started at 256±7°C in all films. The structural and thermo-mechanical characteristics of synthesized nanocomposites make them promising candidates for medical and food safety applications.

ACKNOWLEDGEMENTS

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REFERENCES

[1] W. Maniukiewicz, *Chitin, Chitosan, Oligosaccharides and Their Derivatives*, CRC Press, 83–94, 2010.
[2] H. V. Tran, *et. al*, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 360, 32–40, 2010.
[3] A. Šileikaitė, *et. al*, Materials Science, vol. 12, 1319–1324, 2006.
[4] A. Revina, *Bionanotechnology*, CRC Press, 161-167, 2008.
[5] J. Kumirska, *et. al*, Marine Drugs, vol. 8, 1567–1636, 2010.
[6] HDI Test Methods Task Group (D-42a), IPC, 1998.
[7] I. Quijada-Garrido, *et. al*, *Carbohydrate Polymers*, vol. 68, 173–186, 2007.