Effect of Changes in Relative Humidity and Temperature on Ultrathin Chitosan Films

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We have prepared uniform films of chitosan with thicknesses 20 nm $< h <$ 200 nm by spincoating solutions of chitosan dissolved in dilute acetic acid onto silicon substrates while controlling the spin speed and the relative humidity inside the spincoater. After neutralizing the films, they readily absorbed water in the presence of high humidity. Heating of the films to elevated temperatures caused a large irreversible decrease in the film thickness, a small increase in the index of refraction, and a reduction in water absorption, as measured using ellipsometry. Comparisons of infrared absorption measurements of chitosan films collected before and after heating indicate an increase in the degree of acetylation with heating. Collectively, these observations are consistent with the release of bound water and a chemical change similar to acetylation at elevated temperatures.

Introduction

Biodegradable polymers have attracted considerable interest in the past decade.[1] They not only contribute to solving the problems of diminishing landfill space and petroleum supplies created by the increased use of synthetic plastics, but they are also promising candidates for use in drug delivery systems[2] and medical implants[3] because of their biocompatibility and their ability to be gradually absorbed into the body.

Chitosan is an abundant but underused biopolymer.[4,5] It is derived primarily from chitin, the second most abundant carbohydrate on earth (after cellulose), which plays a structural role in the exoskeletons of invertebrates. Alkali treatment of chitin replaces the acetyl side group on the chitin repeat units with an amine group, converting them to chitosan. The percentage of repeat units with acetyl side groups is specified as the degree of acetylation (DA), with pure chitin corresponding to DA = 100% and pure chitosan corresponding to DA = 0%.[6] Chitosan is a semicrystalline polysaccharide that, unlike many biodegradable polymers, is insoluble in water at neutral pH. It cannot be melted and processed as a typical thermoplastic because of the large number of inter- and intramolecular bonds that are responsible for its rigid, semicrystalline structure,[7] but it can be dissolved in weakly acidic aqueous solutions and be made into hydrogels, either through the addition of chemical cross-linking agents such as gluteraldehyde[3] or because of physical entanglement for high molecular weight molecules.[8] The hydrogel form of chitosan can absorb up to 2000% of its own weight in water.[9] In addition, the ability of chitosan hydrogels to absorb water depends on the pH of the surrounding medium which makes them attractive candidates for drug delivery systems that are specific to certain parts of the digestive tract.[2] For applications that require mechanical rigidity and improved stability with respect to changes in relative humidity, it is preferable to convert chitosan to chitin, and this is typically accomplished by exposing the chitosan to acetic anhydride. Unfortunately, the toxic nature of acetic anhydride makes the chemical conversion of chitosan to chitin environmentally unfriendly.

We have used our experience in the preparation of thin films of synthetic polymers,[10] together with a procedure described in a previous study for the deposition of chitosan films,[11] to develop a protocol for spincoating ultrathin chitosan films onto silicon substrates while controlling the spin speed and the relative humidity (RH) inside the spincoater. Chitosan films are of technological importance because of their potential for use in applications such as sensors and coatings, as well as layers incorporated into multilayer packaging. In addition, the thin film geometry allows the use of a variety of thin film and surface science experimental techniques to characterize the physical and chemical properties of the chitosan material.

Following deposition of the chitosan films, they swell dramatically with increasing RH, which is easily observed by eye and by optical microscopy because of corresponding changes in the color of the films and can be measured accurately using ellipsometry. We find that heating of the films to temperatures 150 °C $< T <$ 200 °C causes a large decrease in the thickness and a small increase in the index of refraction. The amount of swelling with increasing RH also decreases with time spent at elevated temperatures. We show that the observed changes are not due to oxidation or thermal degradation of the films, and we suggest that the release of water from the films at elevated temperatures is responsible for these changes. In infrared (IR) absorption spectroscopy measurements, we observed a corresponding increase in the degree of acetylation[12] for films heated to temperatures 150 °C $< T <$ 200 °C. Collectively, the results suggest that a chemical change occurs in the chitosan films at elevated temperatures, corresponding to a thermally driven conversion of chitosan to a chitinlike material.

Experimental Methods

Most of the experiments in the present study were performed using chitosan with a molecular weight of $M_w \sim 229\,000$ g/mol and a degree of acetylation of DA ∼ 15% (Biosyntech Inc., Laval, Quebec). The

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chitosan was dissolved in 5% acetic acid solutions with chitosan mass concentrations of 0.5−1.5%. The solutions were filtered through Whatman #5 qualitative filter paper to remove any contaminant particles larger than 25 micrometers in diameter. The films were spincoated onto silicon wafers with a 2−3 nm thick native oxide layer that had been placed in a UV/ozone cleaner for 20 min to make the surface hydrophilic. Spincoating was performed using a Headway EC101 spincoater containing an excess of water in the sample chamber to increase the relative humidity (RH) of the environment to RH = 85 ± 5% during spincoating. This produced much slower evaporation than that obtained in the absence of excess water and resulted in more uniform film thicknesses. A Sensirion SHT 11 sensor with a response time of approximately 0.7 s was used to measure the relative humidity in the sample chamber to within 0.1%. Films were spincoated using spin speeds 1500 RPM $< \omega <$ 4000 RPM and a spin time of 2−6 min, resulting in chitosonium acetate films that were uniform in color as observed by eye. The film color was observed to change, but remain uniform, as the film was removed from the spincoating chamber, with RH = 85 ± 5%, to the ambient environment, with lower RH values. The chitosonium acetate films were neutralized by rinsing with 0.1 M NaOH solution for several minutes and with deionized water for several minutes, which restored the free amine groups and produced chitosan films that remained uniform in color at constant relative humidity as observed by eye. Optical microscopy was performed on the films in air using an Olympus BX-60 reflected light microscope with polarized light microscopy capability to inspect the films for defects, to record color images of each film, and to inspect the films for evidence of crystallinity. Atomic force microscopy (AFM) was performed using a Digital Instruments Dimension 3100 atomic force microscope to measure the root-mean-square (rms) roughness of a subset of chitosan films and to inspect the films for evidence of crystallinity.

A set of films was also prepared using chitosan with $M_w \sim 332\,700$ g/mol and DA ∼ 6% (Biosyntech Inc.), dissolved in 5% acetic acid solutions with a chitosan mass concentration of 1% and deposited at a spin speed of 2000 RPM on silicon wafer substrates for infrared (IR) absorption measurements of the degree of acetylation as a function of the temperature to which the films were heated. These films were neutralized using 0.1 M NaOH and deionized water as described above. The thicknesses of these chitosan films following preparation were measured to be within the range 150 ± 2 nm. We chose a relatively large value of the film thickness and a small degree of acetylation for this set of chitosan films to obtain a sufficiently large IR absorption signal and to more easily assess the effect of thermal treatment on the degree of acetylation.

Reflection ellipsometry of the chitosan films was performed using a custom-built self-nulling, single wavelength (λ = 632.8 nm) ellipsometer[13] and a commercial Multiskop instrument from Optrel GbR. In the ellipsometry experiments, the ellipsometric angles P and A corresponding to a null in the intensity at the detector were measured at fixed values of the angle of incidence θ_i ranging from 30^o to 60^o. The ellipsometry measurements were performed in the center of the films to avoid the areas of the film near the edge of the silicon wafer where the film thickness was nonuniform. For the ellipsometry measurements, we used a sample chamber that contained small holes to allow the laser beam to pass into and out of the chamber without the use of glass windows and a gas port that allowed the introduction of air with controlled RH into the chamber, with a typical flow rate of 100 mL/min. We found that this method of controlling the RH in the chamber was more appropriate for the present experiments than the use of saturated salt solutions. The use of saturated salt solutions requires the use of a sealed chamber, which means that windows are required in the ellipsometry cell, complicating the optical path of the ellipsometry experiment and limiting the rate at which the RH can be varied. Within the RH control chamber, the RH sensor was located at a position that differed from the sample position. The difference in RH between the sample position and the sensor position was characterized for 10% < RH < 80% by placing a second Sensirion SHT 11 RH sensor at the sample position. When placed at the same position, the RH readings for the two sensors agreed to within 1.5% over the entire range of RH values. The calibration of the RH sensors supplied by the manufacturer was verified by using a series of saturated LiCl, NaBr, and NaCl salt solutions inside a sealed chamber, with relative humidity values of 11.3%, 57.6%, and 75.5%, respectively.

Following the preparation of each chitosan film, reflection ellipsometry measurements were performed at room temperature with ambient RH = 20 ± 5% to obtain the film thickness and index of refraction. Reflection ellipsometry measurements were also performed at different, fixed values of RH values within the range 10% < RH < 70%, after allowing the RH value to stabilize at a fixed value for 10−15 min, to ensure that RH-related changes in the sample properties had occurred before each ellipsometry measurement was performed. The maximum RH value was limited to 70% to avoid room-temperature condensation of water vapor on the sample. This allowed the determination of the swelling of the films, that is, the increase in film thickness with increasing RH.

To provide an independent measurement of the swelling behavior of the chitosan films, two nominally identical chitosan films with thickness h = 175 nm were measured using ellipsometry, as described above, and using atomic force microscopy (AFM). For the AFM measurement, each film was scratched with a razor blade, which removed the chitosan film and exposed the underlying silicon substrate. The depth of the scratch, and therefore the thickness of the chitosan film, was measured using AFM for different values of RH within the range 20% < RH < 70%, with the RH values stable to within 2%. The RH control chamber used for the AFM measurements is described elsewhere.[14]

Following the preparation and characterization of their initial thickness, index of refraction, and swelling behavior using ellipsometry, the chitosan films were heated using different protocols. One set of chitosan films was heated to a fixed temperature of T = 200 °C, held at this temperature for times ranging from 0.5 to 10 h, and then was cooled to room temperature. The films were then measured again using ellipsometry in the ambient atmosphere (at RH = 20 ± 5%) and as a function of RH. Some of the chitosan films that had been heated to 200 °C for various times and then cooled to room temperature were measured using AFM to obtain the rms roughness. A second set of chitosan films was heated for a fixed time of 2 h at temperatures ranging from T = 50 °C to T = 200 °C in ambient air and also in an oven purged with dry nitrogen and then was measured using ellipsometry in the ambient atmosphere after cooling the films to room temperature. The comparison of the results obtained after heating the films in the dry nitrogen atmosphere and ambient air allowed us to determine whether the films were oxidizing in air for $T <$ 200 °C. Another set of chitosan films was heated for a fixed time of 4 h to temperatures ranging from T = 150 °C to T = 375 °C in an oven purged with dry nitrogen and then was remeasured using ellipsometry in the ambient atmosphere after cooling the films to room temperature. This set of measurements allowed us to identify the temperature above which thermal degradation of the films occurred. AFM and polarized reflected light microscopy were used to inspect the chitosan films that had been heated and subsequently cooled to room temperature for evidence of crystallinity.

Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) was performed on another set of chitosan films with initial thicknesses in the range h = 150 ± 2 nm and a small initial degree of acetylation (DA ∼ 6%). FT-IRRAS is a nondestructive spectroscopic technique with chemical specificity and sufficient sensitivity to allow the measurement of ultrathin films. Following a procedure described by Domszy and Roberts,[12] the degree of acetylation in the films was measured by comparing the area under two peaks in the FT-IRRAS spectra: one peak, centered at a wavenumber of 1655 cm^{-1}, corresponding to the acetyl content, and another peak, centered at 3450 cm^{-1}, corresponding to the hydroxyl group which is used as an internal standard to account for changes in film thickness. The FT-IRRAS spectra were collected at room temperature for films before and after

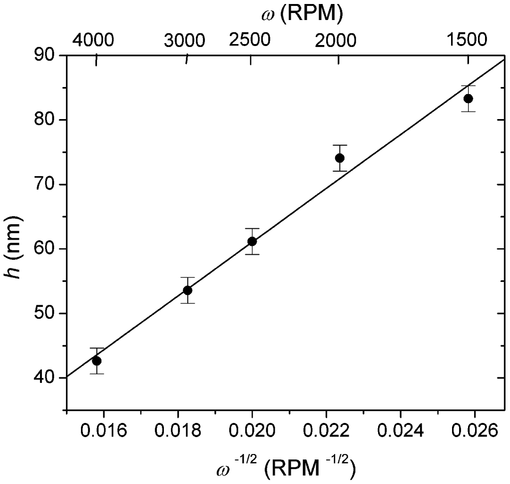

Figure 1. Film thickness *h* of chitosan films versus $\omega^{-1/2}$, where ω is spin speed. The *h* values were obtained from the best fit to reflection ellipsometry data. The straight line indicates the best fit to the form $h = A + B\omega^{-1/2}$, where $A = -18 \pm 5$ nm and $B = 3960 \pm 260$ nm RPM$^{-1/2}$. The representative error bars correspond to the standard deviation of the *h* values obtained for $\omega = 3000$ RPM.

heating for 4 h at fixed temperatures of $T = 150$, 175, 188, 200, 250, and 300 °C using a Nexus 870 Fourier transform infrared reflection absorption spectrometer in a sample chamber that was purged with dry argon for 5 h to eliminate the absorption signatures of water and CO_2.

Results and Discussion

Reflection ellipsometry measurements were performed at room temperature with ambient RH = 20 ± 5% on a series of chitosan films prepared using solutions with chitosan mass concentrations of 1% and different spin speeds ω for RH = 85 ± 5% in the spincoating chamber. The ellipsometry data obtained for each film were fit to an isotropic model of the film, allowing the determination of the dependence of the chitosan film thickness *h* and the index of refraction *n* on the spin speed ω. In Figure 1, we plot the dependence of *h* on spin speed ω which is consistent with $h \propto \omega^{-1/2}$, in agreement with the prediction of simple theories of spincoating.[15] The data were consistent with an index of refraction value of $n = 1.53 \pm 0.01$ which was slightly lower than the value of $n = 1.\ 56 \pm 0.02$ reported for similar films of chitosan.[16] Changes in *h* with ω were also apparent as changes in the color of the films as measured using reflected light microscopy. For spin speeds $\omega > 1000$ RPM, the chitosan films were very smooth, with an rms roughness of ~1 nm over an area of 20 μm × 20 μm, as measured using AFM, and featureless as observed using reflected light microscopy (with and without crossed polarizers).

The film thickness values obtained by fitting ellipsometric data measured at different values of RH in the ellipsometry RH control chamber, after waiting for 10−15 min at each RH value, are shown in Figure 2 for chitosan films with thicknesses ranging from $h = 20$ nm to $h = 200$ nm. In Figure 2, the thickness values have been divided by the value measured for each film at RH = 20%. The relative increase in *h* with increasing RH is similar for a wide range of film thickness values. The increase in film thickness at RH = 70%, for example, corresponds to a volume fraction of water of approximately 25%, which has been estimated by extrapolating the film thickness values to RH = 0% for which the film is assumed to be dry. The measured index of refraction values (data not shown) decrease slightly as the RH value in the sample chamber is increased (a 2−3% reduction over the same RH range as shown in Figure 2 for all film thicknesses). The similarity of the swelling behavior obtained for films of different thicknesses indicates that the films have reached equilibrium and that swelling occurs uniformly across the thickness of the films. This result was confirmed by ellipsometry measurements performed at fixed RH values for extended times (RH held constant at values from RH = 20% to RH = 60% for times greater than 60 min) during which the measured film thickness changed by less than 1% (data not shown). In Figure 2, the film thickness *h* increases approximately linearly with increasing RH for each film, allowing us to define a swelling coefficient corresponding to the slope $(\Delta h/h_i)/\Delta\text{RH}$ for each film, where h_i is the initial film thickness.

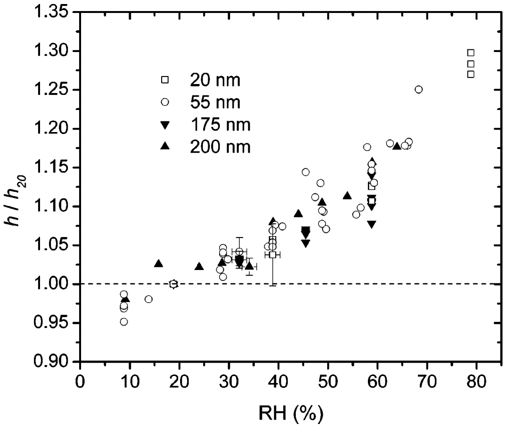

Figure 2. Film thickness *h* divided by the film thickness h_{20} measured at RH = 20%, as a function of relative humidity (RH) in the sample chamber. The film thicknesses were calculated using reflection ellipsometry data, and the RH value in the sample chamber was varied between 10 and 80%.

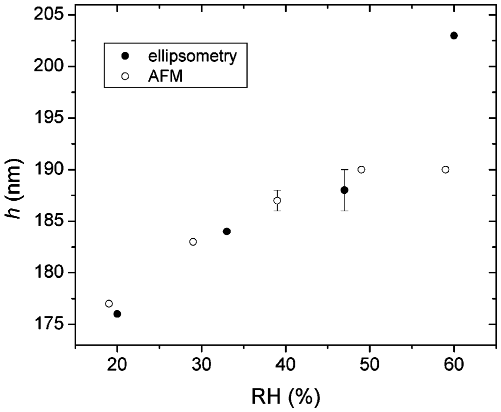

Figure 3. Film thickness *h* as a function of relative humidity (RH) as measured using ellipsometry (closed circles) and atomic force microscopy (open circles).

An independent confirmation of the magnitude of the swelling of the chitosan films with increasing RH was obtained by comparing the swelling behavior of a chitosan film with thickness $h = 175$ nm, as measured using ellipsometry (see Figure 2), to the swelling behavior of a nominally identical chitosan film, as measured using atomic force microscopy. The results of the two measurements were very similar, as shown in Figure 3.

In Figures 4 and 5, we show changes observed in the thickness *h* and the index of refraction *n* for a series of chitosan films that were heated in air to $T = 200$ °C, held at this temperature for different times, cooled to room temperature, and remeasured using ellipsometry. The film thickness *h*

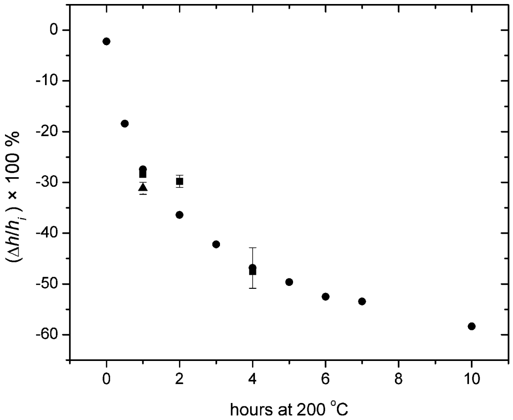

Figure 4. Percent decrease in film thickness, $(\Delta h/h_i) \times 100\%$, of chitosan films held at $T = 200$ °C for different times $0 < t < 10$ h and cooled to room temperature. The h values were obtained from the best fit to reflection ellipsometry data. Data shown include samples with initial thicknesses of $h = 50$ nm (circles), $h = 175$ nm (triangles), and $h = 200$ nm (squares). The uncertainty in the thickness measurements is ±2 nm.

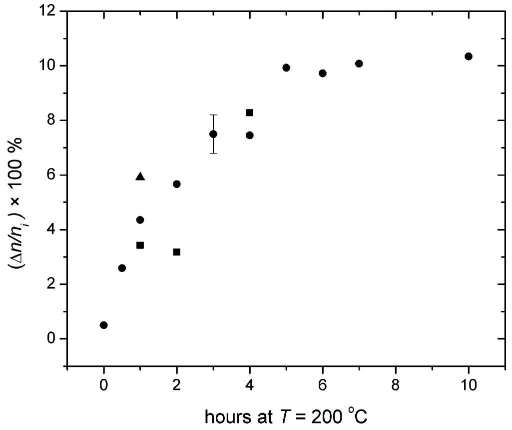

Figure 5. Percent increase in index of refraction, $(\Delta n/n_i) \times 100\%$, of chitosan films held at $T = 200$ °C for different times $0 < t < 10$ h and cooled to room temperature. The n values were obtained from the best fit to reflection ellipsometry data. Data shown include samples with initial thicknesses of $h = 50$ nm (circles), $h = 175$ nm (triangles), and $h = 200$ nm (squares). The uncertainty in the index of refraction measurements is ±0.01, and the average value for the initial index of refraction value is 1.53 ± 0.01.

decreases dramatically with time spent at $T = 200$ °C. The index of refraction n also increases substantially. The percentage changes in thickness and index of refraction are quantitatively similar for films with initial thicknesses ranging from $h = 50$ nm to $h = 200$ nm.

Chitosan films with initial thicknesses h_i within the range 50 ± 4 nm were heated for a fixed time of 2 h at different temperatures between $T = 50$ °C and $T = 200$ °C. One set of films was heated in an oven purged with dry nitrogen and the other set of films was heated in an oven containing air. After cooling the films to room temperature, the films were remeasured using ellipsometry. The percentage change in film thickness Δh because of the heat treatment is plotted versus the temperature to which the films were heated in Figure 6 for films heated in air and heated in dry nitrogen. Within experimental uncertainty, the percentage change in thickness is the same for both sets of films, with significant decreases in the film thickness observed only when the films were heated for a time of 2 h to temperatures greater than $T = 150$ °C. The change in the swelling coefficient $(\Delta h/h_i)/\Delta\mathrm{RH}$, corresponding to the slope of the best linear fit to the h versus RH data for each film, was also measured as a function of the time spent at $T = 200$ °C (data not shown). A large decrease of 80 ± 20% in the swelling coefficient $(\Delta h/h_i)/\Delta\mathrm{RH}$ was observed for times greater than 1 h at $T = 200$ °C.

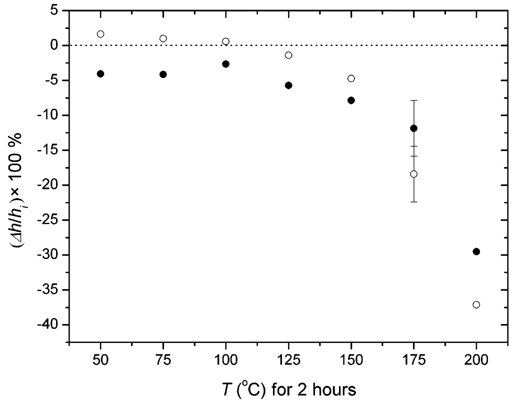

Figure 6. Percentage decrease in film thickness, $(\Delta h/h_i) \times 100\%$, relative to the initial thickness, h_i, of chitosan films held at temperatures from $T = 50$ °C to $T = 200$ °C for a fixed time of 2 h and cooled to room temperature. The solid circles correspond to films that were heated in an oven purged with dry nitrogen, and the open circles correspond to films heated in an oven containing air. The uncertainty in each thickness measurement is ±2 nm, and the initial thicknesses h_i of all films were in the range 50 ± 4 nm.

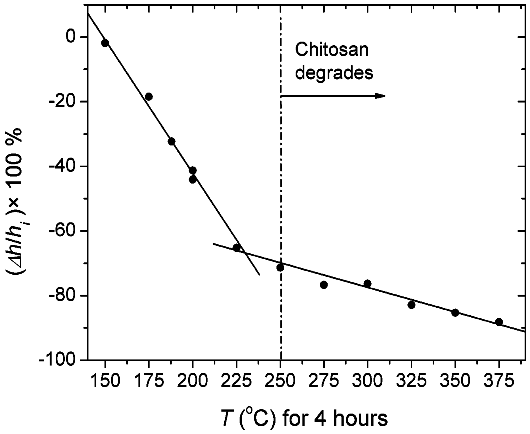

Figure 7. Percentage decrease in film thickness, $(\Delta h/h_i) \times 100\%$, of chitosan films held at temperatures from $T = 150$ °C to $T = 375$ °C for a fixed time of 4 h and cooled to room temperature. Films were heated in an oven purged with dry nitrogen. The uncertainty in each thickness measurement is ±2 nm. The straight lines are intended to only guide the eye.

One possible explanation for the large decreases in film thickness that occur when the chitosan films are heated to temperatures 150 °C $< T <$ 200 °C is that the chitosan is undergoing thermal degradation. If this was true, the decreases observed in the film thickness should increase with increasing temperature. To address this issue, chitosan films were heated for 4 h at temperatures ranging from 150 °C to 375 °C. The percentage decrease in film thickness versus the temperature to which the film was heated is shown in Figure 7. It can be seen that a large decrease in film thickness occurs with increasing temperature up to $T \sim 225$ °C, with a smaller decrease in film thickness with increasing temperature for higher temperatures. This change in slope of percentage decrease in film thickness versus temperature suggests that two different mechanisms determine the behavior: a mechanism that dominates below $T \sim 225$ °C, which we identify below as a chemical change of the chitosan to a chitinlike material, and another mechanism that dominates for temperatures $T > 225$ °C, which is consistent

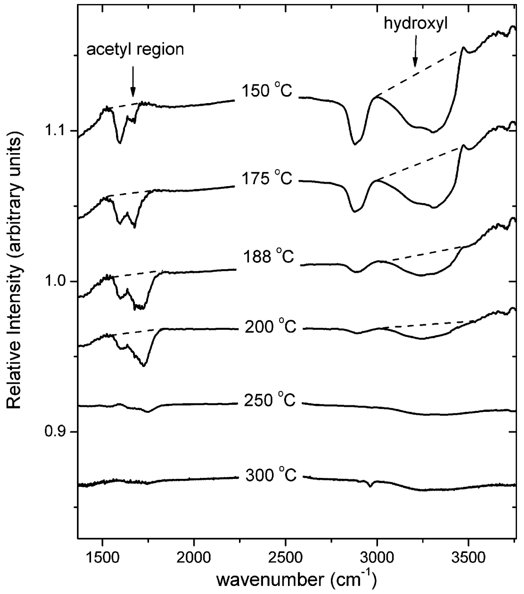

Figure 8. FT-IRRAS spectra of chitosan films after heating in dry nitrogen for 4 h at $T = 150$, 175, 188, 200, 250, 300 °C. The curves have been offset vertically for clarity. The area under the peak centered at a wavenumber of 1655 cm^{-1} is associated with the acetyl group, and the area under the peak centered at a wavenumber of 3450 cm^{-1} is associated with the hydroxyl group. The dashed lines indicate the range of data used to calculate the area for each peak.

with thermal degradation of the chitosan that has been observed previously for temperatures $T > 250$ °C.[17] This interpretation is corroborated by FT-IRRAS measurements performed on ultrathin chitosan films at elevated temperatures, as described below.

We suggest that the changes in the properties of the films obtained for heating to 150 °C $< T <$ 200 °C are caused by the removal of water from the films, with a resulting decrease in the equilibrium water content of the films for all RH values. Following preparation, the chitosan films swell dramatically in the presence of air with high humidity (cf. Figure 2), suggesting that the films are in a hydrogel state, which is consistent with the trapping of solvent within the films during the spincoating deposition process and the subsequent absorption of water molecules when exposed to air with high humidity. The large decrease in film thickness, increase in index of refraction, and large decrease in the swelling coefficient $(\Delta h/h_i)/\Delta\mathrm{RH}$ observed after heating the films to temperatures 150 °C $< T <$ 200 °C are consistent with the expulsion of water from the chitosan network at elevated temperatures which irreversibly reduces the water content of the network. This suggests the possibility of a chemical change, for example, change in bonding, in the chitosan network. This interpretation of our data is consistent with the results of previous differential scanning calorimetry (DSC) measurements of bulk chitosan with a similar degree of acetylation (DA ~ 15%) in which an endothermic peak near $T = 150$ °C was observed that was attributed to the release of trapped water.[17]

To investigate the possibility of a chemical change occurring within the chitosan films because of the thermal treatment, we performed FT-IRRAS (Fourier transform infrared reflection absorption spectroscopy) experiments on films before and after they had been heated for 4 h at $T = 150$, 175, 188, 200, 250, and 300 °C. The corresponding FT-IRRAS spectra are shown in Figure 8. We observe that the area corresponding to the acetyl peak centered at a wavenumber of 1655 cm^{-1} increases with heating, relative to the area of the peak corresponding to the hydroxyl group centered at a wavenumber of 3450 cm^{-1}, for films heated at temperatures up to $T = 200$ °C. For temperatures $T > 250$ °C, chitosan is expected to thermally degrade, and the corresponding spectra for $T = 250$ °C and $T = 300$ °C indicate a large reduction in both absorption peaks.

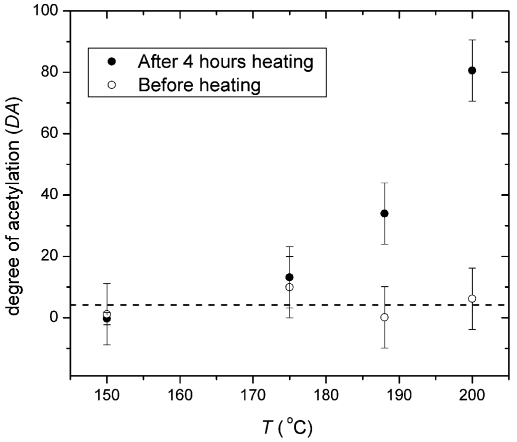

Figure 9. Degree of acetylation (DA) calculated from FT-IRRAS spectra of chitosan films versus the temperature to which the films were heated for a period of 4 h, following the procedure described by Domszy and Roberts.[12] The chitosan films had an initial DA of ~6% and initial film thicknesses *h* within the range of 150 ± 2 nm. The data points measured after exposure to elevated temperatures between $T = 150$ °C and $T = 200$ °C for 4 h are indicated by solid circles, and those measured before heating are indicated by open circles.

The degree of acetylation (DA) was calculated from the ratio of the areas of the absorption peaks corresponding to acetyl groups and hydroxyl groups, A_{1655} and A_{3450}, respectively, according to the formula[12]

$$\mathrm{DA} = (A_{1655}/A_{3450}) \times 100\%/1.33$$

In Figure 9, we plot the calculated DA versus the temperature to which the films were heated for 4 h for temperatures up to $T = 200$ °C. The DA increases monotonically with increasing temperature: for films that have been heated to $T = 200$ °C for 4 h, the calculated DA increased from <10% to approximately 80%. The chitosan films used in the FT-IRRAS experiments were also measured using reflection ellipsometry before and after the heating of the films, and we observed quantitatively similar decreases in thickness and increases in index of refraction with heating for these films as for the $h = 50$ nm, DA ~ 15% films described above: for example, a reduction in film thickness of over 40% was measured for a film heated for 4 h at $T = 200$ °C. The observed increase in DA with heating shown in Figure 9 supports our hypothesis that the decrease in thickness, increase in index of refraction, and decrease in swelling produced by heating the chitosan films to temperatures 150 °C $< T <$ 200 °C is due to the irreversible removal of water from the films. Although the FT-IRRAS measurement does not allow the determination of the water content of the films, since both of the 1655 cm^{-1} and 3450 cm^{-1} absorption peaks scale by the same amount with increased water content,[12] an increase in the DA decreases the solubility of chitosan in water, and it is reasonable to expect that this corresponds to a reduction in the equilibrium water content. The DA was not calculated from the spectra for the films heated to $T = 250$ °C and $T = 300$ °C, since the peaks corresponding to the acetyl group and hydroxyl group were very small. The data shown in Figures 7 and 8 collectively provide strong evidence that thermal degradation does not occur with heating to temperatures $T <$

200 °C and that heating for 4 h at $T = 250$ °C and $T = 300$ °C produces thermal degradation of the chitosan films as expected.

In a previous study, very thick ($h \sim 1$ mm), solution-cast films of a salt of chitosan, chitosonium acetate, were heated to temperatures T ranging from 25 °C to 150 °C, and this produced changes in the physical properties of the films: a mass loss of 9%, increased mechanical strength, and decreased solubility in water were observed after heating films to $T = 110$ °C for 6 h.[18] These changes in the film properties were interpreted as a conversion of chitosonium acetate to an amidized form of chitosan which was similar in properties to chitin.[18] This result suggested that heating of chitosonium acetate to temperatures less than those associated with thermal degradation of the polymer could offer a nontoxic alternative to the conventional method of converting chitosan into chitin by exposure to acetic anhydride. In the present study, the measured decrease in film thickness in thin, neutralized chitosan films heated to $T > 150$ °C corresponds to a similar reduction in mass as is observed for thick chitosonium acetate films heated to similar temperatures. However, the mechanism proposed for this chemical change in ref 18, in which acetate ions provide the “raw material” that converts into acetyl groups, should not be possible in neutralized chitosan films lacking acetate ions.

Conclusions

We have prepared thin, uniform chitosan films by controlling the relative humidity and spin speed during spincoating deposition. The films swell dramatically in the presence of moist air, and we have used reflection ellipsometry to characterize the swelling of the films with increased relative humidity. By heating the films to $T = 200$ °C and cooling them to room temperature, dramatic decreases in the film thickness, increases in the index of refraction, and significant reductions in the swelling of the films are observed. We have verified that these changes are not due to oxidation or thermal degradation of the films. The films contain a significant amount of water following the spincoating deposition, and we suggest that heating of the films irreversibly releases trapped water, possibly because of a chemical change within the chitosan network which increases its stability with respect to changes in relative humidity. FT-IRRAS measurements of a subset of chitosan films before and after heating indicate that the degree of acetylation increases substantially with heating. Collectively, the results of the present study suggest that heating of chitosan to moderate temperatures converts it into a chitinlike material.

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