Improving Wet Performance of Chitosan-Xylan Bioplastic Using a Biobased Additive

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Supervised by

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Abstract

The objective of this study was to improve the water stability and wet strength performance of chitosan-xylan polymer using citric acid as a green and biobased crosslinking agent. Aqueous solution containing chitosan and xylan was added with citric acid at different dosages (0, 0.2, 0.4, 0.8, and 1.6 mmol per gram of polymer). The solution was cast into films for Fourier transform infrared spectroscopic (FTIR) studies, tensile tests, and 24-hour water soaking experiments. The tensile results showed 40% higher wet strength as the citric acid dosage were increased from 0 to 0.4 mmol/g. Higher citric acid dosages (i.e., 0.8 and 1.6 mmol/g), however, resulted in films that were too weak to be tested wet. FTIR results verified the presence of amide linkages, which increased as the citric acid dosage were increased to 0.2 and then to 0.4 mmol/g. The inferred crosslinking was supported by the lower water absorption of the films; the moisture content of the soaked films reduced from 90% (no citric acid) to 52-54%. Additionally, the wet stiffness (modulus of elasticity) of the crosslinked films was improved from 1.2 GPa (control) to 1.6 GPa (citric acid 0.4 mmol/g). An attempt to improve the dry-state ductility (flexibility) of the crosslinked films using adipic acid in partial substitution of citric acid, however, did not turn out to be conclusive under the conditions examined. Overall, findings from this study suggest that the wet mechanical properties and water resistance of chitosan-xylan polymer can be improved through citric acid crosslinking.

Keywords – Chitosan; Xylan; Citric Acid; Crosslinking; Fourier Transform Infrared Spectroscopy (FTIR); Water Absorption; Tensile Properties

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1. Introduction

Chitosan is a renewable polymer produced from the *N*-deacetylation of chitin, a biological polymer found in the exoskeletons of many crustaceans (Chaibakhsh et al. 2013). In fact, chitin (**Figure 1**) is one of the most abundant polysaccharide on earth besides cellulose (Park et al. 2002). Chitosan is a non-toxic and biodegradable polymer that has proven to be a potential replacement for petroleum based materials (Cui et al. 2011). Because of these non-toxic and renewable properties of chitosan, its applications in the medical and food industries has gained much interest in recent years.

Chitosan (**Figure 1**), like other polar polymers (containing, for instance, hydroxyl or amine groups), is susceptible to the influence of water (Cui et al. 2011). A consequence of this is the reduction in mechanical strength and in some cases loss of structural integrity. Water stability and mechanical resistance are important issues, for instance, in chitosan hydrocolloid films that are useful in medical applications (Rivero et al. 2010). These issues can be remedied by chemically crosslinking the molecular chains of chitosan. Crosslinking creates a complex covalently bonded matrix within the polymer network (Fonseca et al. 2016). Thus it reduces water disruption thereby increasing structural integrity and also strength of the polymer (Thiebaud et al. 1997). However, additives such as glutaraldehyde and epichlorohydrin that are commonly used for inducing chemical crosslinking exhibit some toxicity effects, which would limit utilization of the cross-linked chitosan polymer (Shi et al. 2008).

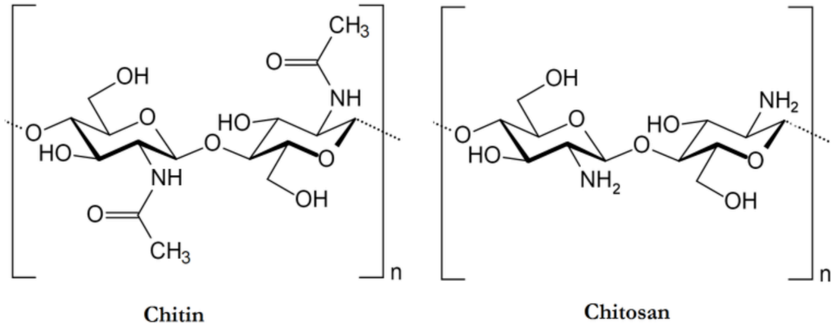

Figure 1. Chitin and chitosan: Copolymers of 2-acetamido-2-deoxy-β-D-glucose and 2-amino-2-deoxy-β-D-glucose (Cui et al. 2011).

The objective of this study was to improve the water stability and wet strength performance of chitosan-based polymer films using a green and biobased crosslinking agent. In essence, this study varied the amount (mole) of crosslinker relative to the mass of matrix polymer to induce varying degrees of crosslinking. The crosslinking agent chosen for this study was citric acid. Citric acid, found most notably in citrus fruits, is a renewable feedstock produced commercially in fermentation processes (Doll et al 2006; Ray and Sivakumar 2009). Citric acid carries carboxylic groups that can interact with hydroxyl or amine functional groups to form, respectively, ester or amide linkages. Citric acid is a tri-carboxylic acid, meaning that each molecule has three carboxylic groups, and so it is possible to form crosslinking with the host polymer (**Figure 2**). Indeed, Cui et al. (2011) demonstrated significant improvement in water repellency of chitosan films that had been reacted with citric acid to form stable amide linkages.

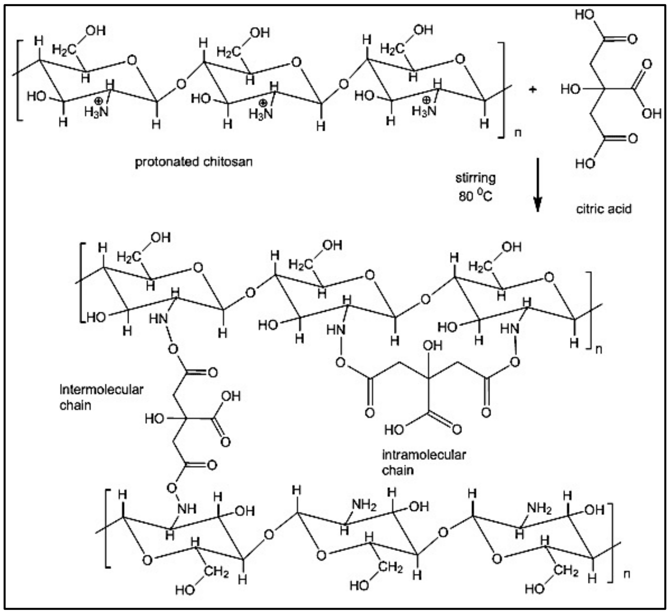

Figure 2: Possible chitosan-citric acid crosslinking mechanism (Lusiana et al. 2016).

Different from previous studies that examined citric acid crosslinking of chitosan, our study focused on a chitosan-xylan hybrid polymer. Xylan (**Figure 3**), also a polysaccharide, constitutes 15-20% of the dry mass of hardwood and grasses. Xylan was reported to have immunomodulatory effects; it improves chitosan hydrogel for bone tissue regeneration (Bush et al. 2016). In the present study, a hypothesis was adopted that adding citric acid would crosslink and enhance the wet performance of chitosan-xylan polymer. To assess these effects, water absorption and changes in tensile properties of the modified polymer were tested after a water soaking experiment.

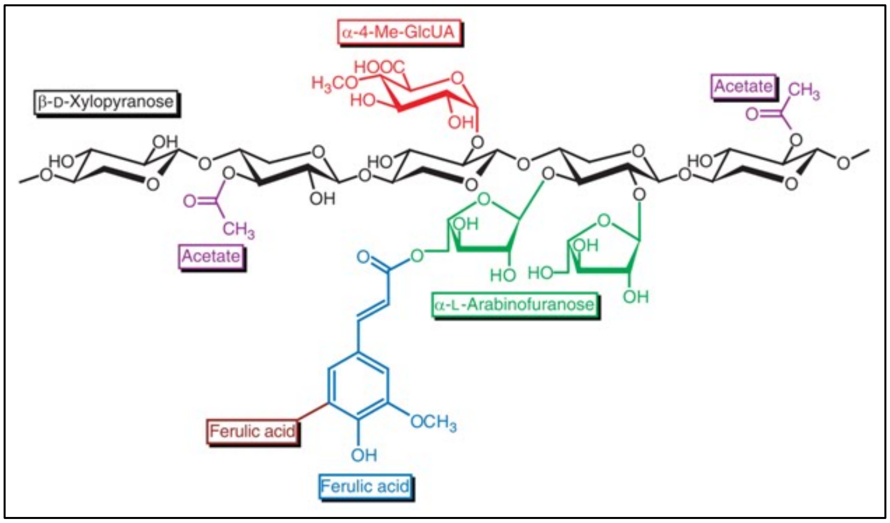

Figure 3: General structure of xylan from a variety of biomass sources (Dodd and Cann 2009)

A concern develops, however, in the crosslinking of polymeric materials because of the increase in brittleness. One way to remediate this issue is to incorporate plasticizers. For example, introduction of glycerol to chitosan-citric acid films resulted in increased ductility (Cui et al. 2011). In the present study, a strategy was attempted to improve/retain ductility while maintaining some degree of crosslinking. This entailed the use of adipic acid, a bi-functional carboxylic acid with carbon spacers (four) longer than that of citric acid.

Summarizing the above, the specific objectives of this study were:

1) Examine chemical linkages in chitosan-xylan films treated with citric acid;
2) Investigate effects of citric acid on tensile and water absorption of chitosan-xylan films;
3) Evaluate the effects of adipic acid as a ductility enhancer for chitosan-xylan films

2. Materials and Methods

2.1. Materials

Medium molecular weight chitosan was purchased from Sigma-Aldrich (St. Louis, MO, USA) with a deacyetelation degree of 75-85% (CAS registry #: 9012-76-4). Xylan from corn core was purchased from TCI chemical company (CAS registry #: 9014-63-5). The following chemicals were also used: adipic acid (CAS registry #: 124-04-9), citric acid (CAS registry #: 77-92-9), and acetic acid (CAS registry #: 64-19-7) from Sigma-Aldrich.

2.2. Film solution preparation

Chitosan solution of 1% (w/v) was prepared by dissolving the compound in 2% (v/v) acetic acid solution with 30 minutes of magnetic stirring (800 rpm) at 40°C (Rivero et al. 2010). Xylan was added to the chitosan solution at a chitosan to xylan mass ratios of 3:1, based on the reported highest fraction of hemicellulose needed to form stable hydrogels (Bush et al. 2016). The chitosan-xylan solution had an average pH of 3.4.

Citric acid (CA) was then added to each batch of dissolved chitosan-xylan solution at different dosages: 0, 0.2, 0.4, 0.8, and 1.6 mmol CA per gram of polymer. The average pH value of the final solution was 3.2. For ductility enhancement studies, the citric acid from a selected (optimized) dosage level was partially substituted with adipic acid (AP), which was dosed at a CA:AP mole ratio of 3:1, 1:1, 1:3, and 0:1 (complete substitution; final solution pH ~3.4). The final solutions were placed in an Isotmep® Vacuum Oven Model 280A (Fisher Scientific) at 50°C and 52 cm-Hg vacuum for 30 minutes. The purpose was to remove bubbles suspended in the solution before the casting procedure.

2.3. Film preparation

Film samples were prepared by casting the prepared solution in Teflon petri dishes of 10-cm inner diameter. The required solution weight for each cast (petri dish) was calculated assuming a solution density of water (1 g/cm^3) to achieve a target dry weight of 0.4 g for the resulted film. For each formulation, four to five films were cast from the same batch of polymer solution. The cast films were left to dry for 48 hours at a relative humidity of 61% and temperature of 24.6°C on average.

2.4. Cross-linking

After 48 hours of drying, the cast films were removed from the Teflon dishes and weighed. The film disk with material build up around its perimeter was trimmed to produce a flat film which was re-weighed. To induce crosslinking, the films were placed in the Isotemp oven at 160°C for 10 minutes with Teflon sheets and metal plates layered over the films. Additionally, a five-pound weight was placed on the metal plates covering the films in the oven to prevent film warping. After removal from the oven, the films were weighed immediately and stored in a 50% controlled relative humidity room. All weight readings collected were for the purpose of tracking solid content, and will not be reported in this paper.

2.5. Tensile testing

The ~10 cm diameter films were die-cut into 0.375” x 2.5” strips based on the dimension ratio specified in the ASTM D-882 standard. Eight strip specimens were cut for each type of tensile sample. For dry testing, the strip specimens were conditioned in a 50% controlled relative humidity room for seven days. After conditioning, the specimen thickness was measured in three locations using a motor-driven micrometer (manufactured by AB Lorentzen & Wettre, Stockholm) equipped with a Mitutoyo Digimatic Indicator. The thickness values were averaged and recorded for tensile testing.

Samples were then tested to failure in the tension mode at an initial gauge length (span) of one inch and loading rate of 0.2 in/min using an INSTRON 5542 fitted with a 500-N load cell. The strain at break (elongation as % of original span), tensile strength, and modulus of elasticity (MOE) were calculated according to the ASTM-D882 method (2012). The MOE was determined from the linear elastic region of the stress-strain curves. Additionally, the broken pieces of all eight specimens were collected and weighed together, and then placed in the oven at 100°C to be dried until constant weight. The moisture content (MC) of the test specimens can be estimated, and it is expressed relative to their oven dry weight:

$$MC\ (\%) = \left[\frac{Weight\ at\ the\ time\ MC\ status\ is\ of\ interest\ - oven\ dry\ weight}{oven\ dry\ weight}\right] \times 100$$

2.6. Water absorption measurements

Strip specimens (0.375” x 2.5”) obtained the same way as in dry tensile tests were used for the soaking experiment. The samples (eight specimens each) were soaked for 24 hours in individual small-mouth beakers filled with water. Once submerged, the specimens were prevented by the beaker shape from floating; this allowed uniform water adsorption. The weight of the specimens was determined before and after soaking to calculate moisture content to indicate the extent of moisture absorption. Before weight measurements, surface water was removed from the specimens by blotting their top and bottom faces using a filter paper (25-μm pores) as the absorbent. The moisture content of the soaked specimen was calculated in the same manner as expressed above relative to its oven dry weight:

$$MC\ (\%) = \left[\frac{weight\ after\ 24\ hr\ soaking - oven\ dry\ weight}{oven\ dry\ weight}\right] \times 100$$

2.7. Fourier transform infrared spectroscopy (FTIR)

Before FTIR study, the specimens were rinsed in water for four minutes to remove any physisorbed or unreacted acid and then dried. The FTIR was conducted in the attenuated reflection (ATR) mode. The spectra were collected at 32 scans using a Nicolet Series II Magna-IR System 750 at a resolution of 4 cm^{-1} in the wavenumber range of 4000 and 600 cm^{-1}. All spectra were baseline-corrected and normalized using the OMNIC™ software (Thermo Fisher Scientific Inc) of the instrument.

3. Results and Discussion

3.1. Cross-linking and functional groups characterization

Figure 4 shows the FTIR spectra of chitosan-xylan films prepared from different citric acid (CA) dosages in the formulation (0, 0.2, and 0.4 mmol CA per gram polymer). Initial observations reveal that all three samples had broad bands centering around 3300 cm^{-1}, corresponding to vibrational stretching of the hydroxyl groups of chitosan and xylan. The –OH band is overlapped by the stretching vibration of N-H, which is present in pristine chitosan (Silva et al. 2012). For films prepared from the two formulations containing citric acids, the OH band observed showed a decrease in slope compared to the control sample. The decreased slope indicates an increase in the broadness of the peak, and it could be attributed to the increased –OH from hydroxyl groups of the added citric acid (Cui et al 2011),

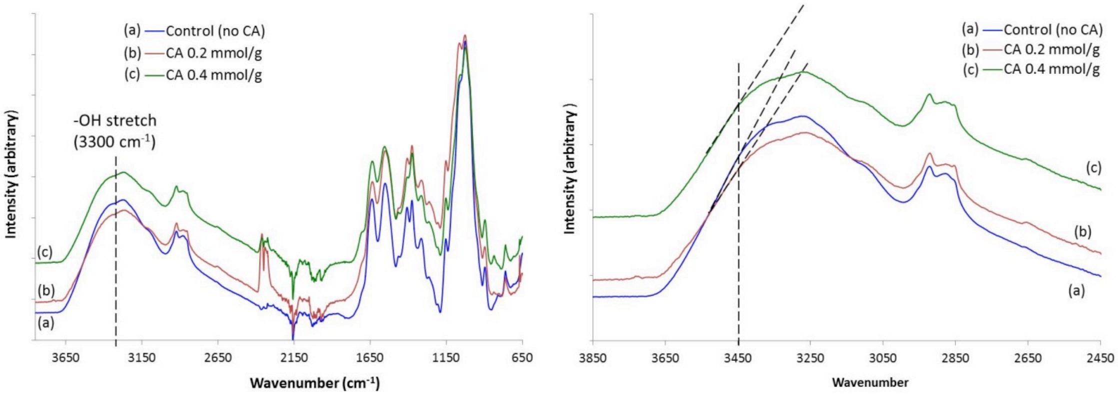

Figure 4: FTIR spectra of chitosan-xylan sample with or without citric acid (CA) in the formulation: whole wavenumber range (left) and focusing on the 3300 cm^{-1} band (right)
Note: The spectra were offset vertically to clearly show individual bands.

Since citric acid could react with hydroxyl groups (of chitosn or xylan) to form ester linkages, it would be of interest to examine the FTIR band near 1730 cm^{-1} to detect the presence of ester. **Figure 5** (left) shows a small band in the control sample at 1710 cm^{-1}, which corresponds to the carbonyl C=O groups. This functional group could be from the carboxylic group in the side chain of xylan polymer (see **Figure 3**). It could also be ascribed to the (15-25%) acetamide groups (see **Figure 2**) that were not deacetylated in our chitosan sample. With citric acid addition, no ester band (1730 cm^{-1}) was visible, suggesting no chemical interaction between the carboxylic acid group of citric acid and the hydroxyl group of chitosan or xylan. Conversely, the 1710 cm^{-1} band increased with increasing citric acid dosage in the film formulation. Previous studies by Ahmad et al (2015) and Salam et al (2011) have shown similar results indicating the peaks could correspond to the carbonyl groups in the amide II linkage of cross-linked chitosan (**Figure 2**). It was suspected that the presence of this peak corresponds to cross-linking reactions similar to the mechanisms shown in **Figure 2** (Ahmad et al 2015). The presence of (and increase in) amide II, however, would need to be verified through other bands that are characteristics of the functional group, which will be discussed next.

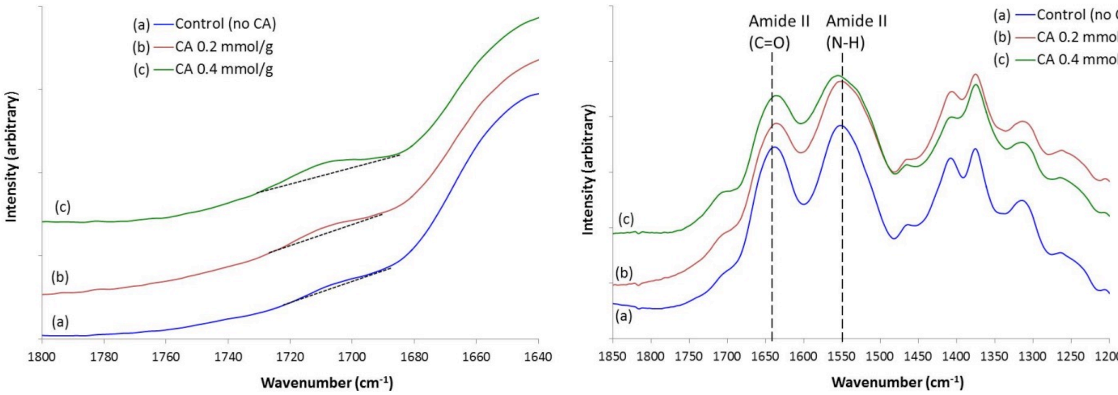

Figure 5: FTIR spectra of carboxyl band region (left) and amide II characteristic bands (right) of chitosan-xylan sample with or without citric acid (CA) in the formulation. Note: The spectra were offset vertically to clearly show individual bands

More conclusive evidence for the presence of amide II was shown in the peak at 1552 cm^{-1} (**Figure 5**; right), corresponding to the N-H stretching of secondary amide (Kumirska et al. 2010). Another observed peak at 1638 cm^{-1} has opposing descriptions in current literature related to cross-linked chitosan. In general, the presence of a strong N-H band (1515-1570 cm^{-1}) combined with the carbonyl band (1630-1680 cm^{-1}) is diagnostic for secondary amide (Smith 1999). Since both bands were present in the control sample, we can verify the presence of amide II, which is reasonable as the chitosan used in this study was of 75-85% deacetylation, meaning that it contains some acetamide (an amide II). As the citric acid dosage was increased, the adjacent 1552 and 1638 cm^{-1} bands became less resolved due to band broadening, suggesting the increasing presence of secondary amide. Since the acetylated portions of the chitosan polymer are unreactive, any increase in the secondary amide would be from the amide linkage formed through the reaction of secondary amine (chitosan) and carboxylic (citric acid) groups. The crosslinking inferred from these amide linkages will be examined using mechanical and soaking tests.

3.2. Mechanical properties of chitosan-xylan films: Effect of citric acid

3.*2.1 Dry and wet strength*

Figure 6 shows the tensile strength of both dry and wet films for various citric acid dosages. The dry strength increased from 44.0 MPa to 67.0 MPa with the addition of 0.2 mmol citric acid per gram of polymer in the formulation. Further increasing the citric acid dosage, however, lowered the dry strength. At 1.6 mmol/g, the strength became 36.0 MPa, i.e., lower than the control sample. Unreacted citric acid (excessive due to high dosages) could act as a plasticizer for the host polymer (Shi et al. 2008) to weaken the film.

The wet strength of films was only measured for samples prepared from citric acid dosages of 0, 0.2, and 0.4 mmol/g. Wet films from higher citric acid dosages (i.e., 0.8 and 1.6 mmol/g) were too weak to be tested. On average, all films tested (citric acid 0, 0.2, and 0.4 mmol/g) showed a 78% decrease in tensile strength after 24-h soaking (**Figure 6**). Films from formulation containing citric acid (0.4 mmol/g) exhibited higher wet strength (13.0 MPa) than the control (9.26 MPa), i.e., a 41 % increase in strength. This supports our hypothesis that citric acid crosslinking improves the wet strength of chitosan-xylan films.

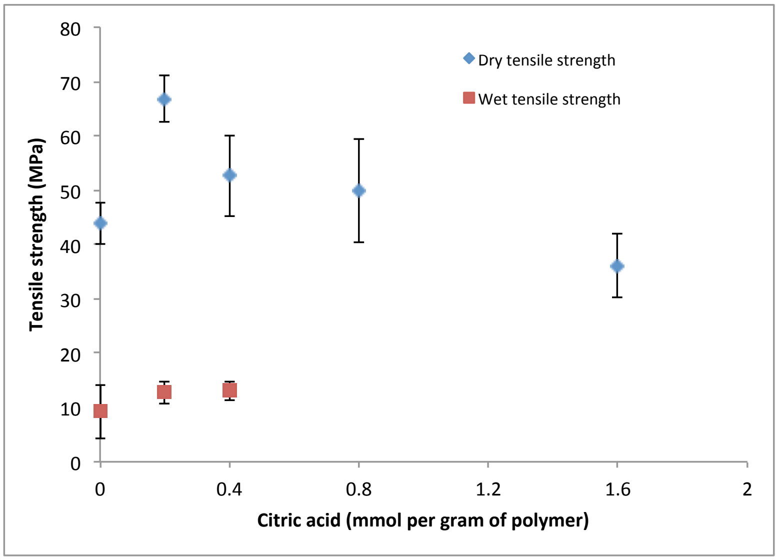

Figure 6: Dry and wet strength of chitosan-xylan films

3.2.2 Dry and wet stiffness and ductility

The stiffness of the film was inferred from the modulus of elasticity (MOE). Addition of citric acid (0.2 and 0.4 mmol/g) resulted in about 20% improvement in dry stiffness (**Figure 7**). The wet stiffness showed a 31% increase over the control when a citric acid dosage of 0.4 mmol/g was used. However, the same dosage level of citric acid resulted in lower dry (1.9 vs. 2.4%) and wet (2.2 vs. 3.4%) fracture strain compared to a lower dosage (0.2 mmol/g); this indicates compromised ductility (flexibility) with excessive crosslinking. When compared to the control, the 0.2 mmol/g dosage of citric acid resulted in stiffer films (both dry and wet) with fracture strain that was larger at dry condition and similar at wet. Overall, these results are consistent with the characteristics of crosslinking, which increases the rigidity of polymer but if done excessively would cause brittleness.

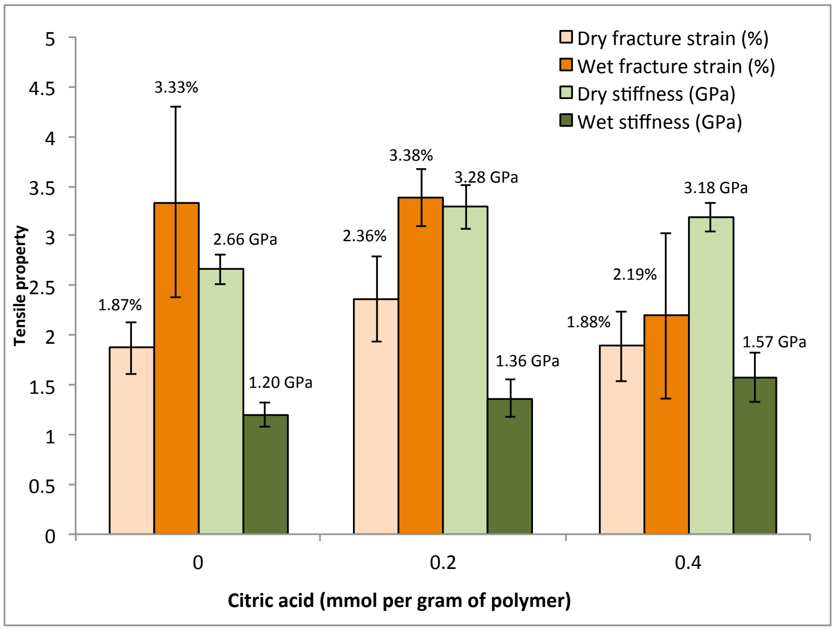

Figure 7: Maximum (fracture) strain and MOE of dry and wet chitosan-xylan films.

3.3. Effects of citric acid on water absorption of chitosan-xylan films

Results of water absorption experiments reaffirm the beneficial effect of crosslinking. The chitosan-xylan films attained 90.0% moisture content (MC) after 24 hours of soaking (**Figure 8**). By contrast, samples from formulations containing citric acid held 52.0% (for 0.2 mmol/g) and 54.0% (for 0.4 mmol/g) water after soaking. This decrease in water uptake could be attributed to crosslinking. The lower moisture content could also explain the higher wet strength discussed earlier for the crosslinked samples. However, between the two citric acid dosages, the samples do not differ considerably in their MC values after 24-h soaking. This observation suggests a potential limit in the water resistance enhancement that could be achieved using citric acid under the treatment conditions adopted in this study.

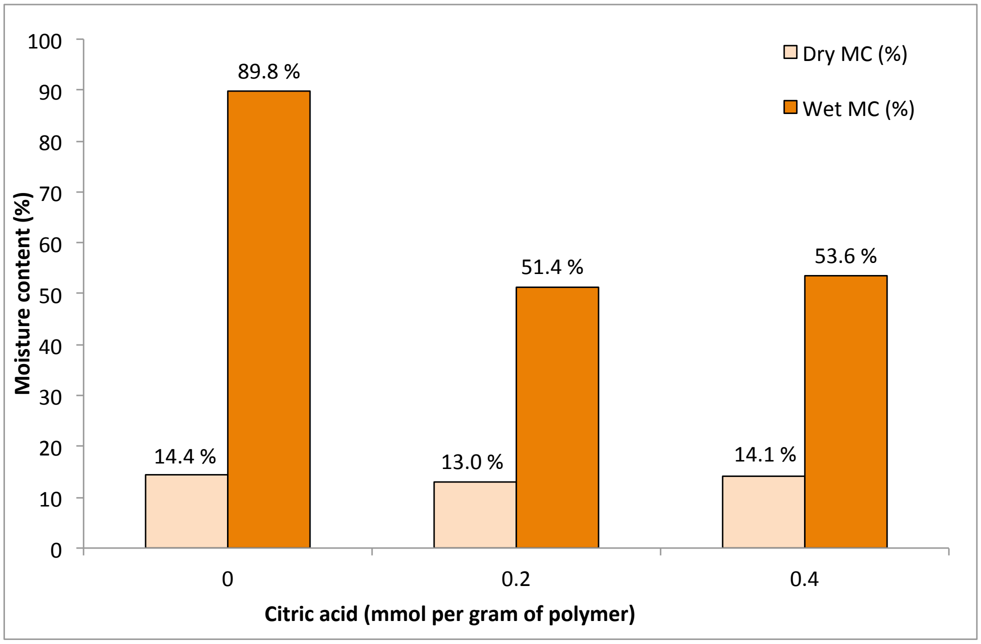

Figure 8: Moisture content of conditioned (unsoaked) and soaked chitosan-xylan films

3.4. Effects of adipic acid on tensile properties of chitosan-xylan films

From the results discussed so far, a polycarboxylic acid (citric acid) dosage of 0.2 mmol/g was selected based on the higher wet and dry tensile properties of the resulted film. To examine if adipic acid (another polycarboxylic acid) would enhance ductility, the acid was added in varying mole ratios relative to citric acid, but the total polycarboxylic acid was maintained at 0.2 mmol/g.

Figure 9 shows little variation in the maximum (fracture) strain values of the polymer films when adipic acid was added. When citric acid was fully substituted with adipic acid, a very subtle increase in the average fracture strain from 2.4% to 2.7% was observed. Other adipic acid ratios showed only small variations. Thus, the intended purpose of adipic acid for improving ductility was not realized. Moreover, the stiffness (MOE) of the film decreased significantly (~33.0%) with the addition of adipic acid (at all ratios) when compared to only using citric acid for the target dosage of polycarboxylic acid. The tensile strength also decreased, with values dropping from 67.0 MPa (only citric acid as crosslinker) to an average of 47.0 MPa (**Figure 10**) when adipic acid was blended to citric acid as mixed polycarboxylics for crosslinking. The lower tensile properties observed could be in part a result of higher film moisture content (average 19.0%) in the case of adipic acid compared to that of citric acid (MC 13.0%). Such MC differences occurred despite that all samples were conditioned in the same manner and for the same amount of duration. Overall, there is no evidence of beneficial effects of adding adipic acid in making chitosan-xylan films, based on the conditions tested in this study.

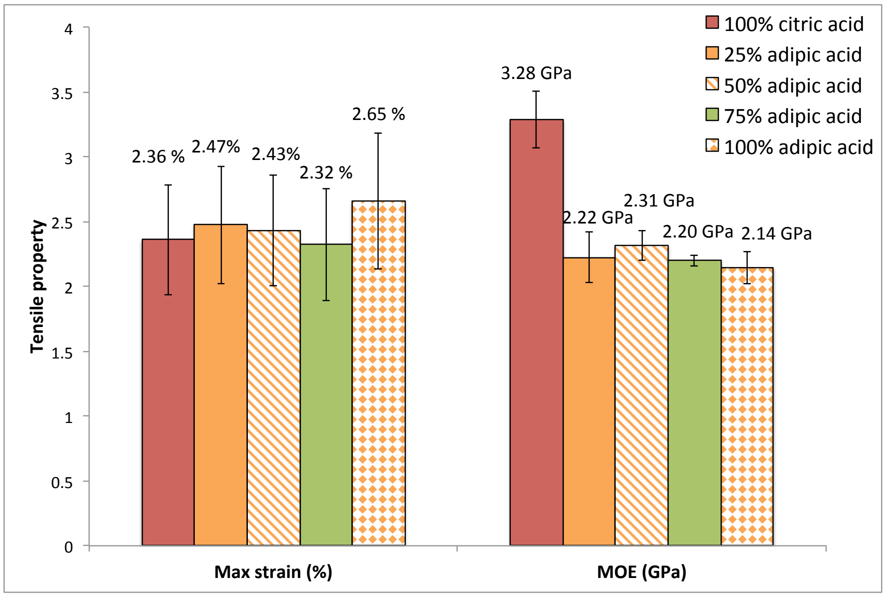

Figure 9: Maximum (fracture) strain and MOE of chitosan-xylan films as citric acid in the formulation was partially and then fully substituted with adipic acid

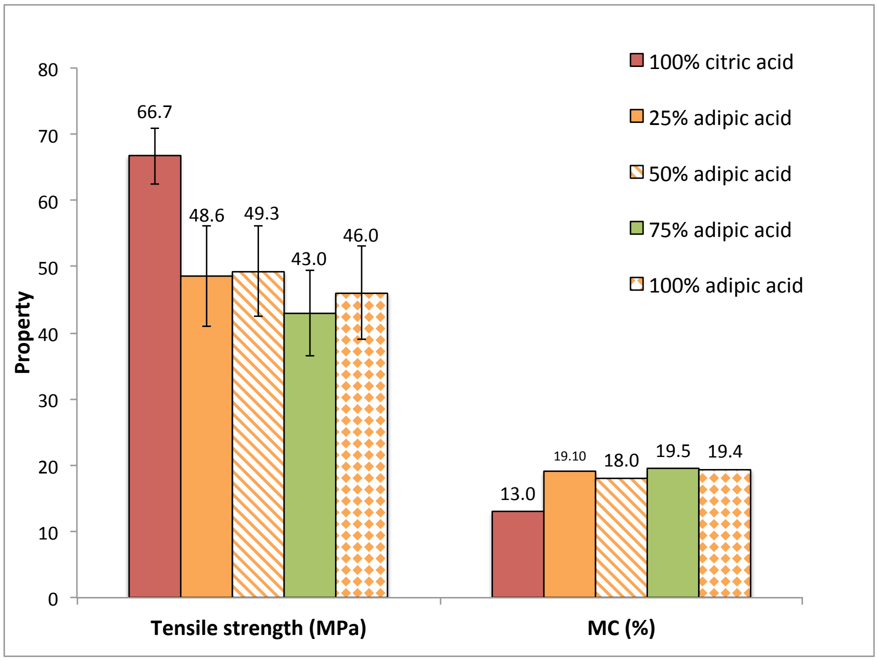

Figure 10: Tensile strength and MC of chitosan-xylan films as citric acid in the formulation was partially and then fully substituted with adipic acid

4. Conclusion

This study examined the wet performance of chitosan-xylan bioplastics crosslinked with citric acid. Film samples were prepared from various dosages of citric acid for FTIR and tensile studies. FTIR results verified the existence of chemical linkages between the amine groups of chitosan and the carboxylic acid groups of citric acid. The inferred crosslinking increased the wet strength of the films. The moisture resistance of the chitosan-xylan film was also improved by crosslinking. There were changes in strength and stiffness of the crosslinked films when citric acid was partially or fully replaced with adipic acid. However, due to differences in moisture content levels of the tested films, the differences could not be conclusively attributed to adipic acid.

The test results show that crosslinking can improve the wet strength and stability of chitosan-xylan hybrid polymer. However, an issue still remains that the wet strength performances of the cross-linked polymer are still significantly lower than when they are dry. Additionally, there seems to be a limit for improving water resistance of chitosan-xylan polymer using citric acid at the treatment conditions adopted in this study. More in-depth research on the crosslinking capacity of the chitosan-xylan polymer is recommended for further optimization of their mechanical properties and water resistance.

Acknowledgments

I would like to thank my faculty mentor in the Bioproducts and Biosystems Engineering Department, Dr. William Tze, for his guidance and support. I also would like to thank Ph.D. candidate Islam Hafez for training and assisting me with the experimental procedure. I acknowledge the University of Minnesota Undergraduate Research Opportunity program for funding this research. Part of this study was also funded by the USDA McIntire Stennis Fund (Project No. MIN-12-053).

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