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Biopolymer films from glucomannan: the effects of citric acid crosslinking on barrier properties

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Abstract

Glucomannan extracted from konjac root is used to form biodegradable films with gas and grease barrier properties for food packaging application. Nano-fibrillated cellulose (NFC) and plasticizers were used to improve the strength properties of the films. Citric acid and sodium hypophosphite (SHP) were used as crosslinking agent and catalyst, respectively, to improve the barrier property of the films against moisture. The film samples were prepared from glucomannan and NFC using a dispersion-casting method. The moisture barrier properties were characterized by the moisture vapor transmission rates (MVTR) and showed a significant decrease of 49.7 % (with 0.35 g citric acid in formulation, cured; marked as CA35-C). The crosslinked glucomannan films were calibrated with increasing mean tensile strength, modulus and elongation.

Keywords: packaging material, composite film, nano-fibrillated cellulose, air permeability, mechanical property

1. Introduction

Biopolymers are a potential alternative source for production of fuels and packaging materials, because they have the capability to be degraded or broken down through the action of naturally occurring organisms leaving behind organic by-products (Othman, 2014). The most common and suitable biopolymers for food packaging applications are naturally occurring materials, such as cellulose, hemicellulose, starch, chitosan and agar. It was recorded that the global bio-plastic demand was 1.4 million metric tons in 2014; and it is expected to reach about 6 million metric tons in 2019 (Chen, 2014). According to studies by Helmut Kaiser Consultancy (2013), bio-plastics are expected to cover approximately 25–30 % of the total plastic market by 2020.

The hydrophilic nature of polysaccharide films offers them good oxygen barrier properties, but their water vapor barrier properties and moisture resistance are relatively poor in comparison with the petroleum-based plastic films (Giancone, et al., 2011), which limits their potential application in packaging materials (Janjarasskul and Krochta, 2010). A high water solubility obviously affects the functionality of hemicellulose-based films as packaging materials. The hydrophilicity of the polysaccharides results in water swelling and impairing their mechanical and barrier properties (Sebti, Delves-Broughton and Coma, 2003). Many studies on hemicellulose-based films report that the water resistance of the films can be improved by chemical or physical crosslinking, during which the polymer chains are crosslinked by covalent bonds (chemical bonds) or weaker physical bonds. The crosslinking reagents could be dicarboxylic or polycarboxylic acids such as citric acid (CA). The crosslinked hemicellulose form three dimensional networks that reduce the mobility of the structure, usually enhancing their water resistance (Figure 1), reducing both water solubility and swelling by water, and boosting their mechanical and barrier properties (Balaguer, et al., 2011).

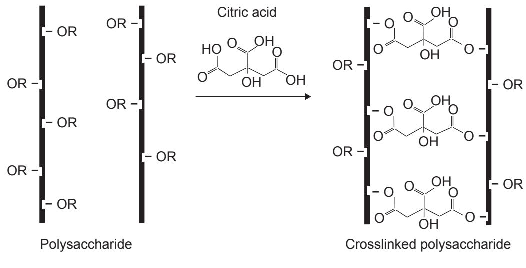

Figure 1: Mechanism for covalent crosslinking between citric acid and a polysaccharide; adapted from Hashem, et al. (2013)

Hemicellulose and nano-fibrillated cellulose are highly promising biopolymers for the production of packaging materials, since they offer films with good tensile and gas barrier properties (Ma, et al., 2017). In addition, they are renewable, available at low cost, and fully biodegradable. However, non-plasticized hemicellulose films are brittle and their hydrophilic character results in poor moisture barrier properties and high water sensitivity compared with petroleum-based plastic films such as polyethylene or polypropylene. A common way to improve the film formation and hydrophobic properties is chemical modification, such as crosslinking. Plasticizers such as water, xylitol or sorbitol reduce the glass transition temperature T_g, of the polymer matrix and prevent the formation of cracks and pinholes (Forssell, et al., 2002; Godbillot, et al., 2006; Stading, Rindlav-Westling and Gatenholm, 2001).

Glucomannan has shown good film-forming capacity, which offers good barrier properties towards air and grease. Several research works and patents have indicated that the development of glucomannan-based films and coatings as sustainable printable packaging materials is commercially promising (Gatenholm, et al., 2008). In the year of 2013, another new patent assigned by Xylophane came out dealing with a method for the production of flexible films or coatings for packaging based on hemicelluloses combined with a crosslinking agent or hydrophobizing agent, to be used as an oxygen, aroma, and/or grease barrier with improved moisture resistance (Gröndahl, et al., 2013).

Nano-fibrillated cellulose (NFC) is a biodegradable film-forming material widely studied for its industrially interesting properties and possible applications in food packaging. Various applications of nano-fibrillated cellulose are under investigation, including its addition as paper fillers (Eriksen, Syverud and Gregerson, 2008), reinforcement in polymer composites (Siqueira, Bras and Dufresne, 2010), coatings for paper and board (Aulin, Gallstedt and Lindström, 2010; Lavoine, Bras and Desloges, 2014; Lavoine, Desloges and Bras, 2014; Lavoine, et al., 2014; Ridgway and Gane, 2012; Syverud, et al., 2009) or stand-alone films (Tammelin, Hippi and Salminen, 2013; Vartiainen, et al., 2016).

However, the focus of this work is on the application of NFC as barrier material used in food packaging and printed electronics. High potential of NFC application as oxygen barrier material on the lab scale was already shown in several works (Aulin, et al., 2010; Aulin, et al., 2013; Honorato, et al., 2015; Kumar, et al., 2014; Rodionova, et al., 2011; Syverud, et al., 2009).

There is a widespread desire and urgent need to replace or partially replace petroleum-based materials with renewable, biodegradable, and eco-friendly packaging materials. Furthermore, there are increasing interests focused on the performance of nano-fibrillated cellulose-containing packaging materials in regard to the end-use properties, such as strength and barrier properties. However, the usage or application of hemicelluloses in packaging is currently limited.

The CA is easily accessible, inexpensive and non-toxic food additive. It has been reported to be utilized as a cross-linking agent to improve the performance of starch, cellulose and PVA/starch films (Coma, et al., 2003; Ma, et al., 2009; Olsson, et al., 2013). The barrier and mechanical properties of plasticized and cross-linked nanocellulose coatings for paper packaging applications has been studied by Herrera, Mathew and Oksman (2017). There has not been information reported using CA as a cross-linking agent in glucomannan/nano-cellulose composite films to enhance the moisture barrier and mechanical properties.

The purpose of this study was to formulate hemicellulose-based stand-alone films with improved moisture barrier and mechanical properties achieved by addition of CA as a crosslinking agent.

The main focus is to explore the optimal film formulations in regard to the barrier and mechanical properties, which will prepare the films for future printing and packaging applications.

2. Experimental

2.1 Materials

Glucomannan from NOW Foods, Inc., in powder form was used. It was derived from the root of *Amorphophalluskonjac* (konjac plant or elephant yam). It is a glucose-mannose polysaccharide in which 5–10 % of the sugars are acetylated. The molecule is structurally related to glucomannan from guar gum. Macroscopically, konjac glucomannan is a soluble, fermentable, and highly viscous fiber.

The NFC (contains: water 95–99 %, cellulose pulp 1–5 %; manufactured by the Department of Chemical and Biological Engineering, University of Maine Process Development Center), in a suspension form was employed in this study. The sample was prepared mechanically by using a pilot scale refiner to break down the wood fibers. The wood fibers were bleached softwood Kraft pulp. The suspensions were obtained at around 3.5 % solids.

Sorbitol in powder form with a purity of 99 %, CA and sodium hypophosphite (SHP) in powder form with a purity of 98 %, from Sigma Aldrich were applied.

Table 1: The crosslinking film formulations and treatment

Formulation	NFC (g)	Glucomannan (g)	Xylitol (g)	CA (g)	SHP as catalyst (g)
N-CA	0.4	1	2	0.00	0.000
CA5-C	0.4	1	2	0.05	0.125
CA15-C	0.4	1	2	0.15	0.125
CA25-C	0.4	1	2	0.25	0.125
CA35-C	0.4	1	2	0.35	0.125
CA25-NC	0.4	1	2	0.25	0.125

2.2 Film formation

The composite film formulations are shown in Table 1. The NFC was added to distilled water for 15 min (10 g / 100 ml) with a mass fraction of 0.5 % of glucomannan (on a NFC basis), a mass fraction of 10 % of sorbitol (on a NFC basis), a mass fraction of 5 %, 15 %, 25 %, and 35 % of CA (on a glucomannan basis), and a mass fraction of 50 % of SHP (on a CA basis) by using a VWR Power Max ELITE Dual Speed Mixer at 45 °C and mixing speed of 450 min^{-1}. The solutions were casted to a mold with the dimensions of 200 mm × 100 mm. Films were dried in the Environmental Test Chambers (Caron Model 6010; temperature range: 5 °C to 70 °C; humidity range: 20 % to 98 % relative humidity (RH)) for 24 hours at 60 °C and 35 % RH. Dried hemicellulose-based films were peeled off manually and then subjected to a curing treatment at 105 °C for 10 min using a fan oven (VWR Model 1305 U). Three film series were prepared following the same procedures, namely, N-CA (films without CA), CA#-C (those added with CA and cured) and CA25-NC (added with 25 % CA and not subjected to the curing treatment).

3. Analytical

Water vapor permeability of the films was evaluated by the gravimetric moisture vapor transmission rate (MVTR) test according to the ASTM E96 desiccant method (American Society for Testing and Materials, 1993). The samples were placed on top of a test cup (Thwing-Albert EZ-Cup 2″) containing sufficient amount of desiccant (anhydrous calcium chloride) to maintain 0 % RH, and the films were sealed to the cup (Figure 2). The assembled cups were placed in the testing room at 23 °C and 50 % RH and weighed every 24 h until constant rate of weight gain was attained. The moisture vapor transmissions (MVT) were calculated by Equation [1].

$$MVT = \frac{G}{(A \times t)} \qquad [1]$$

Where G is the weight change of the film, in grams; A is the area of the tested film, in cm^2; t is the time during which G occurred.

Figure 2: The Thwing-Albert EZ-Cup 2″ and the procedure of film sealing

The typical MVTR barrier values are shown in the Table 2. The water solubility test was conducted on the same specimens that were cut and used for the MVTR measurements. The specimen was a round piece with diameter of 2.5 inch. The film specimens were dried in the oven (VWR Scientific Model 1305 U) at 105 °C for 15 min and then weighed. Then the samples were immersed in 50 ml of distilled water for 6 h at 25 °C with continuous stirring using a magnetic stirrer (Corning Model PC-420). The remaining film pieces were dried and weighed. The insoluble matter was calculated as a percentage of the remaining weight over the initial weight of the film specimen.

The tensile properties of the film samples were assessed according to TAPPI (2006) Standard T494 at 25 °C and 50 % RH using an INSTRON 430I with a 500 N load cell. The specimens were conditioned under 25 °C and 50 % RH for 24 hours prior to testing. The initial gauge length was 100 mm, and the crosshead speed was 25 mm/min. The width of each specimen was 15 mm. The average value and standard deviation of tensile strength, Young's modulus (E) and elongation at break were evaluated for at least five of the tested specimens.

Table 2: Moisture vapor transmission rate permeability properties of plastic films (Khalifa, 2016)

Film type		MVTR at 30 °C, 90 % RH	
		(g/100 in^2 per day)	(g/m^2 per day)
Biaxially–oriented PP	Good MVTR	0.25–0.40	3.9–6.2
HDPE	↑	0.30–0.50	4.7–7.8
Cast PP		0.60–0.70	9.3–11.0
Biax PET		1.00–1.30	16.0–23.0
LDPE		1.00–1.50	16.0–23.0
EVOH		1.40–8.00	22.0–124.0
OPS	↓	7.00–10.00	109.0–155.0
Biax NYLON–6	Poor MVTR	10.00–13.00	155.0–202.0

The surface free energy of the films (CA25-C, CA25-NC and N-CA) was estimated by the FTA200 (First Ten Angstrom Dynamic Contact Angle) measurement apparatus. The FTA200 is a flexible video system for measuring contact angle, surface and interfacial tensions, wettability, and absorption. For the evaluation of the surface free energy, the contact angle of three liquids, deionized ultra-filtered water (DI), hexadecane, and methylene iodide (MI), was measured against surfaces of the N-CA and CA#-C film series, and the critical surface energy was calculated using the Owens-Wendt method (Owens and Wendt, 1969) as well as by the Good-Girifalco modification (Girifalco and Good, 1957) of Young-Dupre equation (Young, 1805; Chaudhury, 1996). Although these methods only estimate the surface free energy of solid, such values are useful for comparing the wettability of solid surfaces and predicting print adhesion. During each measurement, a droplet of liquid (1 µl) was deposited on the film specimen surface through a needle with 0.7 mm diameter. Series of images were captured and analyzed. A minimum of five readings were taken for each sample.

4. Results and Discussion

4.1 Caliper

The caliper of the film samples was measured by the Technidyne PROFILE/Plus Thickness instrument. The calipers of the film samples are shown in Table 3.

Table 3: The caliper of hemicellulose-based films

Sample	Caliper (mm)
N-CA	0.36 ± 0.01
CA5-C	0.35 ± 0.01
CA15-C	0.38 ± 0.03
CA25-C	0.37 ± 0.02
CA35-C	0.37 ± 0.02
CA25-NC	0.36 ± 0.01

The importance to characterize the caliper of the sample films is to ensure the repeatability of the film formation procedures in respect to caliper as well as to eliminate the impact of varying caliper on the barrier properties of the film samples. Thus, consistent caliper will enable to compare film series with various formulations and verify the crosslinking effectiveness. The film caliper was controlled by utilizing equal mass of glucomannan gel to fill the casting mold with identical dimensions.

4.2 Moisture vapor transmission rate

The MVTR of the films characterizing the volume of water vapor passing through a film per unit area and time under specified conditions was measured at a steady state. The expectation for the CA#-C films is lower MVTR and higher strength. The water vapor transfer rate for a packaging material such as low density polyethylene (LDPE) is 16–23 g/m^2 per day for film with 1 mm thickness (Khalifa, 2016). In this study, the CA#-C film series fulfilled this requirement. The N-CA films also fulfilled this requirement, but hornification occurred and resulted in higher opacity and rougher surface, which could lead to poor printability.

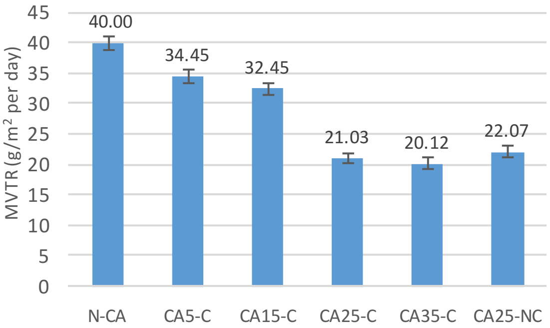

Figure 3: The moisture vapor transmission rate for the hemicellulose-based films

The values (Figure 3) show a reduction of MVTR with addition of CA. The MVTR tended to decrease with the addition of CA. The fall of MVTR values may be caused by a decreased solubility of water in the amorphous regions of the hemicellulose structure thanks to an increasing fraction of the acetylated hydroxyl groups, or simply more thorough crosslinking.

The relatively low air permeability of the films indicates that there were few connected pores through the cross section of the films. Therefore, it would be of interest to investigate the oxygen transmission rate (OTR) in the future work of this study, since it is a very important property for food packaging materials. The gas permeability depends on the dissolution of oxygen and its rate of diffusion in the material when there are no pores allowing for gas to flow through it.

4.3 Tensile Properties

Tensile properties for the different film series are presented in Table 4. Some studies have reported that CA not only effects moisture barrier properties of polysaccharide films, but also functions as plasticizer to improve their tensile properties (Abdillahi, et al., 2013). Correspondingly, this study presented that these effects apparently coexists. On one hand, CA addition decreased the MVTR and soluble matter of the films by approximately 13 %, indicating the crosslinking reaction between glucomannan and CA. On the other hand, the tensile strength, modulus and elongation at break increased with addition of CA, reflecting a functioning of CA as plasticizer. According to the study of Wang, et al. (2014), the plasticizing effect of CA was attributed to increasing interstitial volume of the film or increasing molecular mobility, making the polymeric structure less dense. However, over crosslinked (CA30-C) hemicellulose is brittle and lack of elasticity.

4.4 Surface free energy

When it comes to printing, it is essential to understand the behavior of ink on the chosen substrate. Surface free energy / surface tension is responsible for the surface behavior (atmosphere–solid contact) and the wetting phenomena (liquid–solid contact).

Estimated surface free energy value of the CA#-C film surface is 40.92 mJ/m^2, while the surface tension of the nano-silver conductive ink is 32–36 mN/m (Table 5). This predicts good wetting with ink and high ink adhesion on the N-CA film surface. Hemicellulose is hydrophilic in nature, hence hemicellulose-based films are generally hygroscopic, which means they will absorb moisture. During the surface free energy estimation test, the water drops spread on the films and totally wet the surface. However, the methylene iodide drops bead up on the film surface. This is because the hemicellulose has abundant free hydroxyl groups distributed along the main and side chains and is affinitive to water.

4.5 Solubility

The solubility and the degree of swelling are very important properties for food packaging. The solubility usually decreases as the degrees of crosslinking are increased (Zou, Qu and Zou, 2007). The solubility val-

Table 4: The tensile properties of the hemicellulose-based films

Sample	N-CA	CA5-C	CA15-C	CA25-C	CA35-C
Tensile strength (N/m^2)	2.49 ± 0.11	2.47 ± 0.22	2.89 ± 0.25	3.47 ± 0.12	2.98 ± 0.11
Modulus (N/m^2)	0.011 ± 0.002	0.013 ± 0.001	0.013 ± 0.001	0.016 ± 0.001	0.013 ± 0.002
Elongation (%)	23.38 ± 1.20	22.12 ± 2.10	23.31 ± 2.30	25.55 ± 1.80	22.50 ± 1.30

Table 5: The surface energy estimation of the selected film surfaces

Sample	Surface free energy (mJ/m^2)	Dispersive part (mJ/m^2)	Polar part (mJ/m^2)
N-CA	64.96	20.18	44.78
CA25-NC	42.65	35.43	7.22
CA25-C	40.92	38.78	2.14

Table 6: The solubility values of the film series

Sample	N-CA	CA5-C	CA15-C	CA25-C	CA35-C	CA-NC
Initial weight (g)	1.02	1.05	1.05	1.04	1.03	1.02
Dry weight (g)	0.36	0.39	0.44	0.51	1.03	0.49
Solubility (%)	64.20	62.85	58.09	51.14	45.63	51.96

ues of the N-CA, CA#-C and CA-NC films are found in the Table 6. The CA-NC film has lower solubility than the N-CA film sample, while there is no significant difference of solubility between the CA-NC and CA#-C film samples. This indicates the crosslinking may happen during the mixing and drying process even without film curing. The CA#-C and CA-NC films result in lower solubility, which corresponds to their lower MVTR values.

5. Conclusions

In summary, the glucomannan/NFC stand-alone films were successfully formulated from the solution through mixing, followed by film casting in the presence of CA. The addition of CA led to a significant enhancement in moisture barrier properties. The CA was shown to be effective as a crosslinker, and it decreased water solubility and water vapor permeability of innovatively formulated glucomannan/NFC composite films. The CA also functions as plasticizer to increase the tensile properties of the hemicellulose-based films, proved by higher tensile strength and elongation. Moreover, the crosslinked glucomannan film resulted in a lower solubility. Due to the biodegradability and biocompatibility, this biopolymer film based on glucomannan nano-fibrillated cellulose with improved moisture barrier properties possess potential in food packaging and offers an alternative to petroleum derived products. This work was done in laboratory scale, and therefore more experiments need to be done to scale up stand-alone films production into industrial settings.

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