

Rheology of Glucomannan-Xylan Film-forming Solutions In the Process of Manufacturing Biofilms for Food Packaging

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Keywords: blend biofilms, filmogenic, NFC, film-forming solutions, shear-thinning, frequency sweep, storage, loss, moduli, G' and G'' .

Abstract

Glucomannan-xylan blend films were prepared and their film-forming solutions 'rheological properties were tested using Anton Paar Rheometer at 25°C at shear rates 0.1- 100 1/s. The viscoelastic properties were tested under constant shear strain 5% and frequency sweep 0.1-100 rad/s. Nano fibrillated cellulose (NFC) was added to the mixture to improve the strength property of the blend films. The viscosity of the film-forming solution of all samples showed that it is increased when the concentration of the glucomannan is higher and the NFC is added to the formulas. The solutions proved to be shear-thinning, their fluidity was visible at lower frequencies; gel formation was hindered by higher values of glucomannan concentrations in the blends which means longer drying time, but NFC addition contributed to gel formation in all samples.

1. Introduction

The search for green alternatives of plastic or petroleum-based food packaging films led to creation of biofilms from natural polysaccharides, lipids and proteins. Plastic wrapping films are stretchable, hold the moisture and gases inside the food, transparent, easy to print on, light weight and cheap. However, they do not biodegrade or recycle easily in the environment (Honarvar, 2016), (Fakhoury *et al.*, 2012). Konjac glucomannan is one of the natural polysaccharides which received great interest in biofilm synthesis. Pure glucomannan has a high molecular weight, is viscous and soluble in water, but the films do not keep the moisture and gases inside the food (Cheng *et al.*, 2002), nor stretch easily (Jonas, 2006). One way to improve the properties of glucomannan films is to blend with another polymer and producing a composite film that has a reinforced strength or strong barrier

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properties, for example, starch (Yoshimura, 1998), chitosan (Wu *et al.*, 2019), Nano-fibrillated cellulose, NFC, (Ma *et al.*, 2017) and others. Pure xylan films are brittle, moisture sensitive and have poor mechanical strength. The semi crystalline structure of xylan and its brittleness is owing to its strong hydrogen bonding (Zhong *et al.*, 2013), (Marchand, 2018). Xylan is the plentiful hemicellulose in the primary cell wall of hardwood trees while glucomannan is prevalent in softwoods. The backbone of xylan is xylopyranosyl units; where glucomannan's backbone is composed of β -(1 $\rightarrow$ 4)- D-mannose and D-glucose. Figure 1 shows the chemical structure of both biopolymers (Nechita and Iana-Roman, 2020).

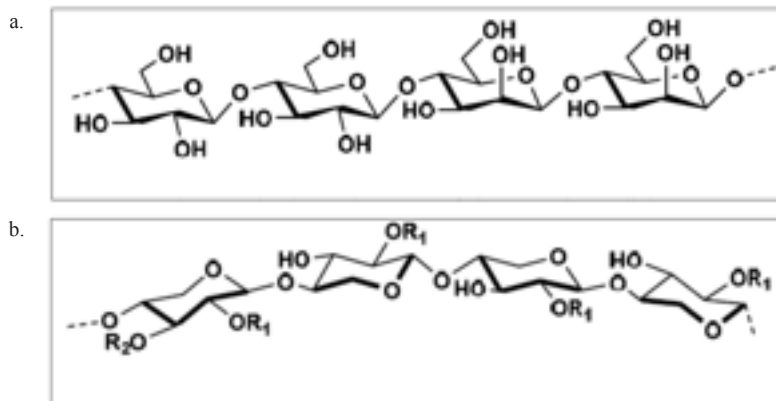


Figure 1. The chemical structure of glucomannan (a) and xylan (b) (Nechita, 2020)

Rheology parameters of filmogenic or film forming solutions, such as apparent viscosity, storage modulus for liquids, loss modulus for solids, complex modulus and $\tan \delta$, have a big influence on polymer's ease of flow during production processes and quality control (Picout, 2003), (Lopez, 2021). For oscillatory tests, storage and loss moduli, G' and G'' , are functions of the angular frequency; if $G'' > G'$, the polymer is liquid in nature and a gel if the reverse. The stress wave usually has δ a phase angle, such that, $\tan \delta$ measures viscosity to elasticity at angular frequency ω , $\tan \delta = G''/G'$. The overall behavior is identified by $\tan \delta$, if $\tan \delta > 1$ then it is more viscous than elastic (Picout, 2003). The goal of this work is to better understand rheology of mixtures of biopolymers, and their contribution to film formation.

2. Materials and Methods

2.1 Materials

Glucomannan (NOW Food Company); Xylan (Alfa Chemistry), Sorbitol (Alfa Aesar); Surfynol 104 PA (Air Products and Chemical Inc). and deionized water from Western Michigan University were used.

2.2 Film formation procedures for glucomannan-xylan reinforced with NFC films:

A casting method was followed in synthesis of the films. The experiments were divided into three groups: preparation of glucomannan-only films, glucomannan-xylan films and glucomannan-xylan reinforced with NFC films. Glucomannan was dissolved in 100 ml of DI water in a 500 ml beaker at room temperature, then heated in a water bath at 35 °C. The solution was mixed for 15 minutes by a rotary mixer at a speed of 6000 rpm. The surfactant was added and mixed for 5 minutes, followed by Xylan and mixed for 5 minutes, lastly Sorbitol was added and mixed for 5 more minutes. For rheology tests, 5-10 ml of the film-forming solutions were taken, and the rest was poured into a Petri dish then dried and then were tested. Table 1 shows 3 sets of the experiments.

Film	Film name	Glucomannan [g]	Xylan [g]	NFC [g]	Surfynol 104PA [g]	Sorbitol [g]
Pure	Gluc100	1	0	0	0.1	0.2
	Gluc90	0.9	0.1	0	0.1	0.2
	Gluc80	0.8	0.2	0	0.1	0.2
	Gluc70	0.7	0.3	0	0.1	0.2
	Gluc60	0.6	0.4	0	0.1	0.2
	Gluc50	0.5	0.5	0	0.1	0.2
	Gluc40	0.4	0.6	0	0.1	0.2
	Gluc90	0.9	0.1	0.1	0.1	0.2
	Gluc80	0.8	0.2	0.1	0.1	0.2
	Gluc70	0.7	0.3	0.1	0.1	0.2
	Gluc60	0.6	0.4	0.1	0.1	0.2
	Gluc50	0.5	0.5	0.1	0.1	0.2
	Gluc40	0.4	0.6	0.1	0.1	0.2

Table 1: Glucomannan films showing NFC contributions (In 100 ml DI)

2.4 Rheological measurements

The viscoelastic tests were performed by Anton Paar Rheometer instrument using parallel plates geometry. The plates were 1 mm apart and the sample filled this space during oscillatory testing. The rheometer applies a rotational speed necessary to deform the sample at 25°C and shear rates 0.1- 100 sec-1. The viscoelastic properties were tested under constant shear strain 5% and frequency sweep 0.1-100 Hz.

3. Results and Discussion

3.1 Viscosity

The viscous behavior of the three groups of glucomannan against shear rate is illustrated in Figure 2 for pure glucomannan and Figure 3 for glucomannan-xylan and reinforced glucomannan-xylan films.

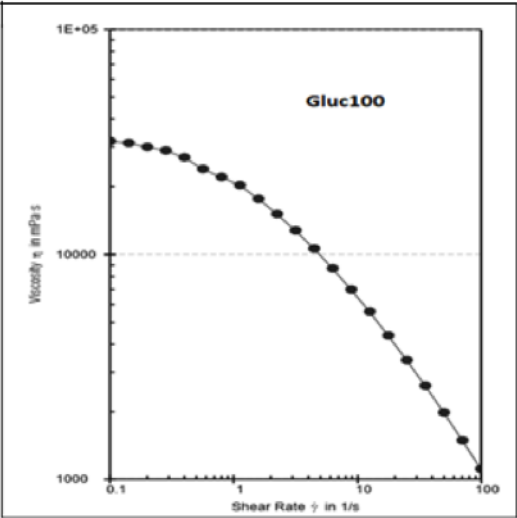


Figure 2: The viscosity vs. shear rate for pure glucomannan film-forming solution

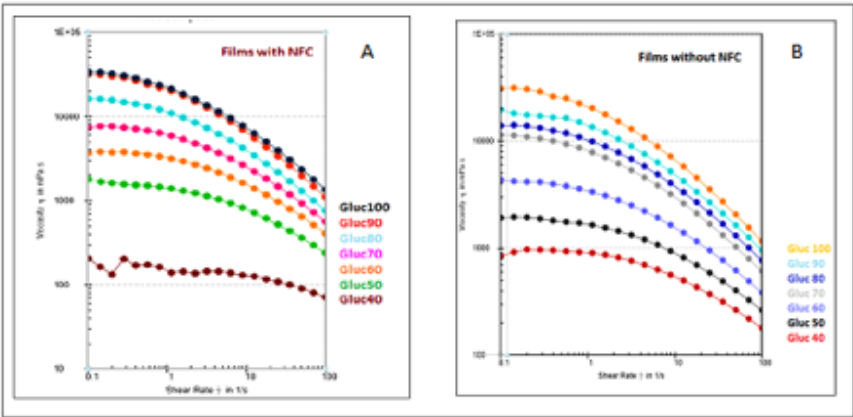


Figure 3: The viscosity vs. shear rate of glucomannan-xylan film-forming solutions.

The Figures A and B, show that the viscosity is decreasing with increasing the shear rate. This indicates that the glucomannan film-forming solutions are shear-thinning ones (Nair *et al.*, 2011); the glucomannan concentration effect on the apparent viscosity of the film-forming solutions is directly proportional, it seems that since the viscosity of glucomannan is naturally high, the fluidity of the solution increased. NFC increased the viscosity; comparing the viscosity of Gluc100, for example, at 0.1 s⁻¹ shear rate is 37348 mPa.s, but for reinforced Gluc100 it is 31996 mPa.s. The viscosity is important for the thickness and uniformity of the films and spreadability of inks on the films(Chakravartula *et al.*, 2019).

3.2 Dynamic viscoelastic measurements

Storage and loss moduli of the 13 film-forming solutions were tested as a function of angular frequency and illustrated in Figures 5, 6 and 7.

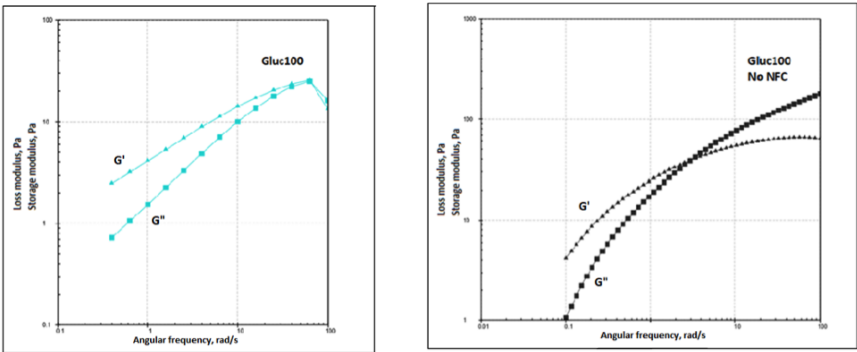


Figure 5: Frequency sweep for pure glucomannan film-forming solutions

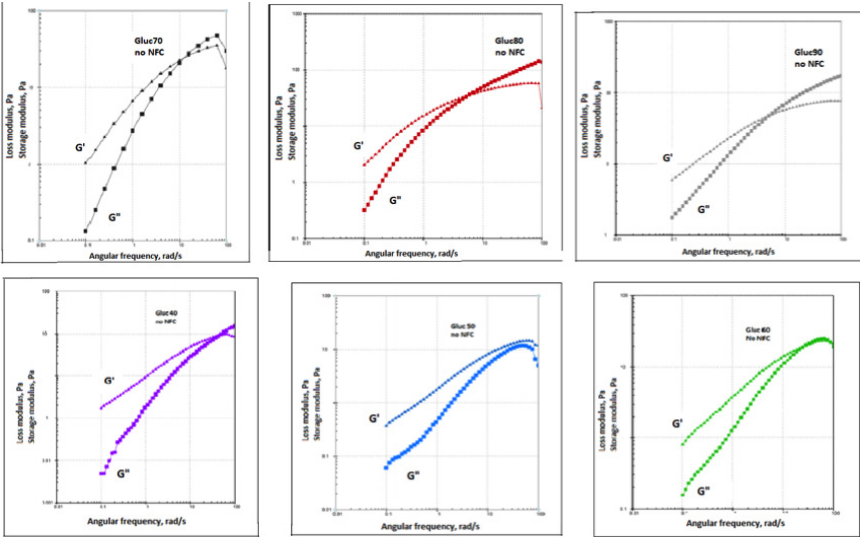


Figure 6: Frequency sweep for different glucomannan-xylan film-forming solutions

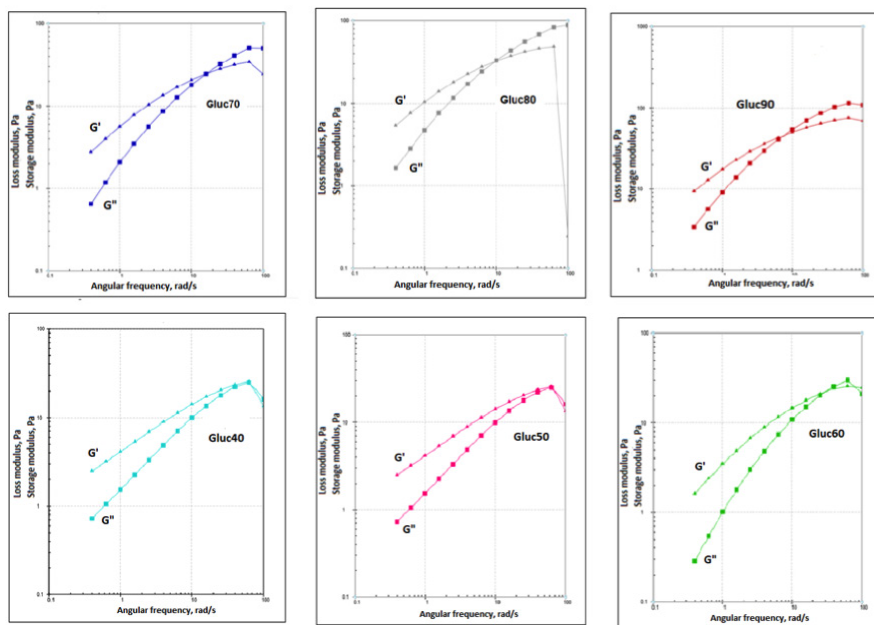


Figure 7: Frequency sweep for different glucomannan-xylan film-forming solution with NFC

All the solutions proved to be liquid in the low region of ω and turned to be a gel at higher ω where $G'' > G'$. The turn over point was shifted to higher values of frequency as the concentration of glucomannan was lowered, where in glucomannan-starch mixture it was the reverse (Yoshimura, 1998), this also corresponds to less viscous solutions. NFC addition contributed to larger G'' and gel formation in all samples, that will increase the drying time of the films and its leveling in the mold. All film forming solutions were transparent, which will affect the transparency of the formed films and the printability process.

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