Hemicellulose Based Printable Films

Ruoxi Ma, Alexandra Pekarovicova, Shreyas Pathak, and Jan Pekarovic

Keywords: bio-film, nanocellulose, gravure, printing

Abstract

Flexible PET or LDPE films have been the most common substrates used in the printing and packaging industry because of its balance properties in relation to other thermoplastic polymers. However, the global sustainability calls for more environmentally, biodegradable and biocompatible materials.

This paper presents results from the experimental programme of formulating a hemicellulose based printable films. The biodegradable glucomannan films were formed with nanofibrilated cellulose, which reinforces the mechanical strength of the film and impart the film with good heretic integrity. The film shows a good potential to be a alternative or substitute of the PET film in printing and packaging industry.

Introduction

Flexible PET films are currently the main substrate for food packaging but global sustainability focus relies more on biodegradable and biocompatible materials. Natural polymers, such as polysaccharides, are ideal starting materials for these kinds of composites due to their biodegradability, biocompatibility, low toxicity and renewability [Juho, 2013]. Depending on the particular plant material, the chemical structure of hemicelluloses vastly differs, as shown in the **Table 1**. However, films made of pure hemicelluloses lack flexibility and have poor thermo-mechanical properties, thus they need to be modified. Xylan films alone without modification are brittle, but they can be derivatized with the aim to decrease water uptake, and increase their flexibility. Enhanced mechanical properties of hardwood xylan films can be improved with addition of nanofibrilated cellulose [Vuoti, 2013; Stevanic, 2012], nanocrystalline cellulose and sorbitol as a plasticizer [Saxena, 2011], or plant protein such as gluten [Kayserilioglu, 2003]. Micro- and nano-fibrilliated cellulose was successfully used for film reinforcement in composite materials [Khalil et al., 2012]. Hemicelluloses may be obtained from plant material by

Western Michigan University

chemical or by more gentle enzymatic treatment [Oinonen, 2011], or combination of both. Obviously, the original source of xylan, or other hemicelluloses can dramatically affect mechanical properties of composite film [Egues, 2013]. Linear xylans are available from corncobs, glucuronoxylans from hardwoods, arabinoxylans from barley, oat, rye, and other cereal brans [Lu, 2000; Pekarovic 2012]. Biodegradable films were prepared from galactoglucomannans, or xylans isolated from wheat straw and blended with carrageenan and locust bean gum [Ruiz, 2013]. Galactoglucomannans were hydrophobized and used for packaging applications. Moreover, film-forming properties of xylan hemicelluloses can be enhanced by acetylation [Blazej, 1985], or by reinforcing with cellulose nanofibrils [Saito, 2013].

Type of hemicellulose	Source	Amount [%]
Arabinoglucuronoxylan	Softwood	7-10
Arabinogalactan	Larchwood	5-35
Arabinoxylans	Annual plants, bran	Variable
Galactoglucomannan	Softwoods	20
Glucomannan	Hardwood	2-5
Glucuronoxylan	Hardwoods	15-30

Table 1: *Hemicelluloses and their sources [Sjostrom, 1993; Stevanic, 2012]*

Besides packaging applications [Hansen, 2008] biodegradable hemicellulose films can be used for biomedical applications because of their non-toxicity, biodegradability, and biocompatibility [Ten, 2013]. Biomedical applications include controlled drug release, or improved medical imaging [Arola, 2013]. Nanocellulose films made from micro fibrillated cellulose, cellulose nanofibers or nanocellulose crystals are being developed for many new applications including diagnostics, transparent conductive films for electronics [Gao, 2013; Nogi, 2013; Zhu, 2014], smart clothing [Gao, 2013], optically transparent electronic displays [Eichhorn, 2010] and membrane applications which comprise fuel cells [Liu, 2003]. The aim of this work was to prepare hemicellulose films from glucomannan, and examine possible reinforcement with nano-fibrillated cellulose (NFC) and use them as a printing substrate.

EXPERIMENTAL

Film Preparation

Glucomannan (Fig.1. NOW Foods, Inc) solution (0.5%-1% w/w) was prepared in a 250ml beaker during continuous stirring at 25ºC. Aqueous Nano-fibrillated Cellulose (NFC, 0.1%-0.2%) solution was added. Then 1% lignin (Powder form, 95% purity, purchased from Sigma Aldrich), 0.1% Surfynol® CT111 (surfactant), 0.5%-1% sorbitol (plasticizer) and 1% xylan (Powder form, purchased form Sigma Aldrich) were directly poured into the glucomannan solution during continuous mixing. The formulations of the film (table.1) were designed according to different

ratio of NFC, glucomannan and lignin, with purpose to decide the strength and optical affects they could impart to the films. The mixture was further homogenized using a magnetic stirrer (Corning Model PC-420) at 45ºC and mixing speed of 600 RPM. Films were then cast by applying 100ml of the film-forming glucomannan solution onto a dish covered by aluminum foil (100mm×100mm) and made even by using Meyer Rod # 6 in order to control the film caliper. It is allowed to dry in the oven for 8 hour, at 60ºC and 35% relative humidity (RH). Dried water-soluble films were peeled off manually and stored in polyethylene bags prior to characterization.

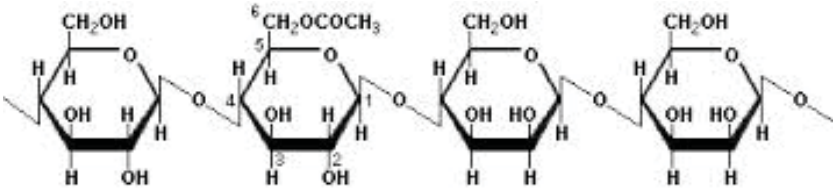

Figure 1: *Glucomannan composed of β-D-glucopyranose and β-D-mannopyranose units linked by 1→4 bonds (second glucopyranose unit is esterified)*

Analytical

Selected surface and strength properties of the film were measured in the paper-testing lab and were compared with the PET (from DePont. Corp.) film and uncoated kraft paper (97GSM). For each measurement, five replicates in each sample were tested. Tensile strength of the films was measured according to TAPPI Standard T494 by using INSTRON 430I with a 500 N load cell. Porosity of the films was measured using Parker Print Surf instrument according to TAPPI Standard T460. Film caliper was measured with Technidyne caliper tester.

Ingredient	Film 1	Film 2	Film 3	Film 4
Water/g	100	100	100	100
Xylan/g	1	1	0	0
Sorbitol/g	0.5	0.5	0	1
Glucomannan/g	0.5	1	0.5	1
Lignin/g	1	0	0.5	1
Nano-cellulose/g	0	0.1	0	0.2
Surfactant/g	0.1	0.1	0.1	0.1

Table 1. *Formulations of bio-films*

Tensile Strength

The tensile strength and elongation at break for the films were assessed at 25ºC and 50% RH using INSTRON 430I with a 500 N load cell. The specimens were aged under these conditions for at least 2 days prior to testing. The initial gauge length was 10mm, and the crosshead speed was 1mm/min. The width of the specimen was 10mm, and the length was no less than 40mm. The results are expressed as the means of five specimens.

Tensile strengths of the films are presented in Fig. 2. Compared to xylan and lignin, nanocellulose has a clearly better reinforcement effect on the films.

Tensile tests measure the force required to break the sample specimen and the extent to which the specimen stretches or elongates to that breaking point. The resulting tensile test data can help specify optimal film formulations.

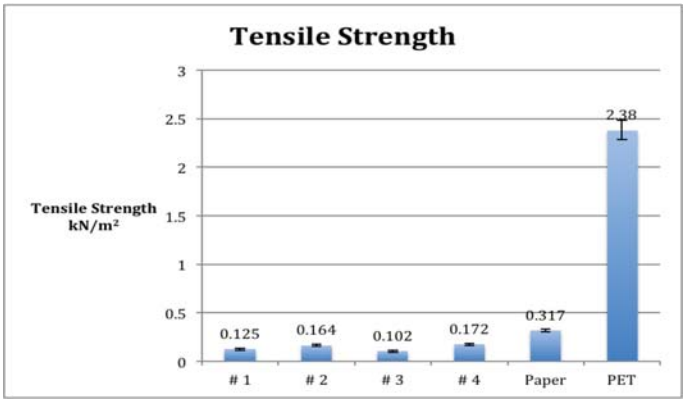

Fig.2 *The tensile strength of the hemicellulose based films, craft paper and PET film*

The tensile strength of the hemicellulose films are not as good as PET film, but are relatively comparable with kraft paper. Among the 4 formulations of the film, #4 has the highest tensile strength, probably due to the addition of Nano-cellulose.

#1 made of lignin and sorbitol lacks of flexibility. #3 made of glucomannan and lignin without plasticizer is brittle.

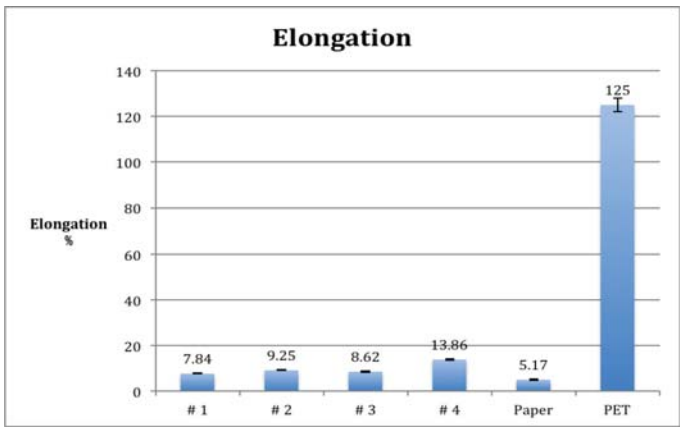

Fig 3. *The elongation of the hemicellulose based films, kraft paper and PET film*

Bursting Strength

Bursting strength tests are generally used for paper and board where there are definite warp and weft directions due to the fiber bonding. Hoverer, the biofilm made of hemicellulose and lignin does not have such distinct directions where the strength is at a maximum. In other words, the film is homogeneous, which means during bursting test, the film undergo the same extension in all directions. This could be proved by the uniform rupture of the film samples.

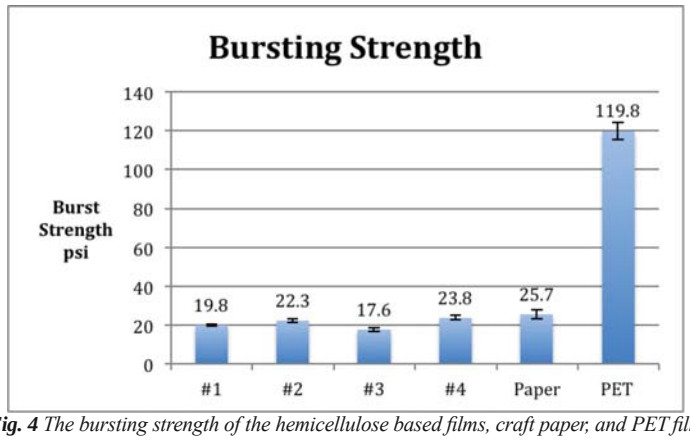

Fig. 4 *The bursting strength of the hemicellulose based films, craft paper, and PET film*

The bursting strength of the biofilms are close to the kraft paper, which could be an evidence for the statement that those films could function as packaging materials. Among all the formulations, #4 has the highest bursting strength, which is coherent with its highest tensile strength. However, there is still long way to go for all the biofilms to be comparable with the PET film.

Porosity

Porosity affects how much and how quickly inks are absorbed in to a paper. However, plastic films are considered a non-porous substrate due to their low porosity in terms of both air and liquid. This non-porous property enables the films function as packaging substrate for special products such as food, pharmacy and chemicals.

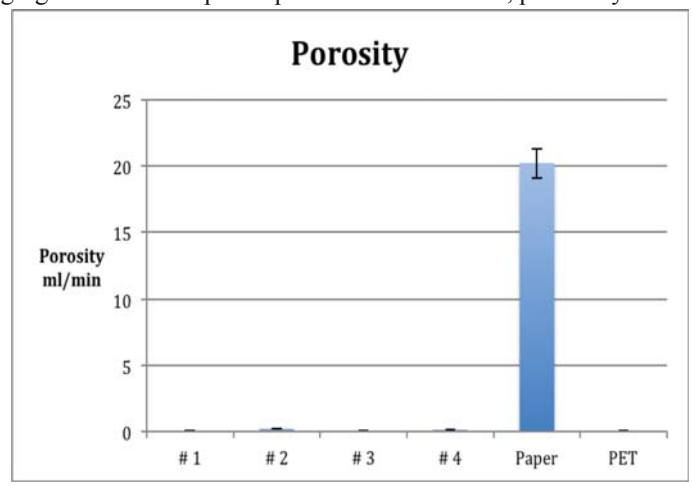

Fig 5 *The porosity of hemicellulose based films, kraft paper and PET film*

All the films are non-porous, with readings of "out of range" on the Parker Print-surf tester. The non-porous property imparts the film with a potential to serve as food packaging with good heretic integrity.

Roughness

For the contacting-type printing processes such as offset and gravure printing, the ink film will transfer to the substrate surface upon physical contact. When the voids in the substrate surface are deep enough to prevent such contact, in transfer will not be uniform and cause poor print quality.

Compared to #1, the surface of #3 and #4 are less even and large pores can be observed on the surface. This is due to the much bubbles that are introduced to the suspension during mixing and drying process.

The wire side is smoother than the top side due to its contact with the supporting foil backing. While the top side has many tiny bubbles that are introduced to the suspension during mixing and spreading process, which leads to a rougher surface on the top side and make it difficult to print on.

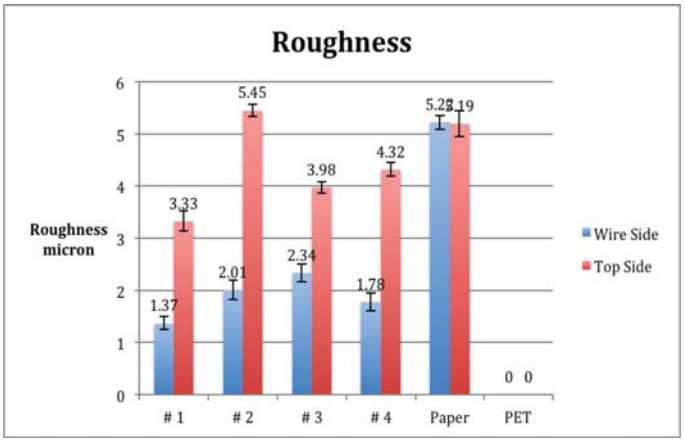

Fig 6. *The roughness of hemicellulose based films, kraft paper and PET film*

Caliper

The caliper of the film is controlled during the spreading by using the Meyer rod #6. The thickness of the films increased with the amount of added NFC due to the fibrous structure of cellulose. The difference between the thickness of the films containing the NFC was not significant, e.g. the #4

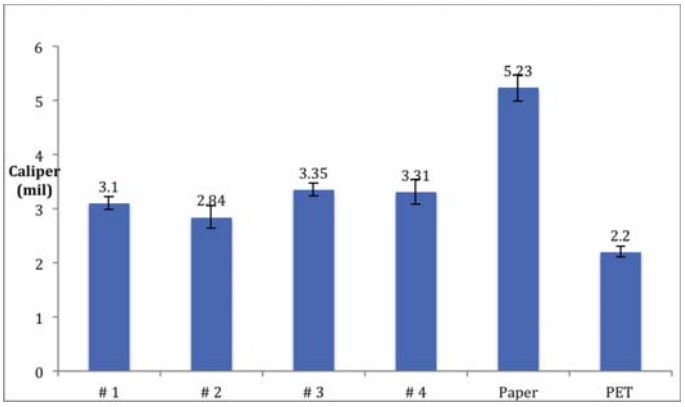

Fig 7. *The caliper of hemicellulose based films, kraft paper and PET film*

Print Evaluation

Prepared films were used as substrates for printing. The gravure printing was demonstrated with a laboratory gravure proofing press K-Printing Proofer (Testing Machines Inc.). The graphic ink (TFC-PR-020, golden) from InkTec Corp was used without further modification. During printing, the impression roll, the film, and the doctor blade move forward at a speed of 40m/min. The image on the plate is a solid patch with a fine resolution of 200 lines per inch. The patterns on the plate were transferred to the film and the doctor blade wipes off the excess ink. The

printed films were placed in the laboratory at controlled conditions (23ºC, 50% RH; Relative Humidity) for 24 hours conditioning prior to optical density measurement with X-Rite 530 Spectro Densiometer.

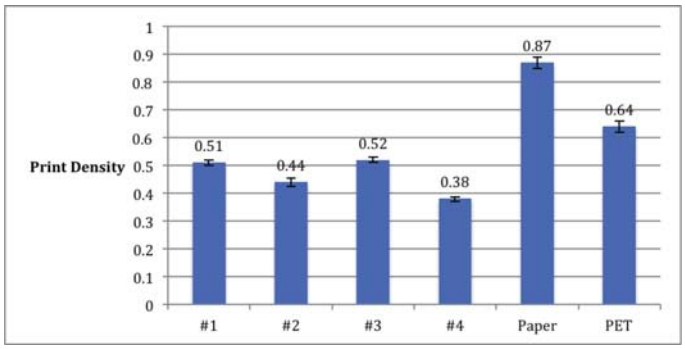

Fig 8. *The print density of hemicellulose based films, kraft paper and PET film*

Both #4 and # 2 have rougher surface due to the non-uniform blended Nano-cellulose, hence lower print density.

CONCLUSIONS

Biodegradable glucomannan films were formed with and without reinforcement with nanofibrilated cellulose. Nanofibrilated cellulose increased the strength of glucomannan films. The glucomannan films were non-porous, which may be useful property with a potential use as food packaging material with good barrier properties. The preliminary printability test shows good potential of the glucomannan films with printable surface. Further study needs to be done with a focus on the topography and improvement of the micro-roughness and wettability of the film surface.

Future work

1. In order to obtain better wettability of the film, the surface energy of the film surface needs to be measured. The printed samples all have adhesion problem, attested by easily rub off when crinkled. Surface treatments such as plasma or corona are needed in order to improve the surface energy of the biofilm.
2. NFC is proved to be able to impart better strength properties for the biofilm. However, the introduction of nano-cellulose leads to non-uniform blend and rougher surfaces, which results in a poor print quality. Therefore, more focus needs to be put on a better way to blend nano-cellulose.
3. The humidity and temperature changes of the surroundings affect the opacity of the biofilm, making it less transparent.

4. The FTIR should be done to observe the molecular interactions of components due to the incorporation. Also, the SEM should be done to analyze the surface morphology, and the XRD should be done to analyze the crystallinity due to the addition of NFC.
5. Barrier properties, grease barrier property and water vapor permeability, e.g., should be measured to determine whether the films are capable as packaging materials.

References

1 Juho A.S., Aleksi K. "Biocomposite cellulose-alginate films: Promising packaging materials", Food Chemistry, 2013

2 Abdul Khalil, H.P.S., Bhat, A.H., & Ireana Yusra, A.F. (2012). Green composites from sustainable cellulose nanofibrils: A review. Carbohydrate Polymers, 87,963-979.

3 Arola S., Malho J.M., Laaksonen P., Lille M., Linder M.B., "The role of hemicellulose in nanofibrilated cellulose networks", Soft Matter, 9, 4, 2013,1319-1326.

4 Blazej A., Kosik M., Fytomasa ako chemicka surovina, Veda, Slovak Academy of Science, Bratislava, 1985, 402 pp.

5 Boulton A.J.M.,"The diabetic foot", Medicine, 38, 12, 2010, pp.644-648.

6 Egues I., Eceiza A., Labidi J., "Effect of different hemicelluloses characteristics on film", Industrial Crops and Products, 47(2013), 331-338.

7 Hansen NM, Plackett D., "Sustainable films and coatings from hemicelluloses: a review". Biomacromolecules, 9 (6), 2008, 1493-505.

8 Illing, M, Krumm D., and Hubler A.C., "Development of a printed sensor for plantar foot pressure measurement", 40th International Research Conference of IARGIAI, Chemnitz, DE, September 8-11, 2013.

9 Kayserilioglu, B.S., Bakir U., Yilmaz L., Akkas N., "Bioresour". Technol. 87, (3) 2003, 239-246.

10 Lu Z.X., Walker K., Muir J., Mascara T, O'Dea K., "Arabinoxylan fiber, a byproduct of wheat flour processing, reduces postprandial glucose response in normoglycemic subjects", Am.J.Clin.Nutr., 71, 5, 2000, 1123-1128.

11 Oinonen P., Areskogh D., Henriksson G., "The processing and upgrading of hemicellulose mixtures", 16th International Symposium on Wood, Fiber, and Pulping Chemistry, ISWFPC, v.2, p. 1028-1031, 2011.

12 Pekarovic J., Busso M., Raycraft L., and Pekarovicova A., "Bioenergy and Value-added Products from Switchgrass", Power Engineering 2012, Proceedings 3rd International Scientific Conference OZE2012: Renewable Energy Resources, High Tatras, Slovakia, EU, May 2012.

13 Ruiz H., Cerqueira H.D., Silva H.D., Rosa M., Rodriguez-Jasso M., "Biorefinery valorization of autohydrolysis wheat straw hemicellulose to be applied in a polymer blend film", Carbohydrate poymers, 92(2013), 2154-2162.

14 Saito T., Kuramae R., Wohlert J., Berglund L., Isogai A., "An ultrastrong nanofibrillar biomaterial: The strength of single cellulose nanofibrils revealed via sonication-induced fragmentation", Biomacromolecules, 14, 1, 2013, 248-253.
15 K. Gao, Z. Shao, X. Wu, X. Wang, J. Li, Y. Zhang, W. Wang, F. Wang, "Cellulose nanofibers/reduced grapheme oxide flexible transparent conductive paper", Carbhydr. Polym. 97, 1, 2013, 243-251
16 Saxena A., Elder T., Ragauskas A.J., "Moisture barrier properties of xylan composite film", Carbohydrate Polymers, 84, 4, 2011, 1371-1377.
17 Sjostrom E., "Wood Chemistry, Academic Press", San Diego, 2nd Ed., 1993, 293 pp.
18 Ten, E., Vermerris, W., "Functionalized polymers from lignocellulosic biomass: State of the art", Polymers, Vol. 5, 2, 2013, 600-642.
19 Vuoti S., Talija R., Johansson L.S., Heikkinen H., Tammelin T., "Solvent impact on esterification and film formation ability of nanofibrillated cellulose", Cellulose, 20(5), 2013, 2379-2392.
20 Stevanic J.S., Bergstrom E.M., Gatenholm P., Berglund L., Salmen L., "Arabinoxylan/nanofibrilated cellulose", J. Materials Science, 47, 18, 2012, 6724-6732.
21 Zhu H., Xiao Z., Liu D., Weadock N.J., Fang Z., Huang J. Hu L., "Biodegradable transparent substrates for flexible organic light emitting diodes", Energy and Environmental Science, 6, 2013, 2105-2111.

Acknowledgements

The authors would like to acknowledge the following companies for their help in the project, InkTec Corp., NOW Foods Inc., Sigma Aldrich Inc.

The authors would like to acknowledge the following PIA/GATF staff: John Bodnar, M. Bohan and J. workman. Additional thanks to Dr. Alexandra Pekarovicova, Dr. Dan. Fleming, Dr. Margret Joyce, and Matt Stoops.