Hemicellulose-base Barrier Coatings for Packaging

Ruoxi Ma, Alexandra Pekarovicova, and Paul D. Fleming, III

Abstract

The use of new biomaterials for medical and packaging application has increased rapidly over the past quarter of a century. Biofilms and biopolymers have been studied with the target uses of packaging and coatings for foodstuffs as well as for biomedical applications. Therefore, there is a need for a better understanding of the interactions between biomaterials and functional inks, which is required to optimize printability, mechanical, and functional properties for the creation of more robust and efficient printed devices and smart packaging. This research aims to advance the knowledge of the material properties of hemicellulose-based biofilms, their interactions with conductive inks, and gravure printability.

Introduction

Flexible PET (Polyethylene Terephthalate) or LDPE (Low-density polyethylene) films are currently the main substrates for food and pharmaceutical packaging. Plastics have been the dominant packaging materials because of their much better barrier properties compared to traditional paper packaging. However, the common plastic films can't be easily degraded, which causes serious pollution and sustainability issues. For example, the incineration of some plastics such as PVC increases dioxin and furan content of air emissions. Therefore, the 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, non-toxicity and renewability[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 to reach decreased water uptake, and increased flexibility. Enhanced mechanical properties

Western Michigan University

of hardwood xylan films can be improved with addition of nanofibrilated cellulose, nanocrystalline cellulose[2,3], and sorbitol as a plasticizer[4], or plant protein such as gluten[5]. Micro- and nano-fibrillated cellulose were successfully used for film reinforcement in composite materials[6]. Hemicelluloses may be obtained from plant material by chemical or by more gentle enzymatic treatment[7], or a combination of both. Obviously, the original source of xylan, or other hemicelluloses can dramatically affect mechanical properties of composite films[8]. Linear xylans are available from corncobs, glucuronoxylans from hardwoods, arabinoxylans from barley, oat, rye, and other cereal brans[9, 10]. Depending on the particular plant material, the chemical composition of hemicelluloses vastly differs, as shown in Table 1[11]. Biodegradable films were prepared from galactoglucomannans and xylans isolated from wheat straw and blended with carrageenan and locust bean gum[12]. Film-forming properties of xylan hemicelluloses can be enhanced by acetylation[13], or by reinforcing with cellulose nanofibrils. Galactoglucomannans were hydrophobized and used for packaging applications, too[14].

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[11]

Lignocellulosic biomass from trees, annual grasses, cereals, and other plants have become the main focus of the developing bio-refining industry[15]. As the main components of plants, cellulose, lignin and hemicelluloses have received a lot of attention in terms of material applications. Hemicellulose is defined as the alkali-soluble polysaccharide remaining after the elimination of pectic substances from plant cell walls[16]. Hemicelluloses (see Fig. 1[17]), depending on their plant material source and sugar composition can be divided into five main groups, which can be defined according to their primary structure as follows: arabinoglucuronoxylans, galactoglucomannans, arabinogalactans, glucomannans, and glucuronoxylans[18].
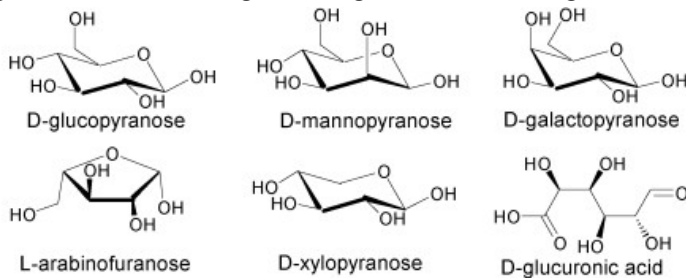

Figure 1. The main constituents of hemicelluloses[17]

The research on hemicelluloses and their packaging and medical applications has been extensive. The konjac glucomannan, which is derived from the plant of genus Amorphophallus, has been used commercially for many years because of its gel- and film-forming properties and the biocompatibility and biodegradability[17]. There are several ways to obtain hemicelluloses from plant resources, including extraction with alkali, dimethyl sulfoxide or methanol/water, as well as steam or microwave treatment[19]. Depending on different pretreatment procedures, the composition of the hemicelluloses could be varying. Sun et al[20] reported the dependency of composition on the isolation procedure, as the pretreatment of wheat straw samples with various organic solvents before extraction resulted in very different hemicellulosic products[20].

Hemicelluloses are hydrophilic in nature, hence hemicellulose-based films are generally hygroscopic, which means they will absorb moisture and degrade with high humidity. This is because they have abundant free hydroxyl groups distributed along the main and side chains and they are ideal candidates for chemical functionalization. Many researchers have been focusing on modifying the properties such as crystallinity, solubility and hydrophilicity of hemicelluloses through techniques such as esterification, etherification or grafting methods. Through the chemical modifications, the hemicellulose-based films could have lower oxygen permeability, lower water vapor permeability and higher mechanical strength and flexibility. Grondahl et al.[21] reported the films made of glucuronoxylan from aspen wood showing improved oxygen barrier properties and the addition of plasticizer resulted in increasing tensile strength.

Hemicelluloses, besides cellulose and lignin are main components of the plant cell wall, and are bound to lignin.

The composition of hemicelluloses is different depending on various raw materials. For example, a study from Lai et.al. reported that the main components vary a lot in four kinds of rice straw, containing arabinose (5%-23%), xylose (17%-40%), and glucose (36%-55%)[22].

The films that are made on the basis of hemicellulose with addition of plasticizers were reported as early as 1949 by Smart and Whistler[23]. The reason to use plasticizers in hemicellulose-based films is to ensure flexibility and the most commonly used plasticizers are sorbitol, glycerol and xylitol (Fig. 2[18]). Besides packaging applications[24], biodegradable hemicellulose films can be used for biomedical applications because of their non-toxicity, biodegradability, and biocompatibility[25]. Biomedical applications include controlled drug release, or improved medical imaging[26].
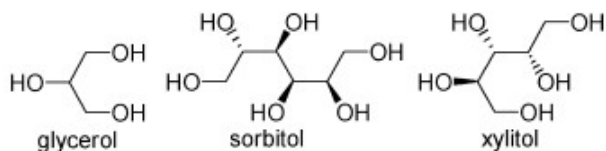
Figure 2. Commonly used plasticizers for the hemicellulose-based films[18]

In this work, the biodegradable glucomannan films were formulated with and without nanofibrillated cellulose, with the aim to reinforce the mechanical strength of the film and impart the film with improved barrier properties. Another aim was to characterize selected physical properties of formulated films, and assess possible printability.

Experimental

Biofilm Preparation

Glucomannan from NOW Foods, Inc. (Fig. 3[23]) solution (0.5%-1% w/w) was prepared in a 250 ml beaker during continuous stirring at 25°C. Nano-fibrillated cellulose (NFC contains: Water 95%-99%, Cellulose pulp 1-5%; manufactured by the Department of Chemical and Biological Engineering, University of Maine) in suspension form was added to the glucomannan separately. Then 1% lignin in powder form, 95% purity, (Sigma Aldrich), and 0.1% Surfynol® CT111 (Air Products and Chemical, Inc.) were added. The formulations of the films (Table 7) were designed with different dosage of NFC, glucomannan and plasticizers, with the purpose to decide how they affect strength properties. The mixture was further homogenized using a magnetic stirrer (Corning Model PC-420) at 45 °C at mixing speed of 450 RPM. The solutions were casted to a mold with the dimensions of 100 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% RH) for 8 hours at 60 °C and 35% RH). Dried hemicellulose-based films were peeled off manually and stored in polyethylene bags prior to characterization.
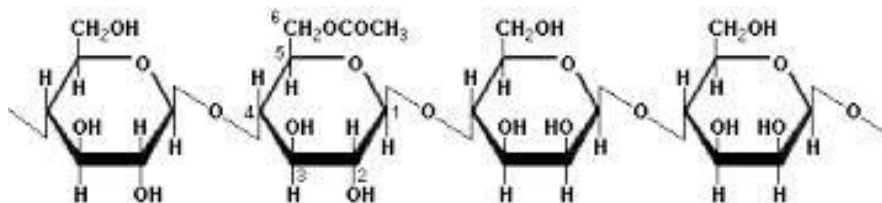

Figure 3. Glucomannan composed of β-D-glucopyranose and β-D-mannopyranose units linked by 1→4 β-D- glycosidic bonds (second glucopyranose unit is esterified)[23]

Films Characterization

Selected mechanical properties, and surface energy of the films were tested. The LDPE film (from Dupont LLC.), along with uncoated paper with a basis weight of 118 g/m2 (from Western Michigan University Pilot Plant) were also analyzed as a control samples. For each test five replicates were done per each film.

Surface Free Energy

When it comes to printing, it is essential to understand the behavior of ink on the chosen substrate. Surface energy/tension is responsible for the surface behavior (atmosphere-solid contact) and the wetting phenomena (liquid-solid contact) (Figure 4[28]).
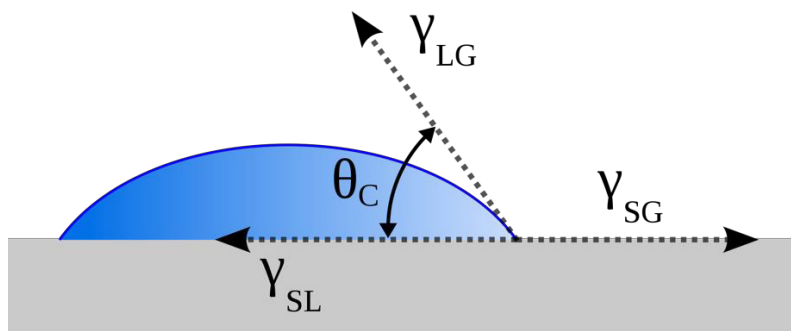

Figure 4. *Contact angle of liquid on a substrate* [28]

The surface energy of the films was estimated by the FTA200 (First Ten Angstrom Dynamic Contact Angle) measurement apparatus. Pendant drop analysis was used for the surface tension measurements of liquid phases. Sessile drop analysis was used for the contact angle measurements. The actions of the droplet appear live on the computer screen and the salient images are captured to the computer's memory for later image analysis. The camera frame rate is 60.9 frames per second. The surface energy is calculated by the program by using Owens- Wendt method using 1 angle of each of 2 liquids on 1 solid. For each kind of liquid, the software captured 300 images of the fluid dropping, hitting the substrate and reaching and equilibrium on the substrate. The measurement was conducted in the condition of 23°C, and 25% RH.

The FTA200 is a flexible video system for measuring contact angle, surface and interfacial tensions, wettability, and absorption. For the evaluation of the surface energy, the contact angle of three liquids, deionized ultra-filtered water (DI), hexadecane, and methylene iodide (MI), was measured against the biofilm surfaces, and the critical surface free energy was calculated using Owens-Wendt[27] method. Although these methods only estimate the solid surface energy, such values are useful for comparing the wettability of solid surfaces and predicting print adhesion.

Contact angle measurement is the ideal method for the characterization of surface energy and surface wettability, and is a widely used technique for studying the loss and recovery of hydrophobicity of the films. Therefore, this method can be used to accurately measure the hydrophilic characteristic of a surface of a hemicellulose-based film. This method enables the surface energetics of a solid surface to be determined by its free surface energy. Often, it is defined on the basis of the static contact angle between the surface and a liquid droplet. The fundamental equation for measurement of solid surface tension by contact angle measurements is described by the Young's equation[28]. Contact angles of deionized ultra-filtered water (DI), hexadecane, and methylene iodide (MI), were measured against the biofilm surfaces, and the critical surface energy was calculated using Owens-Wendt[27] method measurements on a solid substrate.

Tensile Strength

The tensile strength and elongation at break for the films were assessed according to TAPPI 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.

Gravure Printing

Gravure printing was demonstrated with a laboratory gravure proofing press K-Printing Proofer (Testing Machines Inc.) 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 black gravure ink was acquired from Western Michigan University pilot plant. The ink is toluene based with a viscosity of 15 centipoise. The printed films were placed in the laboratory at controlled conditions (23°C, 50% RH) for 24 hours conditioning prior to optical density measurement with X-Rite 530 SpectroDensiometer. The density measurement conditions are in absolute mode with statue T, with a white backing.

Results and Discussion

The preliminary biofilms were formulated based on literature review; few components are chosen to try out if they could form strong films (Table 2). Films were formulated with various amounts of xylan, glucomannan, nanocellulose, lignin, sorbitol, and surfactant. It was observed that the xylan and lignin make the films more brittle, and on the other hand, nanocellulose showed strengthening effect of the films. To find out how if individual components are statistically important and how they affected strength of the films, ANOVA analysis was performed. Then the formulations are optimized by generating a full factorial DoE formulation by Minitab 17.

Ingredient [g]	Film 1	Film 2	Film 3	Film 4
Water	100	100	100	100
Xylan	1	1	0	0
Sorbitol	0.5	0.5	0	1
Glucomannan	0.5	1	0.5	1
Lignin	1	0	0.5	1
Nanocellulose	0	0.1	0	0.2
Surfactant	0.1	0.1	0.1	0.1

Table 2. Formulation of biofilms

Optimization of Biofilm Formulation

The main factors in the film formulations are the portion of nannocellulose, sorbitol and glucomannan. In order to analyze the results of the film formulation, a one-way ANOVA of Tensile versus the main factors, was performed using the Minitab® 17 software package (Minitab Inc.). The full ANOVA was not performed because of no degrees of freedom for factors. ANOVAs were performed on the data pertaining to nanocellulose content versus tensile strength, sorbitol as a plasticizer amount, and level of glucomannan added (Table 3). The significance level for each ANOVA is set as 0.05.

Factor	Level (mass fraction %)		
Nanocellulose	0	0.1	0.2
Sorbitol	0	0.5	1
Glucomannan	0.5	1	N/A

Table 3. The factors and levels in ANOVA analysis for the film formulations

The results are shown in the Table 4. Although the preliminary formulations of the biofilm represent unbalanced design, it is instructive to investigate which factor is contributive to the tensile strength and thus optimize the film formulation design in the future work. For nanocellulose and sorbitol, there are 3 levels of the factor and 5 replicates for each level. For glucomannan, there are 2 levels and 5 replicates for each level (Table 3). The program computed the F ratio F-Value= 176.88 and we can compare this result to an appropriate upper-tail percentage point of the $F_{2,12}$ distribution. Suppose the α=0.05, $F_{0.05,2,12}$=3.89[29]. Because F_0=176.88>3.89, we reject H_0 and conclude that the treatment means differ, that is, the amount of nano-cellose significantly affects the mean tensile strength of the films. For the tensile strength versus sorbitol, the F_0=216.62>$F_{0.05,2,12}$=3.89[29], which means the amount of sorbitol also significantly affects the mean tensile strength of the films (Table 5). For tensile strength versus glucomannan, the F_0=165.5>$F_{0.05,1,8}$=5.32[29], which means the amount of glucomannan significantly affects the mean tensile strength of the films, too (Table 6).

Source	Degree of Freedom	Adj. SS	Adj. MS	F-value	P-value
Nanocellulose	2	0.00644	0.00322	176.88	0.000
Error	12	0.00022	0.00002		
Total	14	0.00666			

Table 4. *ANOVA for tensile strength versus nanocellulose.*

Source	Degree of Freedom	Adj. SS	Adj. MS	F-value	P-value
Sorbitol	2	0.01264	0.00632	216.62	0.000
Error	12	0.00035	0.00003		
Total	14	0.01299			

Table 5. *The ANOVA table for tensile strength versus sorbitol.*

Source	Degree of Freedom	Adj. SS	Adj. MS	F-value	P-value
Glucomannan	2	0.00388	0.00388	165.50	0.000
Error	12	0.00019	0.00002		
Total	14	0.00407			

Table 6. *The ANOVA table for tensile strength versus glucomannan.*

Based on the ANOVA results, the significant factors are chosen to generate a 4-factor, 2-level full factorial biofilm formulations by Minitab 17. The 16 formulations (see Table 7) are formed in accordance to the run order given by Minitab 17, followed by the surface and mechanical properties characterizations.

StdOrder	RunOrder	Nano-cellulose [g]	Glucomannan [g]	Type of plasticizer	Level of plasticizer [g]
4	1	0.4	1.5	Sorbitol	1
12	2	0.4	1.5	Xylitol	2
3	3	0.2	1.5	Sorbitol	1
8	4	0.4	1.5	Sorbitol	1
14	5	0.4	1	Xylitol	2
1	6	0.2	1	Sorbitol	1
11	7	0.2	1.5	Xylitol	2
15	8	0.2	1.5	Xylitol	2
16	9	0.4	1.5	Xylitol	2
6	10	0.4	1	Sorbitol	1
5	11	0.2	1	Sorbitol	1
7	12	0.2	1.5	Sorbitol	1
2	13	0.4	1	Sorbitol	1
9	14	0.2	1	Xylitol	2
13	15	0.2	1	Xylitol	2
10	16	0.4	1	Xylitol	2

Table 7. *The Full factorial DoE of biofilm formulations.*

Tensile strength

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 tensile strength data can help specify optimal film formulations. Tensile strength of the films is shown in Figure 5. Compared to xylan and lignin, nanocellulose has a clearly better strengthening effect on the films. The tensile strength of the hemicellulose films is higher than LDPE film and paper. Among the 16 hemicellulose film formulations, the film #16 had the highest tensile strength, probably due to highest addition of nano-fibrillated cellulose.
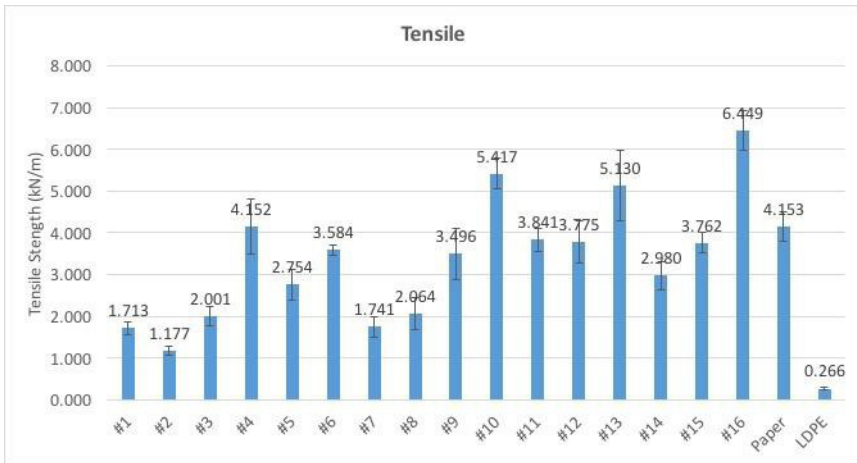

Figure 5. The tensile strength of the hemicellulose based films, paper and LDPE

Elongation

Elongation is the ratio between changed length and initial length after breakage of the test material. It expresses the capability of a material to resist the changes of shape without crack formation. For elastomers and packaging films (e.g. LDPE), the ultimate elongation values could be several hundred percent. For rigid plastic, such as fiber reinforced PET films, the elongation values are under 5%. The combination of high tensile strength and high elongation leads to materials of high toughness. Elongation of hemicellulose biofilms was bigger than that of paper (Fig 6).
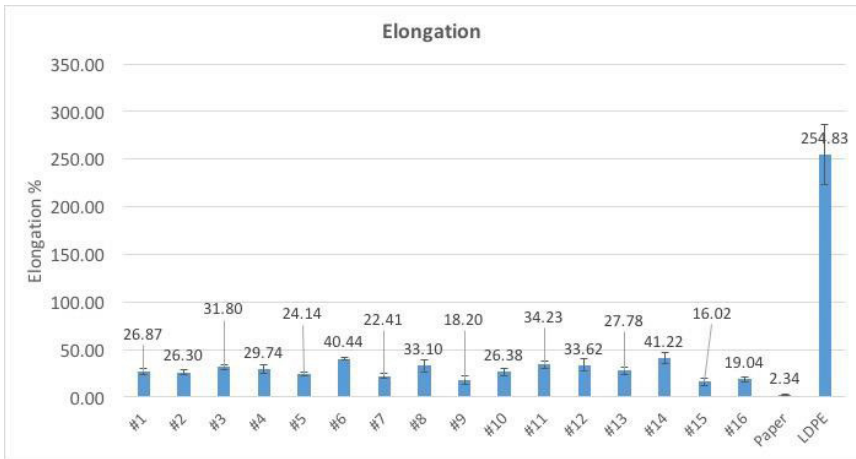
Figure 6. The elongation of the hemicellulose-based films, paper and PET

Air permeability

Permeability describes how easily a fluid is able to move through the porous material. It is calculated using a formula widely known as Darcy's Law.

Darcy's Law

$$Q = K\Delta P * A / \eta \Delta L \qquad (1)$$

Where
Q=flow rate (m3/s)
K=permeability coefficient, (m2)
ΔP = pressure drop or difference, (Pa)
L = flow length or thickness of test sample, (m)
A = area of cross-sectional area to flow, (m2)
η =fluid viscosity, (Pa-s)

The standard parameters for the PPS tester used were as follows[30]:
Fluid (air) viscosity (η): 1.80075 E-05 Pa-s (Ns/m2) at 23C°
Standard pressure drop (ΔP): 6.17 KPa
Area of cross-section (A): 10 cm^2
Therefore, the permeability coefficient,

$$K (\mu m2) = 0.048838 * Q (ml/min) * L (m) \quad [31] \quad (2)$$

An example calculation of the permeability coefficient for a hemicellulose-based film using equation (2) follows:

Parker Print Surf flow rate (Q) at 1000 KPa: 0.59 ml/min
Thickness of the sample film (L): 223.6 µm
Permeability coefficient K= 6.44 x10-06 µm2

Air permeability is a good measure of how much and how quickly inks are absorbed in to a substrate. However, plastic films are considered non-porous substrates due to their low porosity in terms of both air and liquid penetration.

This non-porous property enables the films function as packaging substrate for special products such as foods, pharmaceutical products and chemicals. All the films are non-porous (Fig. 7), which means that films have potential to serve as food packaging with good barrier property.
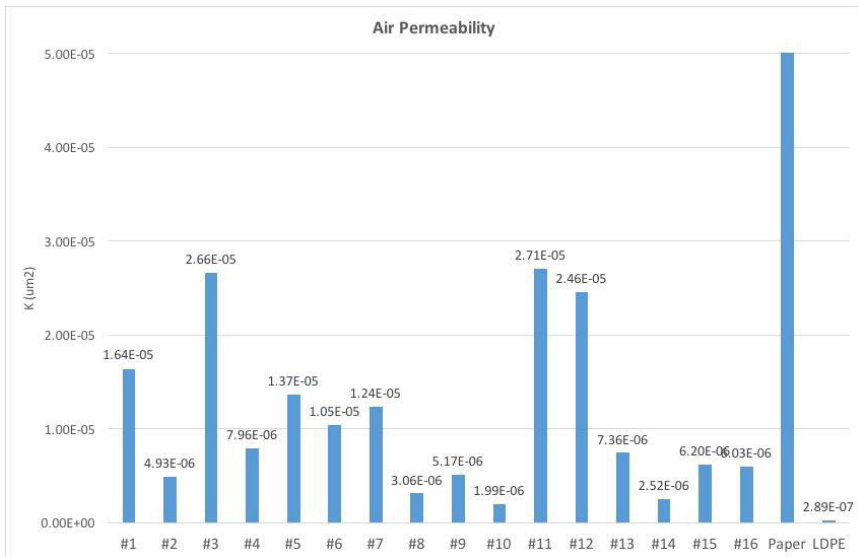

Figure 7. *The air permeability of hemicellulose based films, paper and LDPE*

Surface Free Energy

Because the mechanical test (tensile strength) showed that #16 film formulation produced the strongest film, therefore the #16 film was selected to perform the surface energy test, along with the LDPE and paper as compared group.

Table 8 shows the surface tension of the liquid phases and the contact angles on the biofilm substrate measured with the liquid phases. The surface tension values in Table 8 were entered to the FTA32 software, in which the Owens-Wendt method requires contact angle of each of two known liquids on the substrate to estimate the surface energy. The surface energy results of each liquid pair- MI/DI and

DI/HE, were calculated by the software and presented in Table 9. The Owens-Wendt equation resulted in slightly different surface energy values for the same substrate when the probe liquids were paired differently.

Liquids	γ_{LV}	$\gamma_{LV\text{-}Disp.}$	γ_{LV_Polar}	Contact Angle on Biofilm	Density (g/cc)
DI water (DI)	71.40±0.8	21.80	49.60	23.98±2.43	1.000
Diiodomethane (MI)	48.00±0.6	45.75	2.25	28.33±3.26	3.325
Hexadecane (HE)	21.30±0.2	21.30	0	5.40±1.43	0.770

Table 8. *Surface tension of liquid phases with values of dispersion and polar components used in Owens-Wendt calculations.*

Estimated surface free energy value of 55.33 mJ/m2 is relatively high, which predicts excellent wetting with ink and high ink adhesion. Hemicellulose is hydrophilic in nature, hence hemicellulose-based films are generally hygroscopic, which means they will absorb moisture. 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.

Owens-Wendt	Total (mJ/m^2)	Dispersive (mJ/m^2)	Polar (mJ/m^2)
DI / MI	55.33	32.49	22.83
MI / Hexadecane	51.49	21.10	30.39

Table 9. *Owens-Wendt method of estimating surface free energy values of hemicellulose film #16 (DI- distilled water, MI- methylene iodide)*

Owens-Wendt	Total (mJ/m^2)	Dispersive (mJ/m^2)	Polar (mJ/m^2)
DI / MI	45.80	38.70	7.10

Table 10. *Owens-Wendt method of estimating surface energy values of LDPE film (DI- distilled water, MI-methylene iodide)*

Owens-Wendt	Total (mJ/m^2)	Dispersive (mJ/m^2)	Polar (mJ/m^2)
DI / Methylene iodide	60.88	1.76	59.12

Table 11. *Owens-Wendt method of estimating surface energy values of kraft paper (DI- distilled water, MI-methylene iodide)*

Gravure Printing

Preliminary printing experiments were done using K-Printing Proofer in gravure mode, mimicking rotogravure printing. Optical density of the printed films is illustrated on Figure 8. With similar surface free energy to the paper, the biofilm has higher print density with the same gravure ink. This is probably due to the lower roughness of the film surface. Further study will investigate the topography of the biofilm surface by using the Bruker white light interferometer.
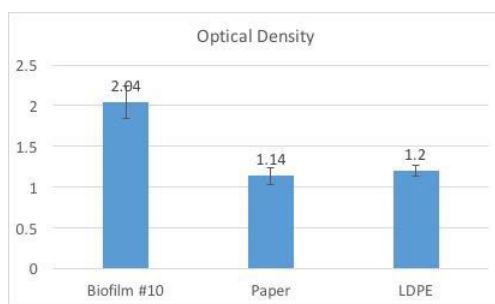
Figure 8. Optical density of solid black patch printed on glucomannan films, paper and LDPE.

Conclusions

Biodegradable glucomannan films were formulated with and without reinforcement with nano-fibrillated cellulose. Statistical analysis of individual components addition showed that glucomannan, sorbitol and nanocellulose all significantly affected mechanical properties of films measured as tensile strength. Nano-fibrillated cellulose increased the mechanical strength of glucomannan films, which was attested by the increased tensile and bursting strength. The glucomannan films were non-porous, which may be useful property with a potential use as a food packaging material with good integrity. The surface energy of the hemicellulose films was found to be relatively high, because the hemicellulose is hydrophilic in nature. High surface energy of films was beneficial for ink adhesion. The films were gravure printed with solvent based ink using gravure K-proofing press. Print density of hemicellulose films were slightly lower than those found on kraft paper and PET film, but biofilms exhibited potential to be used as a packaging material.

References

1. Juho A.S., Aleksi K. "Biocomposite cellulose-alginate films: Promising packaging materials", Food Chemistry, Volume 151, 2014, Pages 343-351.
2. 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.
3. Stevanic J.S., Bergstrom E.M., Gatenholm P., Berglund L., Salmen L., "Arabinoxylan/nanofibrilated cellulose", J. Materials Science, 47, 18, 2012, 6724-6732.
4. Saxena A., Elder T., Ragauskas A.J., "Moisture barrier properties of xylan composite film", Carbohydrate Polymers, 84, 4, 2011, 1371-1377.
5. Kayserilioglu, B.S., Bakir U., Yilmaz L., Akkas N., "Bioresour". Technol. 87, (3) 2003, 239-246.
6. 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.

7. 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.

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

9. 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.

10. 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.

11. Sjostrom E., "Wood Chemistry, Academic Press", San Diego, 2nd Ed., 1993, 293 pp.

12. 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 Polymers, 92(2013), 2154-2162.

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

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. Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick,

W. J., Hallett, J. P., Leak, D. J., Liotta, C. L., Mielenz, J.R., Templer, R., Tschaplinski, T. Science (2006) The path forward for biofuels and biomaterials, Issue 311, Pages: 484-489.

16. Sun. R. C., Sun, X. F., Tomkinson J. In hemicellulose: Science and Technology; Gatenholm, P., Tenkanen, M., Eds., American Chemical Society: Washington, DC, 2004; pp2-22.

17. Ebringerova, A. (2006) Hemicellulose, Macromol. Symp., Volume 232, Pages 1.

18. Ebringerova, A.; Hroomadkova, Z.; Heinze, T. (2005) Polysaccharides I, Structure, Characterization and Use, Adv. Polym. Sci. Volume 186, Issue 1, Pages 1-67.

19. Lindblad, M. S., Albertsson, A. C., (2005) In polysaccharides: Structural diversity and functional versatility, Dumitriu, S., Ed., Marcel Dekker: New York, pp491-508.

20. Sun, X. F., Xu, F., Zhao, H., Sun, R. C., Fowler, P., Baird, M. S., (2005) Characteristics of degraded cellulose obtained from steam-exploded wheat straw, Carbohydr. Res., Volume 66, Issue 1, Pages 97-106.

21. Grondahl, M., Eriksson, L., Gatenholm, P., (2004) Material properties of plasticized hardwood xylans for potential applications as oxygen barrier films, Biomacromolecules, Volume 5, Issue 4, Pages 1528-1535.

22. Lai, V. M. F., Lu, S., He, W. H., Chen, H. H., (2006) Non-starch polysaccharide compositions of rice grains with respect to rice variety and degree of milling, Food Chem., Volume 101, Issue 3, Pages 1205-1210.

23. Smart, C. L., Whistler, R. L., (1949) Films from hemicellulose acetates, Science, Volume 110, Pages 713-714.

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

25. Ten, E. , Vermerris, W., "Functionalized polymers from lignocellulosic biomass: State of the art", Polymers, Vol. 5, 2, 2013, 600-642.

26. 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.

27. Owens, D.K.; Wendt, R.C. "Estimation of the Surface Free Energy of Polymers", J. of Applied Polymer Science vol. 13, 1741-1747 (1969).

28. Young, T. Philos. Trans. R. Soc. London 1805, 95, 65–87.

29. Douglas C. Montgomery, (2005) Design and Analysis of Experiment, Chapter 4, John Wiley & Sons, Inc.

30. Operating and Maintenance Instructions for the Parker Print-Surf Roughness and Porosity Tester, H. E. Messmer Ltd., Britain

31. Lokendra Pal, Margaret K. Joyce and P. D. Fleming, "A Simple Method for Calculation of Permeability Coefficient of Porous Media", TAPPI J., September 2006, p 10.