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EVALUATION OF BARRIER PROPERTIES OF FOOD PACKAGING PAPERS COATED WITH HEMICELLULOSE BIOPOLYMERS

BY

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Abstract. The existing food packaging papers are obtained by coating with aluminium/plastic foils and synthetic polymers. Due to the use of non-renewable resources, poor recyclability and lack of biodegradability, these solutions are not sustainable. In this paper are presented the results on utilisation of xylan hemicelluloses as biopolymers in coating of paper to improve its characteristics for food packaging. In this scope, biopolymer coatings based on xylan and xylan derivatives (acetylated and hydrophobized xylan) were applied in single and successive layers on paper surface. The structural and barrier (to water, gases, oil and grease) properties of coated paper samples showed the good performance to be used in food packaging applications. These findings will make possible obtaining of packaging papers with functional properties, recyclable, biodegradable and compostable that will contribute to reduce of plastic packaging utilisation.

Keywords: xylan; coatings; paper; food packaging; barrier characteristics.

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1. Introduction

Based on their inherent advantages, paper and boards are considered important candidates for food packaging applications. These materials are from renewable resources, non-toxic and biodegradable, but due to the hydrophilic character of cellulose fibres have poor barrier properties to be adequate for food packaging. The existing technologies to obtain food packaging papers with appropriate barrier properties consist of synthetic polymers treatment and metallic or plastic foils lamination. These solutions have negative impact on the environmental, use the non-renewable resources, have low rate of recyclability and are non-biodegradables (Mujtaba *et al*., 2022).

As result of environmental concerns, biopolymers gained increased attention because they not only replace the existing synthetic polymers in different applications but also can provide new combinations of functional properties. In addition, the biopolymers are appropriate matrix to embed the functional compounds as antimicrobial additives to improve the other functional properties of coatings when these are used for food packaging applications (Reichert *et al*., 2020).

There is a high number of studies regarding the utilisation of synthetic polymers to obtain the functional properties of food packaging materials, but only few of them are addressed to food packaging papers. The most studied biopolymer for food contact packaging including paper is Polylactic acid (PLA). However, production of packaging paper coated with PLA and make it competitive with oil-based polymers is still a challenge (Smithers, 2018) because this bio-based polymer is not thermally stable. This involves the utilisation of thermal stabilizers to improve its processing that reduces the biodegradability (Helanto *et al*., 2019).

Based on their biodegradability and non-toxicity, film forming ability and good affinity with paper substrate, the polysaccharides are considered as main candidates to substitute oil-based polymers in food paper coating. In addition, polysaccharides improve the mechanical strength and can provide good barrier to aroma, gases and liquids. However, there are some weaknesses of polysaccharides coatings/films regarding their hydrophilic nature, crystalline structure and properties dependence on the environment humidity as low water resistance or poor barrier to water vapours (Rastogi and Samyn, 2015).

The hemicelluloses (HCs) are polysaccharides that exist in combination with cellulose in the cell walls of lignocellulosic biomass, representing 20-35% of this, as a function of biomass source (Ramos *et al*., 2017).

Additionally, xylans polysaccharides are the most abundant component of hemicelluloses, being available in large quantity in secondary cell wall of wood, agro-residues (wheat straw, corn stalks and cobs), or as secondary product of pulp and paper industry, and is not compete with other resources from agro foods chain. Thus, it can be available in huge amounts as low cost products from forestry, agriculture, and pulp and paper industry (Ebringerová *et al*., 2005).

Until now the commercial applications of xylan hemicelluloses are limited to the xylitol and biofuels obtaining by biological conversion of sugar, starch and vegetable oils. In packaging industry, xylan is already being used as additive for plastics to increase strength and biodegradability. Recent studies on its modification and functionalization have shown their potential wider application in film and coating for food as well as biomedical products (Petzold-Welcke *et al*., 2014).

There are many review reports on main applications of hemicelluloses as food packaging films and coatings for fresh vegetables, but only few of them being related to coatings for paper packaging (Vartiainen *et al*., 2014). In this context, some research studies reported that the uniform films based on xylan/glucomannan exhibit adequate barriers properties (i.e. against oxygen, grease, aroma etc.) that could increase their potential for food paper packaging applications. However, the barrier and strength properties of hemicelluloses films are negative influenced by wet environment (Rastogi and Samyn, 2015; Hartman *et al*., 2006).

Hydrophilicity of hemicellulose limits the range of its industrial applications and the solution is to attach a hydrophobic group onto the hemicellulose chains and thus, improve its hydrophobicity and processability by reducing the H-bonds. Due to the environmental need to produce hydrophobic materials that are biocompatible and may degrade over time in nature, the interest on modification of hemicelluloses is increased in the last decades. This is reflected by the high number of published and cited papers concerning this field. Therefore, for packaging and coating applications, chemical modification with hydrophobic moieties had been applied to enhance the function of hemicelluloses for packaging and coating applications (Zongquan and Xuejun, 2018).

In this paper are presented the results on the utilisation of coatings based on xylan hemicellulose to improve the barrier properties of packaging paper for food packaging applications. With this aim the native hardwood xylan hemicellulose and their acetylated and hydrophobized derivatives were used as coatings in thin layer for paper treatments. The coated paper samples were analysed regarding the main food packaging properties such as: water and oil absorption capacity, grease resistance, barrier to water vapours and gases as we; as the structural characteristics.

2. Experimental

2.1. Materials

Xylan hemicellulose (Xy) from beechwood was purchased from Carl Roth Company, Germany with molecular mass of (132)N. Acetylated xylan

(XyAc) with degree of substitution about 0.48 was obtained by esterification of native xylan with acetic anhydride at 50°C for 1 hour and molar ratio of acetic anhydride to functional hydroxyl groups in the structural unit of xylan about 8:1. Hydrophobized xylan (XyAKD) was obtained by reaction of native xylan with long chain anhydrides as alkyl ketene dimers at 20°C and 24 h of magnetic stirrer at 1500 rpm. Both native xylan and xylan derivatives were used as water dispersion of 2.5% for coating in thin layer of 4.5 g/m^2 weight of commercial base paper of 50 g/m^2 from unbleached cellulose pulp. Alkyl Ketene Dimer (AKD) of milky white liquid, odourless, total solids of 16.2% and viscosity of 4 cPs/ t=25°C (as commercial product AquapelTM 210D -Solenis, USA), was used for xylan hydrophobization and all the other chemical reagents for esterification reaction (acetic anhydride, acetic acid and sulphuric acid) were of analytical purity.

2.2. Experimental methods

2.2.1. Surface treatments (coating) of paper

The coatings based on xylan and xylan derivatives were applied in a single and multi-layer (about 4-5g/m^2) on each side of paper surface using a TQC SHEEN automatic film applicator. In this system the aqueous coating dispersion is applied in front of the wire rod and by automatic rotation of rod over paper substrate a well-defined amount of coating dispersion is applied. The thickness of the coating layer is controlled by the diameter of the wire (Nechita *et al*., 2022). The samples of coated paper were dried for 10 min. at room temperature and 10 min. in an oven at 60°C. The codification of coated samples is presented in the Table 1.

Table 1

The codification of paper coated samples

Sample codification	Description
P0	Base paper (uncoated paper)
P1	Xylan (Xy) coated paper in single layer (about 4-5 g/m^2)
P2	(XyAKD) Hydrophobized xylan coated paper in single layer (about 4-5 g/m^2)
P3	(XyAc) Acetylated xylan coated paper in single layer (about 4-5 g/m^2)
P4	(2Xy)Layered coated paper: 2 layers of xylan (about 4-5 g/m^2)
P5	(Xy+XyAKD) Layered coated paper: base layer of xylan; top layer of hydrophobized (about 4-5 g/m^2)

2.2.2. Testing methods for coated paper samples

Water absorption of paper samples (Cobb60 index), [g/m^2] was measured as described in the standard method SR ISO 535:2014.

Static water contact angle, [°] - according to T-458 cm-04 measured by the static sessile drop method on Ossila contact angle instrument equipped with digital camera and software for recording and processing results. Paper samples were fixed with clamps on the test table and then water drops were deposited on their surface with a micro syringe. The value of the contact angle was recorded after a water-substrate contact time of 5 seconds on samples.

Water vapour transmission rate (WVTR), [g/m^2.day] was evaluated according to the prescriptions of standard method ISO 2528:2018 – using gravimetric (dish) method. The dishes containing a desiccant ($CaCl_2$) were closed and sealed by the paper sample to be tested and then were placed in a controlled atmosphere (23^0C and 50% RH) for 4 days. These dishes were weighed at each 24 h and the WVTR was determined from the increase in mass when this increase has become proportional to the time interval.

Gurley method according to standard ISO 5636-5:2013 (Paper and board – Determination of air permeance (medium range) – Part 5: Gurley method) was used for evaluation of air permeability, [s].

Oil absorption capacity (Unger-Cobb600 index), [g/m^2], was determined as described in the T-441 om-98 standard.

Grease resistance as measured as KIT test according to Tappi T559 standard method. A drop of the solution was applied to the paper surface for 15 s, the excess solution was removed, and the appearance or not of a stain on the back of the paperboard sheet was verified. The solution with the highest Kit number, which remained on the surface of the package without causing stains on the back side, was adopted as the grease-repellency value.

The structural modification of xylan hemicellulose were evaluated by FT-IR analysis using a spectrometer type Nicolet iS50 FT-IR (Thermo Scientific). The spectral range of 4000–400 cm^{-1} at 2 cm^{-1} resolution was used for FT-IR spectra registering.

The scanning electron microscopy (SEM) technique with Quanta 200 system (FEI) was used to investigate the paper surfaces microstructure.

For each sample of coated paper were performed 5 measurements. The results interpretation is based on average value and standard deviation calculated for all measurements.

3. Results and discussions

3.1. Structural analyses of modified xylan by FT-IR

The FT-IR spectra of xylan and xylan derivatives are presented in Fig. 1. Comparing with native xylan, the structural spectra of xylan derivatives indicated the presence of absorption peaks at 1746 cm^{-1} which are associated to C=O vibration stretching from acetyl and -COOH groups (Fig. 1b) and the vibration stretching characteristic absorption peaks of β-ketone ester bond formed between xylan hemicelluloses and AKD within 1602 cm^{-1} and 1733 cm^{-1} (Fig. 1c).

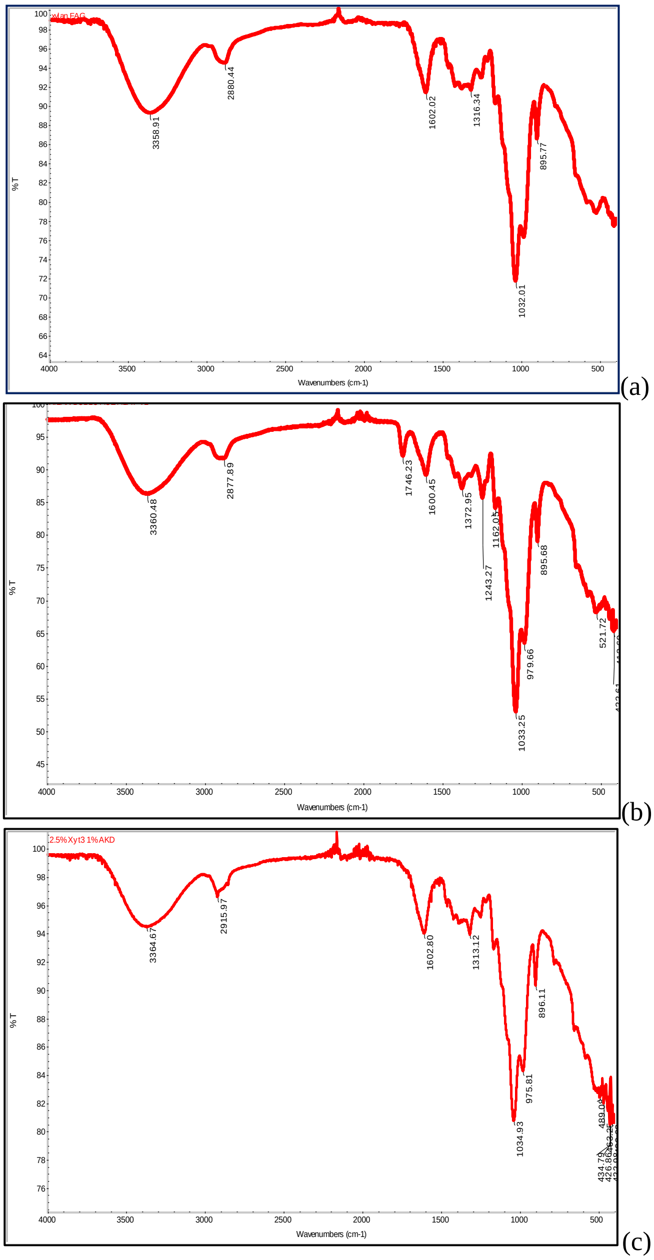
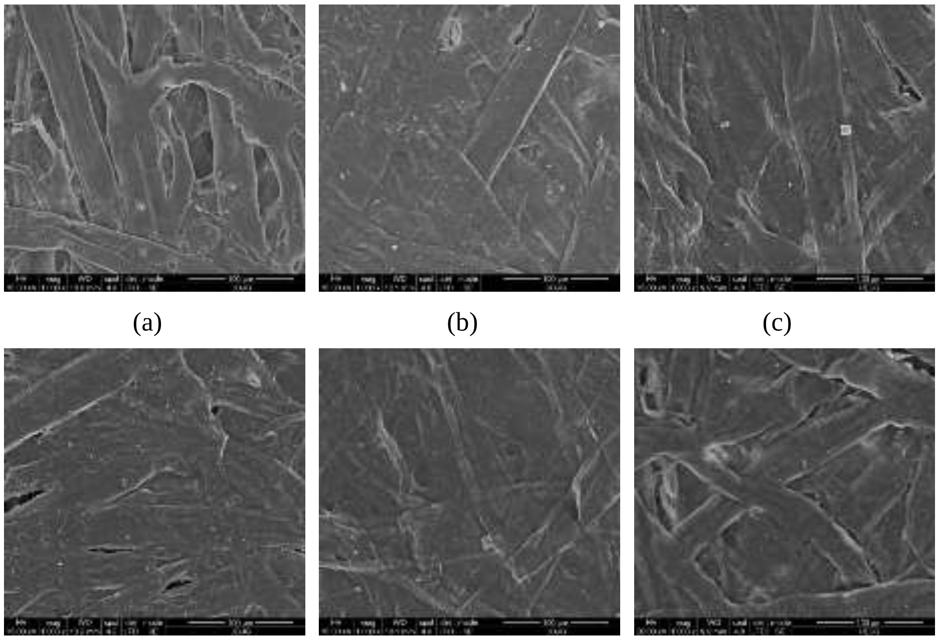


Fig. 1 – FT-IR spectra of (a) hardwood xylan (Xy); (b) acetylated xylan (XyAc); (c) AKD hydrophobized xylan (XyAKD).

3.2. Microstructural analyses of coated paper surface by SEM

The SEM images of coated papers based on xylan hemicellulose and their derivatives are presented in Fig. 2. Compared with untreated paper, the paper samples coated with xylan hemicellulose and their derivatives exhibit a smooth, homogeneous and flat surface (Fig. 2). For the samples coated with XyAKD and XyAc some defects and nonuniformities are observed in the coating layer structure (Fig. 2c, d) that are reduced in case of layered coated samples (Fig. 2e, f).



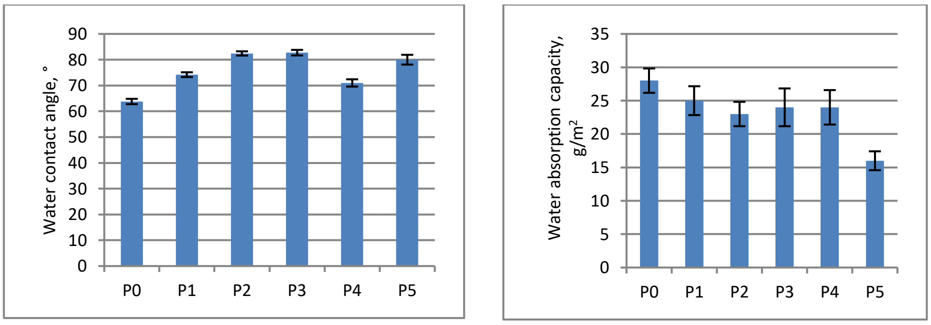
(a) (b) (c)

(d) (e) (f)

Fig. 2 – SEM images of coated paper samples with xylan and xylan derivatives: (a) P0 -base paper; (b) P1- Xy coated paper in single layer; (c) P2 -XyAKD coated paper in single layer; (d) P3 -XyAc coated paper in single layer; (e) P4 –layered coated paper: 2Xy; (f) P5 -Layered coated paper: base layer of Xy; top layer of XyAKD.

3.3. The barrier properties of xylan coated samples

Liquids absorption, gas/vapour permeability and grease and oil resistance are important properties required for packaging papers that came into contact, temporarily or permanently, with wet and fatty foods.

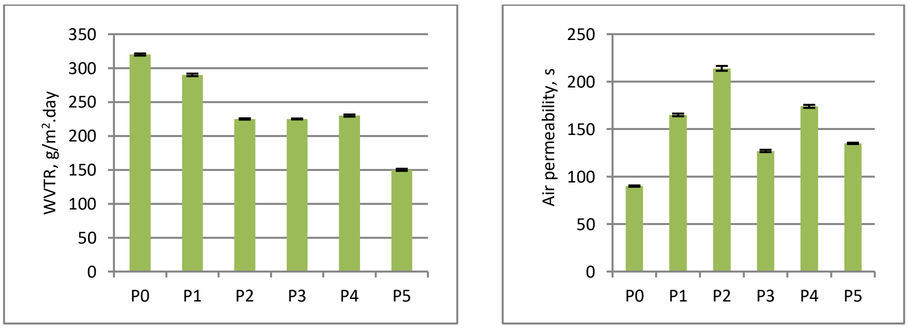


(a) (b)

Fig. 3 – The water barrier properties of xylan coated papers.

In case of single layer coatings the contact angle value of xylan coated samples (P1) was with about 14% higher than that of base paper. For the papers coated with xylan derivatives (P2 and P3) the improving was with about 23% higher comparing with uncoated paper. For the layered coated samples it is observed the similar trend with better results for the P5 sample. In this case the base layer consists of xylan which even if is high hydrophilic, it is able to fill and close the pores on paper surface; this increases the efficiency of the hydrophobized xylan top layer, comparing with the sample P4 coated samples with 2 layers of xylan hemicellulose (P4 sample) (Fig. 3a).

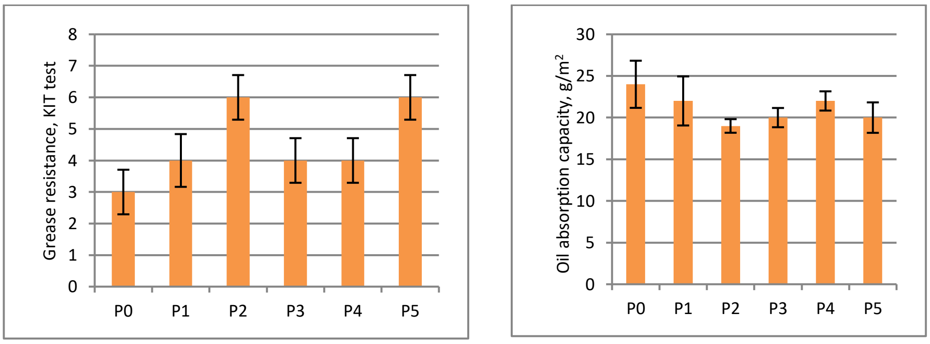
The results of water absorption are correlated with contact angle values, P5 sample exhibiting the better absorption capacity comparing with those of samples P1-P4 (Fig. 3b).



(a) (b)

Fig. 4 – The water vapour and air barrier properties of xylan coated papers.

Regarding the gases barrier properties, all coated samples show improved properties comparing with base paper. It can be observed that the results of water absorption are confirmed by the WVTR and air permeability of xylan coated paper samples. In this case, xylan derivatives coated papers (P2, P3) and those coated with 2 layers (P4, P5) exhibit lower WVTR, with 22.5% lower and 48%, respectively comparing with xylan coated papers (Fig. 4a). The slightly improving of air permeability of P3 and P5 samples (Fig. 4b) is the result of high number of micropores and cracks within the structure of coating layers as it can be observed in SEM images from Fig. 2d and f.



(a) (b)

Fig. 5 – The oil and grease barrier properties of xylan coated papers.

Appropriate results were obtained for grease resistance of xylan coated papers. The KIT test of hydrophobized xylan coated papers, both single and double layer (P2 and P5 samples) was 6 (Fig. 5a). Having in view the low weight of coating layer of about 5 g/m^2, it is considered a good result, comparable with KIT values obtained for paper coated with chitosan and palmitic acid at higher coating weight (11g/m^2) (dos Santos *et al.*, 2022).

Usually, the oil permeation to the base paper surface takes place by capillary flow through pores or cavities of fibrous network. The porous structure allows the intense penetration of oil and grease. It is observed in Fig. 5b, that the oil absorption was only slightly improved for all the coated samples being for the layered coated papers with 8%-16% lower comparing with base paper and respectively, 17% - 21% for the derivatives xylan coated papers P2 and P3. This is result of low weight of coating layer that not close all the pores from paper structure. It is confirmed by the air permeability results of coated paper samples, which were only slight improved, as above mentioned.

4. Conclusions

The dispersions of xylan hemicellulose and their derivatives – AKD hydrophobizated xylan and acetylated xylan were used as coatings to obtain paper with enhanced barrier properties. The structural analysis by FT-IR was highlighted the presence of functional groups in the xylan derivatives structures, as acetyl and keto-esters that impart hydrophobicity with effect on improving of water barrier properties of coated papers. By xylan coating the uniform and flat surface of paper with closed pores is obtained as is observed by SEM analyses. As result the gases and oil/grease penetration are improved. The application of two layers of xylan coatings on paper surface enhanced the barrier propertie of paper. The obtained results indicate that the utilisation of xylan hemicelluloses and their derivatives as coatings on paper surface can be an eco-friendly alternative for petroleum based polymers in food packaging. This could extend the application area of xylan hemicellulose that is an underutilised biopolymer.

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EVALUAREA PROPRIETĂȚILOR DE BARIERĂ
ALE HÂRTIEI DE AMBALAJ ALIMENTAR TRATATĂ CU BIOPOLIMERI
PE BAZĂ DE HEMICELULOZĂ

(Rezumat)

În prezent, tehnologiile utilizate pentru obținerea hârtiei cu proprietăți adecvate pentru ambalarea alimentelor constau în acoperirea hârtiei cu dispersii de polimeri sintetici sau laminarea acesteia cu folii de plastic și aluminiu. Aceste tehnologii nu sunt sustenabile, având la bază materiale din resurse neregenerabile, grad redus de reciclare și biodegradare. În această lucrare sunt prezentate rezultatele utilizării hemicelulozei tip xilan ca biopolimer în dispersiile de acoperire a hârtiei în scopul îmbunătățirii performanțelor de ambalare a alimentelor. Astfel, pastele de acoperire pe bază de xilan și derivații acetilați și hidrofobizați ai acestuia au fost aplicate în simplu și dublu strat la suprafața hârtiei. Caracteristicile structurale și de barieră la apă, aer, uleiuri și grăsimi înregistrate pentru mostrele de hârtii acoperite arată că acestea au performanțe corespunzătoare pentru a fi utilizate în aplicații de ambalare a alimentelor. Aceste rezultate vor face posibilă obținerea hârtiilor de ambalaj cu proprietăți funcționale, reciclabile, biodegradabile și compostabile contribuind astfel reducerea utilizării ambalajelor din materiale plastice.