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SUSTAINABLE FOOD PACKAGING MATERIALS BASED ON HEMICELLULOSE COATED PAPERS

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Abstract: *This paper presents investigations on the utilization of xylan hemicellulose and its derivatives (hydrophobized and acetylated xylan) combined with chitosan biopolymer to improve the barrier and strength properties of paper. In this context, coatings based on hardwood xylan hemicellulose in different combinations, were used for surface treatment of paper. The results demonstrated improved barrier properties to water, gases, oil, and grease, as well as enhanced resistance to microbial attacks and increased mechanical strength of the coated papers. Based on these results, it can be concluded that xylan hemicellulose is a promising biopolymer to substitute synthetic polymers in the treatment of papers for food packaging applications.*

Key words: xylan hemicellulose, coatings, packaging papers, barrier properties

1. INTRODUCTION

The demand for sustainable alternatives is growing, and developing eco-friendly packaging from renewable resources, like lignocellulosic biomass or agricultural residues, could help mitigate environmental harm without competing with food production. These bio-based materials can provide a more sustainable solution by reducing reliance on fossil fuels and promoting biodegradability, thus aligning with circular economy goals (Zhao et al., 2021).

Cellulose-based materials, such as paper and board, are widely regarded as cost-effective and highly promising options due to their numerous inherent advantages. They are less expensive than many alternative materials, highly recyclable, and biodegradable. Additionally, they are easy to convert into containers with specific strength and stiffness properties, offer greater resilience than glass or plastic across a broader temperature range, are lighter in weight, and provide superior printability compared to other materials.

However, when used as food packaging, paper and board face inherent challenges due to their poor barrier properties. The porous structure and hydrophilic nature of cellulose fibers, which form their basic structure, make them ineffective at blocking water vapor, oxygen, flavors, or microbial contamination. Current methods to enhance the barrier properties of paper for agro-food packaging involve coating it with synthetic polymers or laminating it with plastic or aluminum foils. Unfortunately, these modifications negatively impact the sustainability of the packaging by relying on non-renewable resources, reducing recyclability, and hindering biodegradability (Johansson et al., 2012; Liu et al., 2016).

For these reasons, there are both opportunities and challenges in developing cellulose-based packaging materials that meet market performance expectations. The goal is to design suitable barrier and active antimicrobial properties while maintaining their recyclability and biodegradability. Achieving this balance is essential to ensure that these materials offer effective protection for food products without compromising their environmental sustainability.

The utilization of biopolymers to obtain the food packaging papers with appropriate barrier properties, represent a potential alternative to meet the technical, economical and environmental requirements of food packaging industry.

Over the past two decades, research has shown that hemicelluloses, particularly xylan polysaccharides (XyHCs), have significant potential for industrial applications. However, this potential has yet to be realized on a commercial scale. Xylan, the primary hemicellulose in hardwood, is found abundantly in the secondary cell walls of agricultural residues and as a byproduct of the wood and pulp industries. Despite its availability,

the industrial use of XyHCs remains limited due to their hydrophilic properties, which pose challenges for broader application (Ren & Sun, 2010, Wissam, 2018).
The esterification of xylan hemicelluloses (XyHCs) is often reported as a method to produce functionalized xylan films with enhanced properties. This chemical modification improves the water and grease barrier capabilities of the films, while also reducing their oxygen permeability, making them more suitable for industrial applications that require these characteristics.
In this paper are presented the results on the utilization of xylan hemicellulose in native and chemically modified state and chitosan biopolymer in coatings for food packaging papers. Two xylan derivatives (hydrophobized xylan and acetylated xylan) and native chitosan were used in homogenous formula for surface treatment of packaging paper in single and double layer with 4,5 – 5 g/m^2 weight on both sides of paper. The functional properties as barrier to water, oils, greases, mechanical and antimicrobial, specific for food packaging applications were evaluated.

2. METHODS

Two different esterification methods for chemical modification of xylan hemicellulose were employed:

- *acetylation of xylan using acetic anhydride,* at 50°C for 1h and molar ratio of acetic anhydride to functional hydroxyl groups in the structural unit of xylan about 8:1. Resulted acetylated xylan has a degree of substitution (DS) of 0.48 (Roman et al, 2023), and
- *the reaction of xylan with alkyl ketene dimer (AKD),* which reacts with the hydroxyl groups of xylan to form β-keto ester compounds. The reaction was developed at 20°C for 24h using a magnetic stirrer at 1500 rpm (Nechita et al, 2022).

The functionalized xylan was characterized using FT-IR analysis and applied as coating on packaging paper surface.
Colloidal dispersions of xylan or its derivatives and chitosan were prepared by gradually adding the xylan/xylan derivative solution dropwise into the chitosan dispersion at a rate of about 60 mL/h, while stirring continuously with a magnetic stirrer. Once the chitosan addition was complete, the mixture of dispersions was stirred magnetically for 24 h.
A TQC SHEEN automatic film applicator (TQC B.V., Netherlands) was employed to coat paper samples. In this setup, an aqueous coating dispersion was applied in front of a 6 mm diameter rod. The rod automatically rotated over the paper substrate in a longitudinal direction at 100 mbar pressure and a speed of 125 mm/s, ensuring a precise application of the coating dispersion. The coating layer's thickness was controlled by the rod's diameter. A total of 20 coated paper samples, each measuring 20 × 25 cm, were produced and tested for their functional properties. Uncoated paper (base paper) was used as a reference. (Table 1).
The performances of xylan hemicellulose coated papers were assessed by evaluating the barrier properties to water, oil, grease, gases and against the microbial attack and mechanical strength using standardized methods.
The surface morphology of the coated papers was analyzed using a scanning electron microscope (SEM) FEI QUANTA 200 operating at an acceleration voltage of 20 kV.
Barrier to air and water vapours of coated papers were evaluated by measuring the resistance to air passing (Gurley porosity according to ISO 5636-5:2013 and water vapours transmission rate (WVTR) according to the ISO 2528:2018 standard which used the gravimetric (dish) method to measure the rate at which water vapours passe through the paper.
The wettability of coated surface was evaluated by analyzing of water contact angle and water absorption capacity of coated papers.
Oil and Grease Resistance was tested by measuring the oil absorption capacity as Unger-Cobb600 index (TTAPPI T 441 om-09) and as KIT rating of paper samples according to the TAPPI T 559 cm-12, respectively.
The antimicrobial activity of the coated papers was tested against Gram positive bacteria, *Bacillus sp* using a modified and adapted method of the ISO 846 (2000) standard.

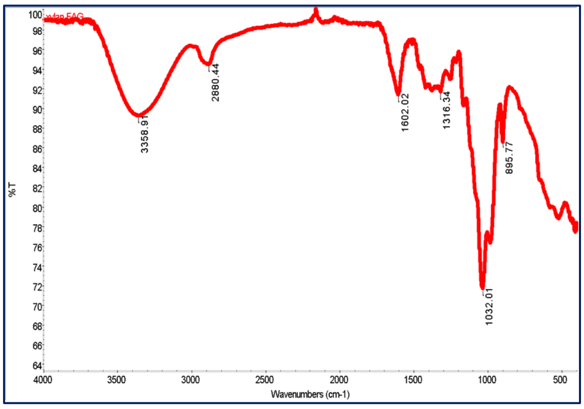
Table 1: The codification and composition of xylan hemicellulose coated papers

Sample codification	Composition					
	Single layer			Double layer		
	Native xylan (Xy)	Acetylated Xylan (XyAc)	Hydrophobised Xylan (XyAKD)	L1: Xy L2: Chi	L1: XyAc L2: Chi	L1: XyAKD L2: Chi
P1	100	-	-	-	-	-
P2	-	100	-	-	-	-
P3	-	-	100	-	-	-
P4	-	-	-	L1:100/ L2:100	-	-
P5	-	-	-	-	L1:100/ L2:100	-
P6	-	-	-	-	-	L1:100/ L2:100

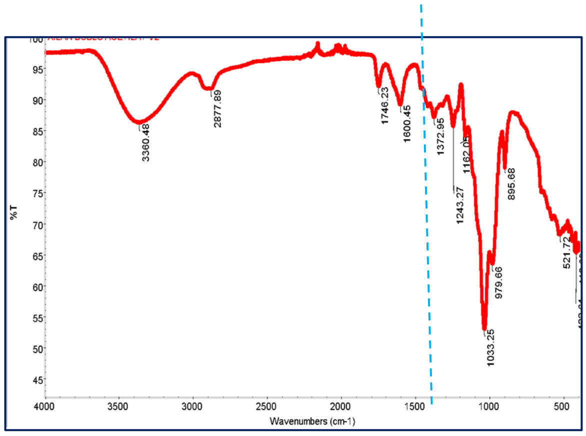
3. RESULTS AND DISCUSSIONS

3.1 Structural characteristics of xylan derivatives

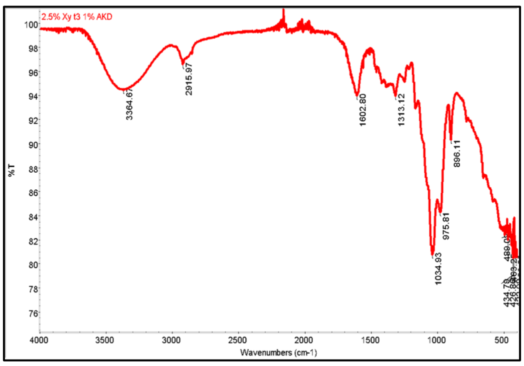
The structural analyses by FT-IR indicated the presence of absorption peaks at 1746 cm^{-1} which are associated to C=O vibration stretching from acetyl and -COOH groups (Figure 1b) and the vibration stretching characteristic absorption peaks of β-ketone ester bond formed between xylan hemicelluloses and AKD at 1602 cm^{-1} and 1733 cm^{-1} (Figure 1c). These confirm the chemical modification of xylan hemicellulose by introducing the new functional groups in the chemical structure (Figure 1a).



(a)



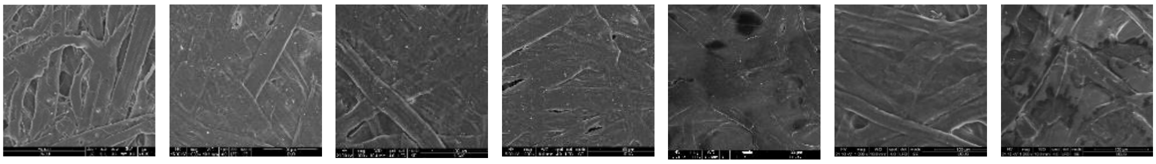
(b)



(c)

Figure 1: FT-IR spectra of: (a) Native xylan; (b) Acetilated xylan XyAc; (c) Hydrophobised xylan XyAKD

3.2 The surface morphology of coated papers



P0 P1 P2 P3 P4 P5 P6

Figure 2: Surface morphology of the polysaccharides coated papers

The surface morphology of hemicellulose-coated papers, as shown in Figure 2 varies depending on the coating combination applied. The uncoated paper (P0) exhibits a porous structure with numerous cavities. Applying a coating layer improves surface uniformity and smoothness. When two successive layers are applied, with chitosan as the top layer, a distinct surface topography is observed. The excellent film-forming ability of chitosan results in a uniform, crack-free surface, in contrast to the samples coated with xylan or its derivatives.

3.3 Barrier to air and water vapors

In general, the air and water vapor barrier properties of paper coated with xylan or xylan derivatives are improved compared to uncoated papers. When two successive layers are applied (P4-P6 samples), a dense structure is formed, significantly reducing air permeability and water vapor transmission rate (WVTR) (Figure 3). Coating with polymer dispersions typically leads to partial or complete filling of the cellulose fibers, resulting in the densification of the paper sheet. This reduces interfiber interactions and limits water vapor diffusion into the substrate.

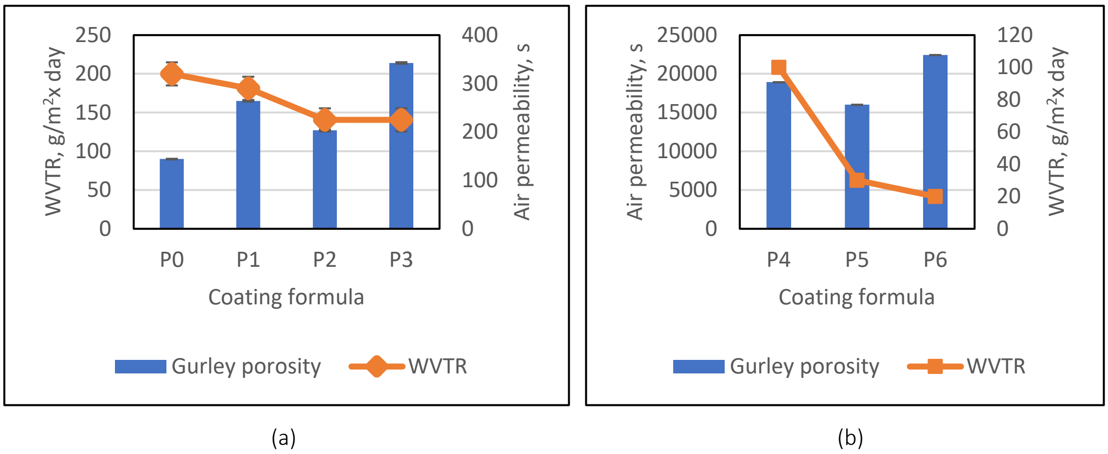
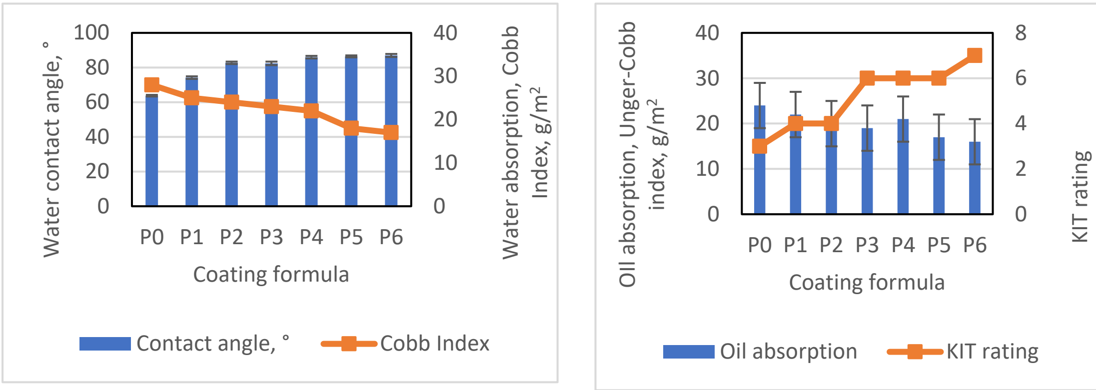


Figure 3: Gases barrier properties of xylan coated papers (a) single layer; (b) double layer

3.4 Barrier to water, oils, and greases of coated papers

In general, the paper samples coated with successive layers of xylan derivatives and chitosan showed improved water absorption and contact angle values compared to papers coated with single layer of native xylan and its derivatives. For samples P5 and P6, water absorption was the lowest, and the contact angle measured 86-87° (Figure 4a). Analyzing the results shown in Figure 4b, it can be observed that the oil and grease resistance of the samples coated with two successive layers of xylan derivatives and chitosan improved, reaching 16 g/m^2 for oil absorption (Unger Cobb test) and 7 in the KIT test (samples P5 and P6). These values are comparable to those of current food packaging papers coated with synthetic polymers or fluorochemical compounds.



(a) (b)

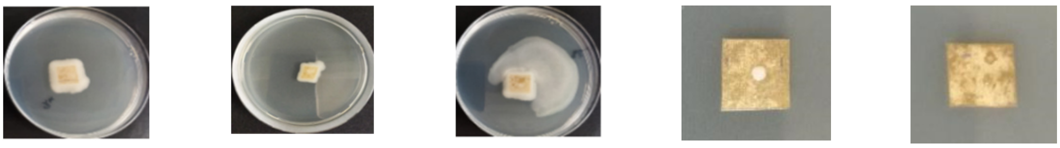
Figure 4: Barrier properties of hemicellulose coated papers to:(a) water; (b) oils and greases

3.5 Antibacterial capacity of coated papers

In general, papers coated with xylan derivatives showed a slight inhibitory effect, indicating that a small inhibition zone can be observed on the surface and around it, as shown in Figure 5. However, papers coated with acetylated xylan exhibit a stronger inhibition effect. These results are consistent with the lower WVTR values observed for these paper samples. The samples coated with xylan derivatives and chitosan in two layers exhibited better inhibition effects, with sample P6 having a total inhibition of *Bacillus sp.*

P1	P2	P3	P5	P6

Inhibition degree after 24h at 37°C



Degree of inhibition, %

45.2	70.3	20.2	95.10	100

Figure 5: The antibacterial activity of hemicellulose coated papers

3.6 Strength properties

In addition to functional properties, mechanical strength is crucial for paper packaging to ensure adequate protection of the packaged material during transport and handling. Compared to uncoated paper, all coated samples exhibited improved bursting strength, a key characteristic for packaging paper (Figure 6). This can be attributed to the fact that, at low coating weights, the additional moisture in the paper substrate due to the hygroscopic nature of xylan coatings is minimal and does not negatively affect the bursting strength of the coated paper (Zachary, 2018).

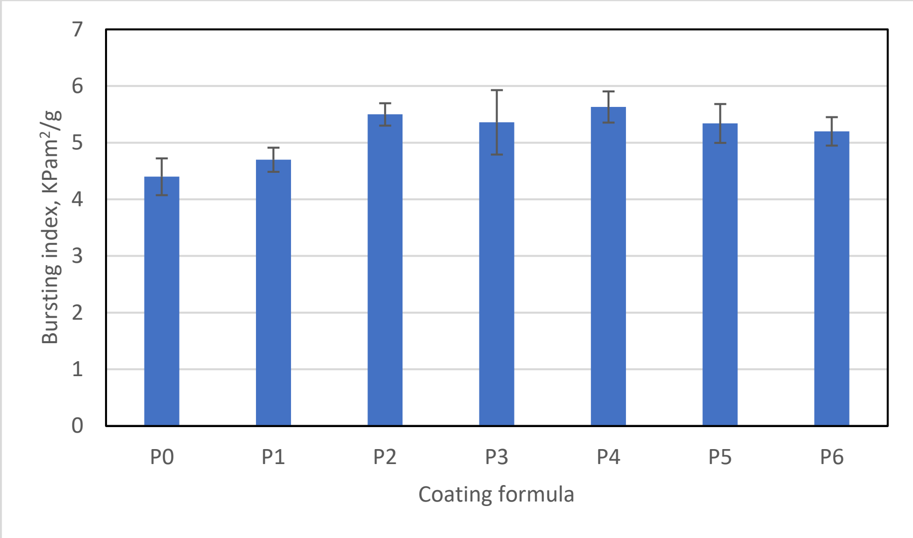


Figure 6: The strength properties of hemicellulose coated papers

4. CONCLUSIONS

Based on the obtained results, it can be concluded that coating paper with xylan hemicellulose leads to improved water, oil, greases and gas barrier properties. Additionally, the xylan coating has a positive effect on the bursting strength of the coated papers, which is one of the most important strength properties for packaging paper.

Coating paper with successive layers, with chitosan as the top layer, resulted in improved inhibition of *Bacillus sp.* after 24 hours. Generally, the antimicrobial properties of coated papers are closely linked to their water barrier properties; samples with reduced water and water vapor permeability tend to inhibit bacterial growth more effectively.

5. ACKNOWLEDGMENTS

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